On the role of penetrant structure in diffusion in structured polymers*

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Marked differences between the diffusional behaviour of linear and non-linear penetrant molecules in structured polymers exist, which remain hitherto unexplained. The existing theories of transport in polymers have been re-examined with a view to explain such differences. Direct and indirect experimental evidence has been analysed to support the view-point that linear molecules diffuse by a segmental motion. A diagnostic method in the context of a modified Maxwell model has been proposed to differentiate between different diffusive phenomena. The role of co-operative segmental motion for the polymer matrix has been quantitatively examined. Possible technological implications of the findings of the work have been elaborated on.

INTRODUCTION

Study of transport in polymers provides a useful tool to investigate polymer structure[1] and to elucidate structure–property relationships in polymers. In addition, knowledge of influence of polymer morphology on transport properties has pragmatic technological implications in the field of polymer applications as barrier materials, controlled rate drug release systems and as membranes. Diffusion and permeation of gases, organic vapours and liquids in structured polymers have been therefore extensively studied.

The functional dependence of diffusivity on crystallinity in semi-crystalline polymers has been explained in the literature on the basis of (a) linear dependence of diffusivity on the amorphous fraction[2], (b) the concept of transmission function[3], (c) a two parameter model suggested by Michaels and Bixler[4] and (d) modification of Maxwell's equation for electrical conductivity of composite systems[5]. Recently Kulkarni and Mashelkar[6] extended the last approach to develop a modified Maxwell model and correlated successfully the diffusion phenomena in crosslinked polymers.

According to the two phase models of transport in semi-crystalline polymers, the polymer consists of a continuous amorphous phase into which the impermeable crystallites are embedded. It must be noted that all the above mentioned models predict a decrease in diffusivity with increase in crystallinity. These models, however, do not take into consideration more subtle aspects of the structure of the amorphous phase. This aspect has been recently considered by Klein[7], who showed on the basis of theoretical considerations that diffusivity of certain long chain molecules increases with increasing crystallinity. These predictions were subsequently substantiated by experimental results[8]. The concept of freely jointed chains, which is used in the development of the Klein theory, precludes the application of it to short chain molecules.

There exists a class of penetrants whose diffusional behaviour cannot be explained on the basis of considerations summarized in the earlier paragraphs. As we shall show later, analysis of experimental observations in these cases made by us indicates that apart from polymer morphology, the structural attributes of diffusant molecules play an important role in the transport process. Thus the mechanism of transport largely depends upon the geometry of the penetrant molecule. Some interesting observations are reported below.

(1) Sefton and Chiang[1] studied the diffusion of iso-octane in sclair polyethylene resins over a wide range of percentage crystallinity and crystallite sizes. Contrary to normal expectations, the authors reported an increase in diffusion coefficient of iso-octane with increasing crystallinity.

(2) Aitken and Barrer[9] reported diffusivity of isomers of butane and pentane in crosslinked rubbers. The diffusivity decreased in the order n-butane > iso-butane and n-pentane > iso-pentane > neo-pentane. An analysis of the data indicated that the diffusivity-crosslink density relationship proposed by Kulkarni and Mashelkar[6] was obeyed only in the case of neo-pentane, but the other isomers did not obey it.

(3) Chen and Ferry[10] studied the diffusion of radioactively tagged n-dodecane and n-hexadecane in natural rubber at various levels of crosslinking. These authors observed that the activation energy for diffusion of such long chain linear molecules was close to that for butane and pentane, which was reported by Aitken and Barrer[9]. Furthermore, the decrease in diffusivity with increase in crosslinking was far more for a smaller molecule such as nitrogen in comparison with that for a larger molecule such as hexadecane.

In summary then, there exist in the literature a number of anomalous observations concerning diffusion of linear molecules in structured polymers, which cannot be explained on the basis of existing theories of diffusive transport in polymers. We propose to re-examine the

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Table 1 Influence of crystallinity on transition temperature of polypropylene (Data in reference 12)

Polypropylene	Specific gravity	T_δ (°C)	Crystallinity (%)
Atactic	0.860	−4.7	9
Isotactic (annealed)	0.899	−4.5	44
Isotactic (quenched)[1]	0.890	−3.5	36
Isotactic (quenched)[11]	0.885	−1.5	32

theories of transport in polymers in the context of the above anomalous observations. The phenomenological differences in diffusion of linear and non-linear molecules in polymers will be demonstrated. These will be explained for the first time on the basis of differences in the mechanism of diffusion and will be substantiated by evaluating the data reported by earlier workers. Technological implications of the results will also be discussed.

