The Effect of Styrene Grafting on the Diffusion and Solubility of Organic Liquids in Polyethylene

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Synopsis

The effect of grafting styrene onto low-density polyethylene on the diffusion and solubility of benzene and n-hexane in the graft copolymer has been investigated. The diffusion coefficient at zero concentration $D_{c=0}$ for both benzene and n-hexane decreased with the amount of styrene grafting in the polyethylene–styrene graft copolymer membrane. The free volume parameters of the polyethylene–styrene graft copolymer were calculated using benzene and n-hexane as the diffusing species. Results show that there is a large decrease in free volume as grafting proceeds and the effect is more pronounced at low levels of grafting. Solubility was found to be a function of the per cent grafting, there being a 50%–90% increase in benzene solubility in a 26% graft compared to polyethylene. The increase in solubility for n-hexane was considerably lower. The effect of crystallinity on the free volume parameters has also been calculated.

INTRODUCTION

The modification of the properties of polymer films by radiation-induced graft copolymerization has been the subject of numerous investigations during the past decade. However, relatively little work has been reported on the effect of graft copolymerization on the transport properties of polymer films. Fels[1] and Huang and Fels[2] recently investigated the permeation and separation of binary organic liquids through polyethylene–styrene graft copolymer membranes. Increased permeation rates and separation factors were observed which resulted in overall improvement in separation efficiencies. Myers et al.[3] and Huang and Kanitz[4] have studied the permeation of permanent gases through polyethylene–styrene graft copolymers. Rogers[5] and Sternberg and Rogers[6] investigated the transport properties of graft copolymer membranes with a gradient of graft concentration across the membrane. Wellons[7] studied the transport of water vapor through cellulose acetate grafted with styrene and reported that the major effect of grafting was to reduce the solubility of water in the graft copolymer. The permeability of a liquid through a polymer membrane can be considered as a composite term which is the product of the solubility

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and diffusion coefficients. Polymer membranes thus exhibit selective permeation behavior toward liquid mixtures and can be used for separation purposes, depending on the solubility and diffusion characteristics of the liquids involved. In order to improve the separation properties of a given polymer membrane by chemical or physical modification, it is necessary to control and influence the diffusion and solubility of the liquids in the modified polymer. It is the purpose of this study to investigate the effect of graft copolymerizing styrene onto polyethylene on the diffusion and solubility coefficients of organic liquids in the resulting graft copolymer. The changes in the free volume parameters of the grafted polyethylene with per cent styrene grafting were also calculated using the method described in a previous paper.[8]

THEORY

Fujita[9] has developed a free volume expression for the diffusion coefficients of organic vapors in polymers. The diffusion coefficient is in the form

$$\frac{D_T}{D_{c=0}} = \ln\left[\frac{v_p}{[f(0,T)]^2/\beta(T)B_d + (f(0,T)/B_d)v_p}\right] \qquad (1)$$

where D_T is the thermodynamic diffusion coefficient, $D_{c=0}$ is the diffusion coefficient at zero concentration of the diffusing species, v_p is the volume fraction of the diffusing species, $f(0,T)$ is the free volume of the polymer at temperature T, $\beta(T)$ is a proportionality factor relating the increase in free volume of the system with added liquid, and B_d is a constant for a given liquid–polymer system and is related to the size of the minimum "hole" for a diffusional step to occur.

In a previous paper,[10] a method was described whereby $D_{c=0}$ and the free volume parameters, $f(0,T)$, $\beta(T)$, and B_d could be obtained by measuring the desorption of a liquid from a polymer film.

EXPERIMENTAL

Desorption Measurements

The equipment for desorption measurements has been described previously.[10] It consisted of a Cahn Electrobalance which enabled a continuous recording to be made of the weight of the sample during desorption. Desorption runs were done using liquid benzene and n-hexane with polyethylene and four polyethylene–styrene graft copolymers having a graft level of about 5%, 11%, 18%, and 26%. Each run was carried out in duplicate.