THEORIES OF DIFFUSIONAL TRANSPORT IN POLYMERS

Above we briefly enumerated the theories of diffusional transport in polymers. In the following paragraphs, salient features of two phase models of transport in polymers elucidated by Michaels and Bixler[4] and by Kulkarni and Mashelkar[6] will be discussed. This will be followed by an analysis of Klein's[7] considerations of topological constraints on diffusion of linear molecules in semi-crystalline polymers.

Michaels and Bixler (MB) model

According to Michaels and Bixler[4], diffusivity (D) in semi-crystalline polymers is given by the equation

$$D = D^*/\tau\beta \qquad (1)$$

Here D^* denotes the diffusivity in purely amorphous polymer, τ denotes the geometric impedence factor and β is the chain immobilization factor.

The geometric impedence factor τ signifies the decrease in diffusion coefficient resulting from the fact that the penetrant has now to diffuse through the amorphous regions of non-uniform cross sectional area. τ increases with crystallinity but is independent of penetrant size.

Depending upon the crystallization conditions, a number of polymer chains encompass both crystalline and amorphous regions. Mobility of a chain in the amorphous region is hindered because of the participation of a segment of the same chain in the crystalline region. The decrease in diffusivity due to this immobilization of chains is accounted for by the chain immobilization factor, β. It increases with crystallinity and decreases with increasing crystallite size if the crystallinity remains unchanged. Although β has been successfully correlated with the molecular diameter of the diffusant, such a correlation does not appear to be based on established concepts. That such a correlation is indeed possible, is explained by the fact that the extent of immobilization remaining the same, its effectiveness in reducing the diffusion coefficient depends upon the molecular diameter of the diffusant[11]. Further, the assumption that degree of immobilization should be a characteristic of the polymer morphology alone, leads to the conclusion that the differences in the energy of activation of diffusion are due to energy of activation for jump of the diffusant only, while the energy of activation for hole formation should be constant. If the energy of activation for hole formation is independent of the crystallinity of the polymer, we would anticipate the transition temperature of semi-crystalline polymers to be independent of the crystallinity. Unfortunately, there have not been many systematic efforts to evaluate the effect of crystallinity alone on glass transition temperature, since other parameters such as stereoregularity and orientation also play an important role. Newman and Cox[12] reported that the crystallinity and stereospecificity have a more pronounced influence on the transition temperature than the contribution from individual parameters. In order to study the effect of these parameters, these authors studied the influence of annealing on transition temperature of polypropylene. From the data on density reported, we have calculated the crystallinity. The data are summarized in *Table 1*, which indicates that the transition temperature is almost independent of the crystallinity and crystallite sizes. Hoffman and Weeks[13] have also reported that increase in crystallinity from 38.8% to 82.2% had no effect on transition temperature of poly(chlorotrifluoroethylene).

It is clear that the explanation of an increase in diffusivity of iso-octane with increase in crystallinity of sclair polyethylenes by MB model poses certain conceptual difficulties. To demonstrate this we evaluated τ from Sefton and Chiang's[2] data. The chain immobilization parameter β was evaluated indirectly in terms of D^*. The results are summarized in *Table 2*. It is clear that the chain immobilization parameter β decreases with increasing crystallinity, a situation which is difficult to visualise physically.

Sefton and Chiang[1] explained their results by pointing out that in sclair polyethylenes, an increase in crystallinity results from fewer number of crystallites of larger size rather than larger number of crystallites of same size. It was further argued that in such a case the geometric impedance factor τ remains unaffected. Sefton and Chiang, however, did not give any reasoning for making such an assumption. On the contrary, β, which was thought to be proportional to the interfacial area of the crystalline/amorphous regions, was assumed to be decreased.

The inverse relationship between crystallite size and the chain immobilization parameter can be easily explained. However, in the literature no data are available to substantiate this. It is probably because of the fact that both crystallinity and crystallite size cannot be controlled at will during crystallization. We detected only one observation supporting the above argument. Gardner and McNally[4] studied the effect of extrusion temperature

Table 2 Evaluation of parameters of Michaels and Bixler's model (Data in reference 1)

Poly-ethylene	Crystal-linity (%)	Diffusivity $D \times 10^8 \mathrm{cm^2\,s^{-1}}$	τ	$(\beta/D^*) \times 10^{-5}$
8107	43	8.2608	3.8	31.856
E341–01	54	14.7826	4.35	15.551
8507	61	28.2608	4.70	7.529
8707	65	36.9565	5.30	5.105
2908	74	48.2608	6.15	3.369

Table 3 Effect of morphology on diffusion of CI disperse yellow in polypropylene (Data in reference 14)

Extrusion temperature	Spherulite radii $\times 10^6$ m	Crystallinity (%)	$D \times 10^8$ cm^2 s^{-1} 72°C	80°C	90°C
210–240	2.56	32	0.86	1.21	1.68
230–260	3.25	31	1.15	1.54	3.61
250–280	5.06	31	2.09	1.94	3.88
260–290	6.31	29	2.36	2.79	4.57

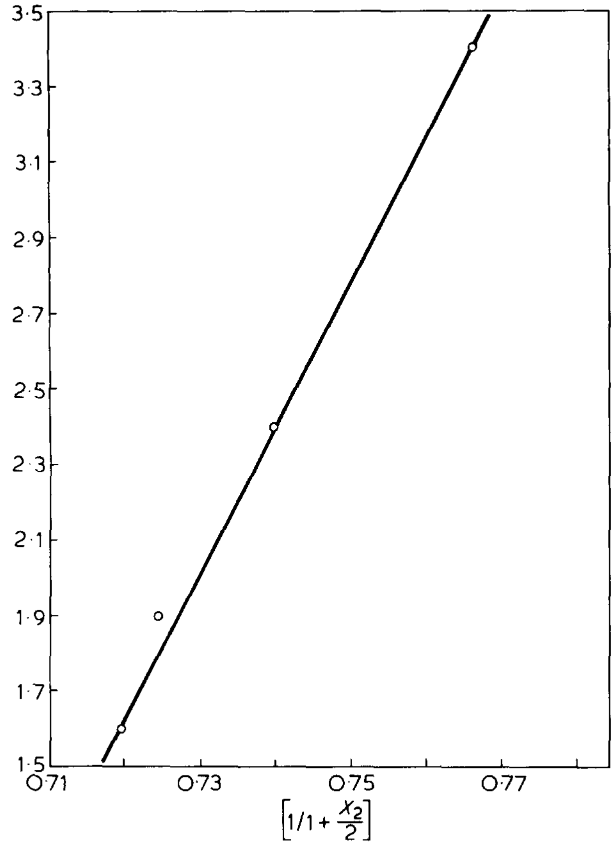


Figure 1 Effect of crystallinity on diffusion of oxygen (*D*) in polythene (Data: reference 17)

on morphology of polypropylene and on the diffusivity of the disperse dye (CI disperse yellow 3) in polypropylene. From the data summarized in *Table 3*, we conclude that in addition to crystallinity, the crystallite diameter has a significant influence on diffusivity. Thus, crystallinity remaining unchanged, diffusivity increases with increasing crystallite size as a result of decrease in β.

Sclair polyethylene resins are unique in the sense that in these systems crystallinity as well as crystallite sizes are increasing. Consequently, an increase in diffusivity with crystallinity can only be explained if it can be assumed that the decrease in β resulting from an increase in crystallite size is greater than the increase in β resulting from an increase in crystallinity and the increase in τ resulting from an increase in crystallinity. This does appear to be improbable.

We can assume that β is related to the interfacial area between the crystalline/amorphous regions. We can then conclude that the polymer chains which encompass the crystalline and amorphous regions play an important role in the diffusion process. We shall discuss this point and its implications in further detail.