Preparation of Graft Copolymer Films

The low-density polyethylene film was supplied by the Plastic Film Division Canadian Industries Ltd., Toronto, Ontario. It contained no

plasticizers or antiblock agents. Its density was 0.9157 g/ml and it had a melt index of 7.0 g/10 min.

The polyethylene film was first deaerated under vacuum and two numbered samples were placed into capped test tubes. Styrene monomer and methanol were mixed in the proportion of 70% methanol and 30% styrene by volume and poured into the test tubes. The addition of a nonsolvent of the polymer and grafted chains results in an increase in the yield of graft with a given amount of radiation. This improvement in grafting with methanol was first reported by Odian et al.[11] and is attributed to the Trommsdorf effect. After degassing of the solution and sample, the samples were kept in contact with the solution for about four days. The graft copolymerization reaction was carried out by gamma-ray irradiation in a 12,000 curie, 220 cobalt-60 unit at the Department of Chemical Engineering at the University of Waterloo. This unit was designed and built by the Commercial Products Division, Atomic Energy of Canada, Ltd. Radiation intensities of up to 1.0 megarads per hour were obtainable in the sample chamber. The temperature during the irradiation was maintained at about 35°C by continuously circulating air into the irradiation chamber.

After irradiation, the test tubes were removed from the Gammacell-220. The films were extracted in benzene for 48 hr in order to remove any homopolymerized polystyrene. The weight of the dried sample was measured to obtain the percent grafting which is defined as

$$\% \text{ grafting } = [(W_2 - W_1)/W_1] \times 100 \tag{2}$$

where W_1, W_2 are the weights of the sample before and after grafting, respectively.

Measurement of Crystallinity

Crystallinity was determined by thermal measurements. This method is based on the fact that amorphous and crystalline regions have different enthalpy–temperature characteristics. Dole[12] gives a practical procedure to evaluate crystallinity which consists of measuring the heat input to the sample as a function of temperature over a fairly large temperature range. The crystalline fraction can be calculated by

$$\gamma_c = \Delta H_s / \Delta H_c \tag{3}$$

where γ_c is the crystalline fraction of the polymer, ΔH_s is the change in enthalpy between T_1 and T_2 of the polymer sample, and ΔH_c is the change in enthalpy of 100% crystalline polyethylene.

The change in enthalpy was measured with a Perkin-Elmer differential scanning calorimeter, Model DSC-1B. The instrument gives a recorder output of the heat input to the sample versus the temperature of the sample. To obtain the ΔH's, the area under the curve between 25°C and 130°C was measured; ΔH_c was estimated by measuring the enthalpy change of a crystalline sample of dotriacontane and found to be 69 cal/g.

DISCUSSION

Diffusion Coefficient at Zero Concentration

The parameter $D_{c=0}$ was obtained directly from the desorption curves. A typical desorption plot of $\ln Q(t)/Q(0)$ against time is shown in Figure 1. From the slope of the straight line at long times, the value of $D_{c=0}$ may be calculated. As discussed in the previous paper,[10] the slope is equal to $D_{c=0}$ $\pi^2/4l^2$. The results obtained are presented in Table I. It is difficult to compare the values for $D_{c=0}$ with previous values reported in the literature because this diffusion coefficient is quite sensitive to the morphology of the film. It would be expected to vary considerably with sample history and preparation. McCall[13] obtains a value of 3.0×10^{-8} cm^2/sec for benzene in DYNK, a low-density polyethylene made by Union Carbide, Bakelite Division. The temperature used in his study was specified only as room temperature. However, his value compares favorably with the value of $D_{c=0}$ of 2.15×10^{-8} cm^2/sec at 30°C found in the present study.