Modified Maxwell (MM) model

Kulkarni and Mashelkar[6] used Maxwell's original considerations of the problem of electrical conductivity in a composite system comprising uniform spheres dispersed in a continuous medium and devised a Modified Maxwell (MM) model to correlate diffusivity in semi-crystalline and crosslinked polymers. The expressions were given by

$$D = D^*\left[\frac{1}{1+\frac{x_2}{2}}\right] + D_0, \quad \text{for semicrystalline polymers} \tag{2}$$

and

$$D = D^*\left[\frac{1}{1+\frac{x_c}{2}}\right] + D_0, \quad \text{for crosslinked polymers} \tag{3}$$

where D^* and D_0 denote parameters that are characteristic of the polymer–penetrant system and x_2 and x_c denote crystalline and crosslink fractions respectively.

Kulkarni and Mashelkar[16] have tested the utility of these relationships for a wide range of polymer–penetrant systems. A typical plot of diffusivity of oxygen as a function of crystallinity of polyethylene is shown in *Figure 1* to demonstrate the validity of equation 2.[17] *Figure 2* shows that equation 3 is obeyed for diffusion of chrysophenine G in crosslinked cellophane[18].

We shall now examine the data reported by Aitken and Barrer[9] on diffusivity of isomers of butane and pentane in natural rubber. These data are plotted in *Figure 3* in the framework of the MM model. It is seen that the relationship proposed by MM model is obeyed in the case of neo-pentane alone. Furthermore the diffusivity of the isomers reduces in the order normal > iso > neo.

Figure 4 shows the data illustrating the influence of crosslinking of natural rubber on diffusivity of hexadecane taken from the studies by Chen and Ferry[10]. The data have been again plotted in the framework of MM model (equation 3). It is clear from the figure that crosslinking has practically no influence on the diffusivity of hexadecane compared to that on diffusivity of nitrogen. Thus, for a marginal increase in crosslink fraction from

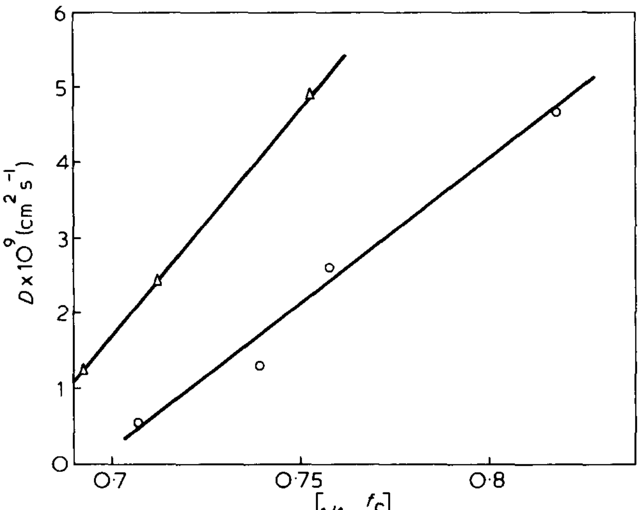


Figure 2 Effect of crosslinking on diffusion of chrysophenine G (*D*) at 70°C in cellophane crosslinked with dimethylol ethylene urea, (○); and Bis hydroxy ethyl sulphone, (△) (Data: reference 18)

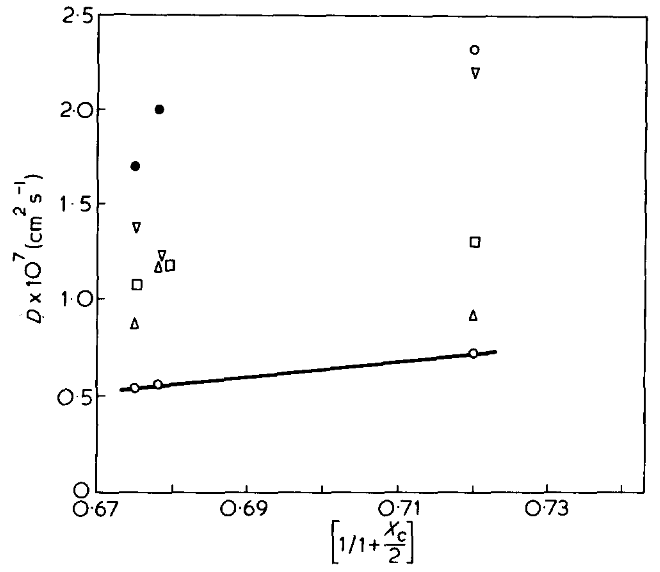


Figure 3 Effect of crosslinking on diffusivit; of n-butane, (●); iso-butane, (□); n-pentane, (△); iso-pentane, (△); and neo-pentane, (○); at 30°C in crosslinked rubber (Data: reference 9)

0.667 to 0.669, diffusivity of nitrogen decreased by 70%, whereas that of hexadecane decreased by only 20% for an increase in crosslink fraction from 0.70 to 0.75. The evidence presented above shows that the linear diffusants with a sufficiently long chain behave in such a way that the conventional two phase model such as MM model cannot correlate their behaviour.

Topological constraints on diffusion of linear molecules: Klein's model

Klein[7] investigated the problem of diffusion of linear molecules in semicrystalline polymers. It was shown that the structural attrubutes of amorphous phase, which do not affect the diffusion of a penetrant of radius less than 4 Å, play an important role in the transport of linear diffusants. Klein showed that diffusion coefficient in such systems is expressed by the equation

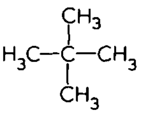
$$D\alpha \frac{(1-x)}{N}[1+2\alpha\lambda(x_\infty - x_0)N^{1/2}+4\alpha^2\lambda^2(x_\infty - x)^2 N]^{-1} \tag{4}$$

where x is crystalline volume fraction, N is the number of freely jointed chain links, α and λ are constants and x_∞ is the crystalline volume fraction in polymer coiled extremely slowly. Equation 4 predicts an increase in diffusivity of chain molecules with increase in crystallinity. The predictions were experimentally confirmed by Klein for diffusion of C_{25}–C_{45} molecules in linear polyethylenes which were cooled at different rates[8].

It must be mentioned at the outset that the semiempirical relationship developed by Klein[7] cannot quantitatively describe the increase in diffusivity of iso-octane with increase in crystallinity of sclair polyethylenes reported by Sefton and Chiang[1]. Nonetheless the basic concept underlying development of equation 4 is important. It was shown by DeGennes[20] that the diffusion of a polymer chain within a network polymer occurs by reptative motion rather than by the motion of the molecule as a whole. Indeed, diffusion by propogation of stored length defect along the contour of the diffusant molecule can occur in linear penetrants of chain lengths, which are much shorter than those proposed by Klein[7]. Thus, in the case of linear diffusants, the segmental motion can be considered to lead to the propagation of stored length defect along the length of the molecule leading to displacement of the centre of the molecule. Thus, it appears that the concept of a subchain instead of using statistical segment as a unit in the chain deformation process might turn out to be useful (see e.g. Marrucci and Hermans[21]).

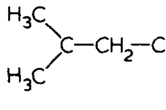
Role of segmental motion in diffusion of linear penetrants

In the light of the above discussion, we now propose a possible explanation of the differences in diffusional behaviour of neo-pentane, iso-pentane and n-pentane (indicated earlier) in the context of segmental motion. Three isometic forms of pentane are shown below.



$$H_3C-\overset{CH_3}{\underset{CH_3}{C}}-CH_3$$

Neo-pentone



Iso-pentone

CH_3–CH_2–CH_2–CH_2–CH_3

n-pentone

It is clear from the structures that none of the bond rotations around any carbon atom can lead to a change in the position of the centre of gravity of the neo-pentane molecule. Diffusion of neo-pentane, therefore, cannot result from segmental motion. In the case of iso-pentane, the rotations of the two methyl groups attached to the carbon atom will have a similar effect, while rotations of the ethyl link attached to the tertiary carbon atom permits certain conformations which will lead to a change in the position of the molecule's centre of gravity. The number of such permissible conformations is much larger in the case of n-pentane, wherein rotation around each carbon atom is possible. It is therefore clear that diffusivities of the three isomers should be in the order n-pentane > iso-pentane > neo-pentane. In the case of neo-pentane alone, diffusion