Figure 2 shows the change in the diffusion coefficient at zero concentration with per cent grafting. It can be seen that for both benzene and n-hexane, $D_{c=0}$ decreases as the amount of styrene grafted to polyethylene increases. $D_{c=0}$ is related to the free volume at zero concentration by the following expression:

$$D_{c=0} = RT \, A_d \exp(-B_d/f(0,T)) \qquad (4)$$

where R is the gas constant and A_d is a constant. This would therefore indicate that the free volume of the polymer network available for diffusion
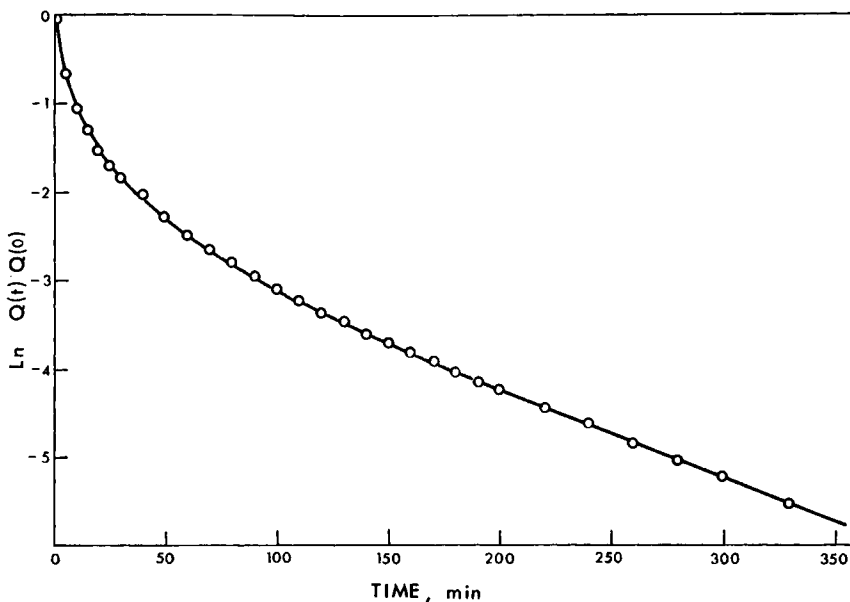

Fig. 1 Desorption of benzene from polyethylene: ln $Q(t)/Q(0)$ vs. time for a typical desorption run.

TABLE I
Diffusion Coefficients at Zero Concentration of
Polyethylene–Styrene Graft Copolymers

Per cent grafting	Diffusing species	$D_{c=0} \times 10^8$, cm^2/sec				
		25°C	30°C	35°C	40°C	45°C
0	n-hexane	1.10	1.33	2.13	2.80	4.49
	benzene	1.25	2.15	2.87	5.03	6.90
5	n-hexane	0.679	0.897	1.16	1.71	2.29
	benzene	1.10	1.48	2.00	2.69	3.80
11	n-hexane	0.769	0.908	1.20	1.56	2.05
	benzene	0.643	0.826	1.18	1.53	2.11
18	n-hexane	0.628	0.808	0.941	1.20	1.43
	benzene	0.386	0.442	0.693	0.947	1.22
26	n-hexane	0.349	0.455	0.612	0.779	0.900
	benzene	0.242	0.370	0.462	0.771	1.00

is decreasing as more styrene is grafted. The following physical interpretation can be made at this point. 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.
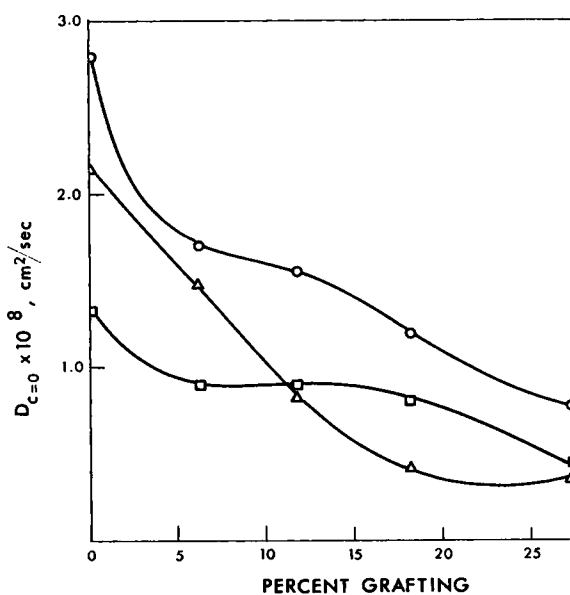

Fig. 2. Change in the diffusion coefficient at zero concentration with per cent grafting: (□) temperature 30°C, n-hexane as diffusing species; (O) temperature 40°C, n-hexane as diffusing species; (Δ) temperature 30°C, benzene as diffusing species.