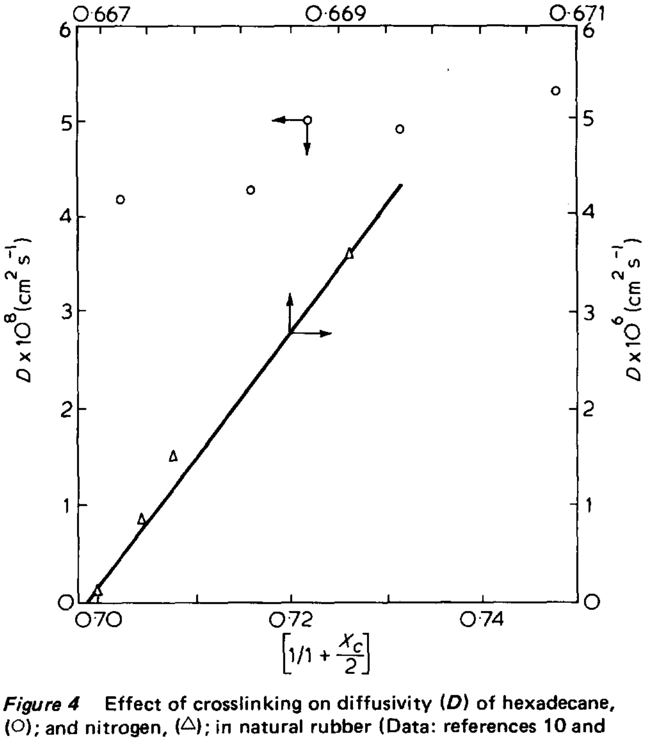


Figure 4 Effect of crosslinking on diffusivity (*D*) of hexadecane, (○); and nitrogen, (△); in natural rubber (Data: references 10 and 19)

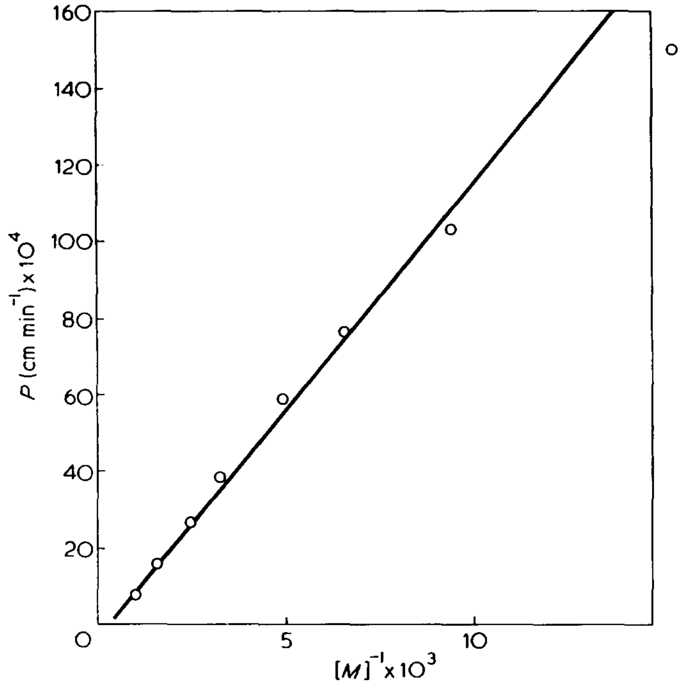


Figure 5 Permeabilities (*P*) of polyethylene glycols in cellophane as a function of permeant molecular weight (*M*) (Data: reference 23), (O), Ethylene glycol

results from the movement of the molecule as a whole and not due to the segmental motion. It is, therefore, not surprising that the MM model relationship observed in the case of diffusion of gases in network polymers, is observed in the case of neo-pentane alone.