A further account of this will be given later when the actual free volume fractions are discussed.

Solubility

Equilibrium solubility data was obtained for the liquids benzene and n-hexane in the polyethylene–styrene graft copolymers at five different temperatures.   These results are calculated by knowing the initial weight at the start of the desorption run and obtaining the final weight at the end of the run.   Some experimental difficulties were encountered in determining the point when the polymer had lost its surface film of liquid.   With improvement in experimental techniques, the difference between duplicate runs was found to average about 0.7%.   The solubility data in cc liquid per cc liquid plus polymer are shown in Table II.

TABLE II
Solubility of Benzene and n-Hexane in Polyethylene and
Polyethylene–Styrene Graft Copolymers

Per cent grafting	Species	Solubility, cc/cc				
		25°C	30°C	35°C	40°C	45°C
0	n-hexane	0.161	0.178	0.193	0.212	0.228
	benzene	0.148	0.175	0.199	0.223	0.234
5	n-hexane	0.159	0.180	0.190	0.205	0.222
	benzene	0.171	0.185	0.205	0.225	0.253
11	n-hexane	0.168	0.182	0.193	0.209	0.227
	benzene	0.203	0.223	0.244	0.257	0.285
18	n-hexane	0.179	0.195	0.208	0.217	0.244
	benzene	0.234	0.245	0.267	0.286	0.309
26	n-hexane	0.188	0.202	0.209	0.233	0.245
	benzene	0.271	0.283	0.291	0.313	0.340

The solubility was found to be a function of the composition of the graft copolymer.   Some typical curves are shown in Figure 3.   As can be seen, the solubility of benzene is affected the most, there being a 50% to 90% increase in solubility in the 26% grafted films over the ungrafted polyethylene.   In contrast, n-hexane shows only a 10% to 16% increase in solubility.

Crystallinity Measurements

The results of the measurements on the crystalline content are presented in Table III.   It is interesting to note that conditioning the film by soaking it in a liquid does not appreciably alter the crystalline content.   This was also previously reported by Choo.[14]   There is an indication that the crystalline content decreases as the level of grafting increases.   It is possible that this may be attributed to some disruption of the crystallites by the growing polystyrene side chains.   However, it should be noted that the presence of grafted side chains may cause significant changes in the enthalpy–tempera-
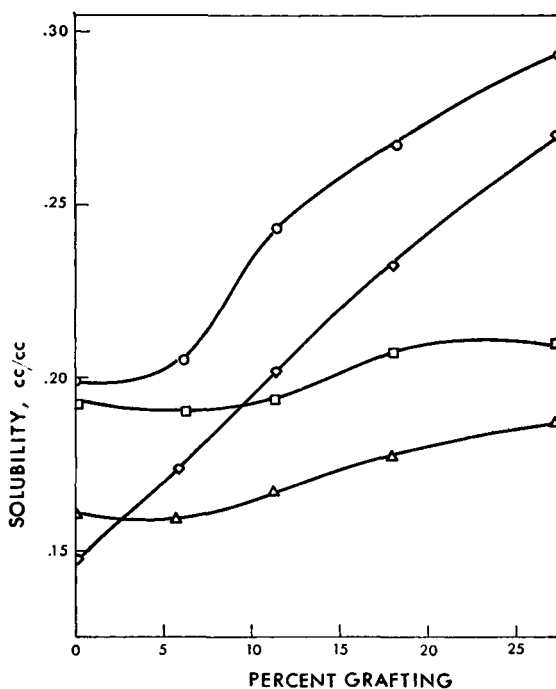
Fig. 3. Solubility of n-hexane and benzene in polyethylene–styrene graft copolymers: (∇) benzene at 25°C; (O) benzene at 35°C; ($\triangle$) n-hexane at 25°C; ($\square$) n-hexane at 35°C.

ture relationship. Therefore the crystallinity values reported here are probably only accurate to ±5%.

Free Volume Parameters

The method for obtaining the free volume parameters, $f(0,T)$, $\beta(T)$ and B_d, has been described in the previous paper.[10] The results for the diffusion of benzene and n-hexane are presented in Tables IV and V, respectively. Several interesting trends can be seen from these results. The first is that

TABLE III
Weight Per cent Crystallinity of Polyethylene
and Polyethylene–Styrene Graft Copolymers

Per cent grafting	Crystallinity, wt-%				
	no treatment	n-hexane at 35°C	benzene at 35°C	n-hexane at 45°C	benzene at 45°C
0	63	65	61	63	59
5	58	60	60	62	62
11	53	58	56	55	56
18	55	51	54	50	54
27	50	48	49	49	51

TABLE IV

Free Volume Parameters for the Diffusion of n-Hexane in Polyethylene and Polyethylene–Styrene Graft Copolymers

Per cent grafting	B_d	25°C		30°C		35°C		40°C		45°C	
		$f(0,T)$	$\beta(T)$	$f(0,T)$	$\beta(T)$	$f(0,T)$	$\beta(T)$	$f(0,T)$	$\beta(T)$	$f(0,T)$	$\beta(T)$
0	0.143	0.0120	0.0522	0.0143	0.0805	0.0162	0.103	0.0169	0.115	0.0180	0.124
5	0.106	0.0064	0.0207	0.0091	0.0454	0.0104	0.0623	0.0115	0.0756	0.0121	0.0861
11	0.108	0.0059	0.0152	0.0082	0.0312	0.0094	0.0432	0.0106	0.0577	0.0112	0.0697
18	0.0851	0.0037	0.00731	0.0049	0.0131	0.0065	0.0257	0.0082	0.0476	0.0092	0.0635
27	0.0824	0.0039	0.0084	0.0046	0.0133	0.0058	0.0230	0.0077	0.0489	0.0089	0.0754

TABLE V

Free Volume Parameters for the Diffusion of Benzene in Polyethylene and Polyethylene–Styrene Graft Copolymers

| Per cent grafting	B_d	25°C		30°C		35°C		40°C		45°C	
		$f(0,T)$	$\beta(T)$	$f(0,T)$	$\beta(T)$	$f(0,T)$	$\beta(T)$	$f(0,T)$	$\beta(T)$	$f(0,T)$	$\beta(T)$
0	0.241	0.0174	0.0795	0.0188	0.0821	0.0212	0.107	0.0231	0.119	0.0265	0.156
5	0.0835	0.0053	0.0185	0.0070	0.0370	0.0082	0.0568	0.0087	0.0670	0.0094	0.0766
11	0.0721	0.0061	0.0334	0.0069	0.0523	0.0074	0.0639	0.0078	0.0812	0.0082	0.0899
18	0.0456	0.0040	0.0252	0.0050	0.0527	0.0052	0.0645	0.0055	0.0821	0.0056	0.0885
27	0.0242	0.0023	0.0179	0.0027	0.0299	0.0029	0.0428	0.0030	0.0511	0.0031	0.0659
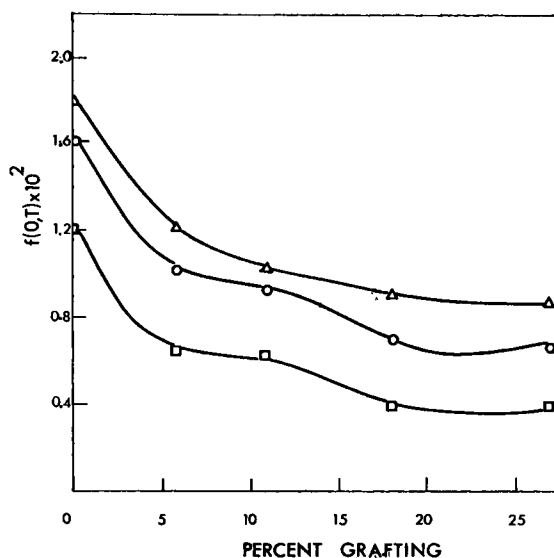
Fig. 4. Change in the fractional free volume of the polymer with per cent grafting, n-hexane: (□) 25°C;   (○) 35°C;   (△) 45°C.

there is a general tendency for the free volume of the polymer to decrease (with only two exceptions) as the amount of styrene grafting is increased. This is shown in Figures 4 and 5.   Therefore, it appears that at the levels of graft copolymerization used in this study, grafting is taking place in the amorphous regions where it would affect the free volume for diffusion. For n-hexane, the free volume of ungrafted polyethylene is two to three times that of a 26% graft.   When benzene is the diffusing species, a factor of seven to eight is involved.   Wellons[7] investigated the diffusion characteristics of cellulose acetate film grafted with polystyrene and describes the role of the grafted polystyrene as "crosslinks."   He feels that the effect of crosslinking arises from the randomly coiled side chains becoming entangled with other molecular chains.

Another interesting observation which can be made from the results of the free volume calculations is that the free volume of the polymer depends to some extent on the permeant used in the desorption experiment. Theoretically, free volume is a polymer property and should be independent of the nature of the permeant.   This discrepancy can be explained in terms of the following considerations.   Before a desorption run is made, the polymer is soaked in the liquid to be desorbed for a relatively long time to ensure that the equilibrium concentration is obtained.   This process leads to a conditioning of the film which is known to alter the distribution of crystallite sizes without altering the level of crystallinity.   The result of this conditioning process can bring about marked changes in the diffusional behavior of polymer membranes.   Since the effect of conditioning depends on the particular liquid used for the process, the free volume of the polymer
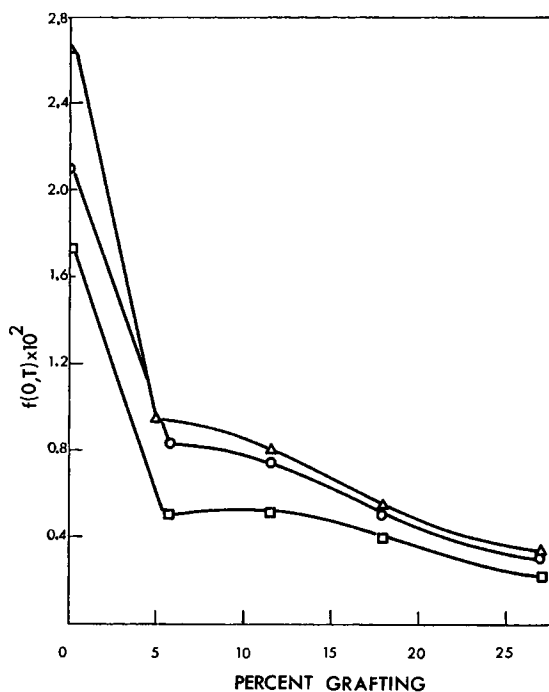
Fig. 5. Change in the fraction free volume of the polymer with per cent grafting, benzene:
(□) 25°C; (O) 35°C; (△) 45°C.

would not be independent of the liquid used as permeant in a semicrystal-
line polymer.   However, in a purely amorphous polymer, the free volume
would be independent of the permeant.

It is interesting to study the effect of the crystallite regions on the free
volume and to compare this effect with that of the grafting.   In order to
do this, it is required to know what the free volume of the polymer would
be if the crystalline regions had no effect on the diffusion, that is, if their
role were simply that of an inert volume which does not impede the diffu-
sion process.   To calculate the effect of crystallinity, the actual free volume
obtained in this study (Tables IV and V) can be compared with this "theo-
retical" free volume.

It has been shown by Williams et al.[15] that the free volume of an amor-
phous polymer is given approximately by the relation

$$f_{am}(0,T) = 0.025 + 4.8 \times 10^{-4} (T - T_g) \tag{5}$$

where $f_{am}(0,T)$ is the free volume of an amorphous polymer at temperature
T and T_g is the glass transition temperature of the polymer.

The "theoretical" free volume of the crystalline polymer can then be
obtained by multiplying the free volume of the 100% amorphous polymer
by the volume fraction of amorphous material in the polymer sample.   In

the absence of experimental data, the glass transition of the copolymer will be calculated by a relationship quoted in Meares[16] as

$$1/T_g = W_a/T_{ga} + W_b/T_{gb} \tag{6}$$

where T_g, T_{ga}, and T_{gb} are the glass transition temperatures of the copolymer, component a, and component b, respectively.

The comparison of the actual free volume obtained experimentally and the "theoretical" one is shown in Tables VI and VII, expressed as (experi-

TABLE VI

Free Volume of Polyethylene and Polyethylene–Styrene
Graft Copolymers as Per Cent of Theoretical Free Volume for
the Diffusion of n-Hexane

Per cent grafting	Free volume, %				
	25°C	30°C	35°C	40°C	45°C
0.00	36.0	38.6	39.7	37.8	36.8
5.67	19.8	25.3	26.2	26.4	25.4
11.3	18.7	23.4	24.3	25.2	24.1
19.3	12.2	14.5	17.5	20.0	20.5
27.3	13.4	14.2	16.1	19.5	20.6

TABLE VII

Free Volume of Polyethylene and Polyethylene–Styrene
Graft Copolymers as Per Cent of Theoretical Free Volume
for the Difference of Benzene

Per cent grafting	Free volume, %				
	25°C	30°C	35°C	40°C	45°C
0.00	52.2	50.8	51.9	51.6	54.2
5.67	16.4	19.5	20.7	20.0	19.8
11.3	19.4	19.7	19.1	18.4	17.7
19.3	13.2	14.8	14.0	13.4	12.5
27.3	7.9	8.3	8.1	7.6	7.2

mental free volume/theoretical free volume) $\times$ 100. There are several interesting observations which can be made from this data. For ungrafted polyethylene, the effect of crystallinity is to decrease the free volume to 50% of the theoretical one in the case of benzene and about 38% in the case of n-hexane. Thus it is apparent that there is a definite impediment of the diffusion process by the crystallite regions. Using eq. (4), which relates the free volume to $D_{c=0}$, the diffusion coefficient at zero concentration could be reduced by a factor of about seven for benzene and about 11 for n-hexane. Although the comparison is not entirely justified, it is noteworthy that Michaels and Parker[17] estimate that the diffusion coefficient of O_2 in a polyethylene film with about the same crystallinity used in the present study would be reduced by a factor of about five.
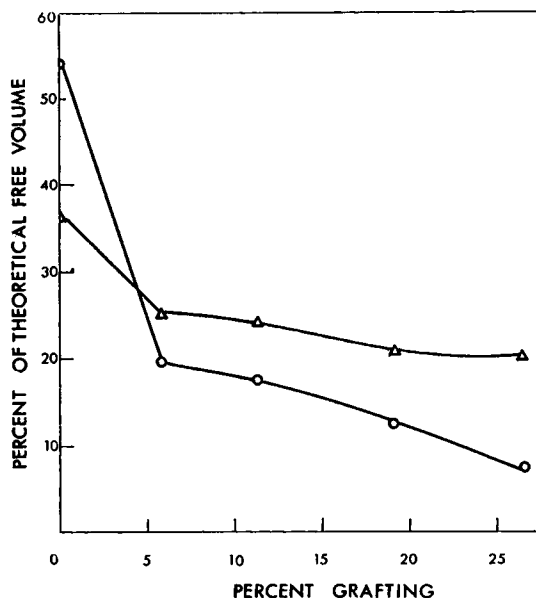
Fig. 6. Effect of grafting on the impediment of free volume of the polymer: (O) n-hexane at 45°C;   (△) benzene at 45°C.

The second feature of note is the change of the free volume impediment with per cent grafting, as shown in Figure 6.   There is a large decrease in the free volume "efficiency" at the 5% level of grafting.   In the case of benzene diffusion, the decrease is from 50% to about 20% and for n-hexane, from 38% to about 26%.   As the grafting is increased beyond this level, the "efficiency" drops relatively slowly.   Thus it is evident that at low levels of grafting, the chains formed are more effective in reducing the free volume than at higher levels of grafting.   A possible explanation of these observations can be made in the following terms.   Before grafting, the film was swollen in the styrene–methanol mixture.   At low levels of grafting, it is likely that the grafting reaction is not diffusion controlled.   This means that there is sufficient monomer dissolved in the film to enable the efficient utilization of free radical sites for graft copolymerization and for the rate of chain termination to be relatively high.   Thus it would be expected that at low levels of grafting, the grafting frequency (number of grafted chains per backbone molecule) would be high and the grafted side chains relatively short.

At higher levels of grafting, it seems that both the growth and termination steps become diffusion controlled because the film, being about 10 mil, is relatively thick.   Stannett et al.[18] found evidence of the diffusion-controlled growth step in a 1-mil cellulose acetate film.   A similar effect may occur for the films used in the present study.   Accordingly, at high levels of grafting, the grafting frequency would be expected to be lower because of slow diffusion of monomer to the free radical sites.   The diffusion-controlled

termination would give rise to an effect analogous to the Trommsdorff effect, with the result that the side chains that are formed are of high molecular weight. There is also the possibility of a nonuniformity of grafting across the film because of the thick film used. This means that the magnitude of the diffusion-controlled factor would be higher at the center of the film than near the edges which are in contact with the styrene-methanol solution. Although it is not possible to obtain data on the molecular weight distribution of the grafted polystyrene chains on polyethylene, Huang and Chandramouli[19] have recently investigated the structure of cellulose–styrene graft copolymers. Their work indicates that the molecular weight distribution of the grafted polystyrene side chains is very broad, indicating a relatively large amount of low molecular weight material. It is plausible, therefore, that short chains which result in higher grafting frequency have a greater effect on the reduction on free volume than do longer chains of relatively low grafting frequency.

Returning now to the relative effects of crystallinity and grafting on the free volume reduction, it is seen that in a 55% crystalline polymer, the free volume is reduced to 50% of the "theoretical" free volume, while the addition of 5% graft results in another 30% to 50% reduction. It therefore appears that on a weight basis, the grafting process presents a greater impediment than does the crystalline phase of the polymer. Accordingly, in a graft copolymer, especially at low levels of grafting, the effect of disruption of crystallite regions on the transport properties would be small unless these disruptions were of major magnitude. An example of this is shown in the behaviour of $D_{c=0}$ as the grafting is increased (Fig. 2). It can now be seen that it is possible for some disruption of crystallites to occur with grafting, but the net effect can still be a lowering of $D_{c=0}$. The results in Tables VI and VII also show that the effect of temperature on the "efficiency" of the free volume is not very pronounced. If there is an effect, its magnitude is too small to show up when compared to the ability of the grafted side chains and crystallites to lower the free volume.

Based on the fundamental parameters obtained, it is possible to discuss some of the important aspects of the effects of grafting on permeation selectivity. One of the major aims of the present investigation is the possible applications of graft copolymers as permselective membranes. For a polymer membrane to be useful for industrial separations, it must combine a high permeability with a good ability to separate the required mixture. In a separate study, Huang and Fels[2] have shown that grafting side chains onto the main backbone of a polymer results in a "tight" structure and enhances the separation of binary organic liquids. In point of fact, it is felt that the major factors involved in the improvement of separation by grafting are (a) a high grafting frequency, (b) short side chain length, and perhaps (c) side chain conformation, although no data on this aspect was obtained in the present study.

However, the results of the present investigation also indicate that because the introduction of grafted polymer side chains decreases the free

volume, the diffusion coefficients are correspondingly lowered. This would mean a lower mixture permeability if the solubility remained constant. Thus, to increase the permeability, an increase in solubility is required. This can be accomplished by choosing the grafting polymer to be one whose solubility parameter is close to the solubility parameter of one of the components in the liquid mixture. The solubility of the component will thus tend to increase as the amount of grafting is increased and offset a lowered diffusion coefficient. Indeed, the increase in solubility might be large enough to result in an increase in permeability with per cent grafting.

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