The ideas of diffusion by segmental motion of the penetrant molecule for a linear penetrant implied in the preceding paragraph can be used to derive, semi-qualitatively, a relationship between the diffusion coefficient and the molecular weight of the penetrant. Following the arguments of Auerbach *et al.*[22] it can be shown that in such a case the diffusion coefficient will vary inversely as the molecular weight. We shall again examine this implication in the light of the data in the literature[23–25]. Huang and Jarvis[23] have presented extensive data on permeation of glycols of different molecular weights in cellophane system. In *Figure 5* we show the values of permeability (proportional to diffusivity) plotted against the molecular weight of the penetrant. It was observed that the proposed reciprocal relationship between diffusivity and molecular weight is obeyed in all the cases except in ethylene glycol. This is to be expected. Ethylene glycol has only two carbon atoms, in which case diffusion cannot occur *via* segmental motion. Higher homologues of the series contain sufficient numbers of carbon atoms to allow for such a motion. Chen and Ferry[10] also observed that in various polymers, the diffusivities of n-hexadecane and n-octane vary inversely with their molecular weights.

The linear relationship between reciprocal of the molecular weight of the diffusant and the diffusivity implies that the friction coefficient for the translational movement of the linear molecules is directly proportional to the molecular weight. This conclusion is significant as it implies that the diffusion coefficients in polymer–polymer systems may be evaluated from the knowledge of diffusion coefficients of the oligomers. The hypothesis can be tested by extending the relationship to polymer–polymer systems. We analysed this hypothesis by evaluating the literature data[26] on diffusion of polyisoprene in nàtural rubber. *Figure 6* shows a plot of diffusivity of polyisoprene in natural rubber as a function of the reciprocal of molecular weight of polyisoprene. The linearity of the curve indicates that our hypothesis may be used as a good approximation for estimating polymer–polymer diffusivity. The evidence provided by us shows that the diffusivity of linear molecules varies inversely with the molecular weight of the diffusant. This also signifies that diffusion is the result of segmental motion.

The ease of rotation around each carbon atom of the linear diffusant enables the molecule to adopt a large number of conformations. Each such displacement will effectively shift the centre of the molecule, i.e. result in diffusion. It then follows that since the segment size of the diffusing molecule remains unchanged, the energy of activation for jump will remain constant. Consequently, the number of CH_2-units in the backbone participating in the cooperative movement leading to hole formation and the energy of activation for hole formation step, remains constant. The net result is that the energy of activation for diffusion becomes independent of the chain length of the diffusing molecule. We have summarized the values of energy of activation for a number of long chain penetrants in *Table 4*. It is seen that the activation energy is approximately of the order of 12 ± 2 kcal mol^{-1}. This lends further support to our hypothesis.

It may be argued that the hydrocarbons studied by Chen and Ferry are much higher in the homologous series. The behaviour of polyglycols can similarly be attributed to the flexibility of the ether linkage. The role of segmental motion in the diffusion of hydrocarbons

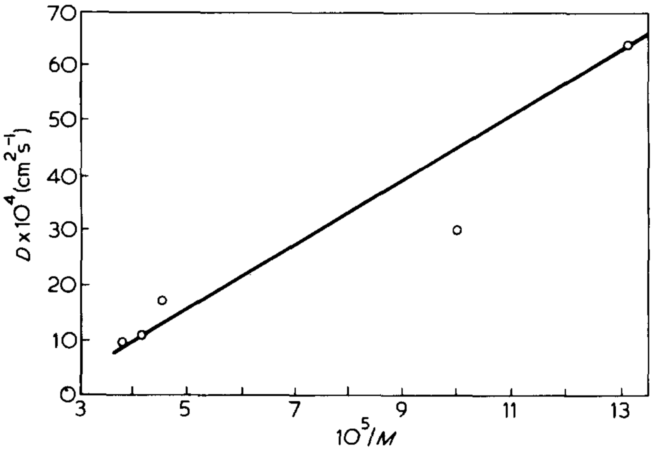


Figure 6 Diffusivity (*D*) of polyisoprene at 100°C in natural rubber as a function of molecular weight (*M*) of polyisoprene (Data: reference 26)

Table 4 Energy of activation for diffusion of various penetrants (Data in references 9, 10)

Penetrant molecule	ΔE_D kcal mol^{-1}
n-Butane	12.2
Iso-butane	13.8
n-Pentane	14.5
Iso-pentane	14.3
Neo-pentane	13.2
n-Hexadecane	10.08
n-Dodecane	10.08

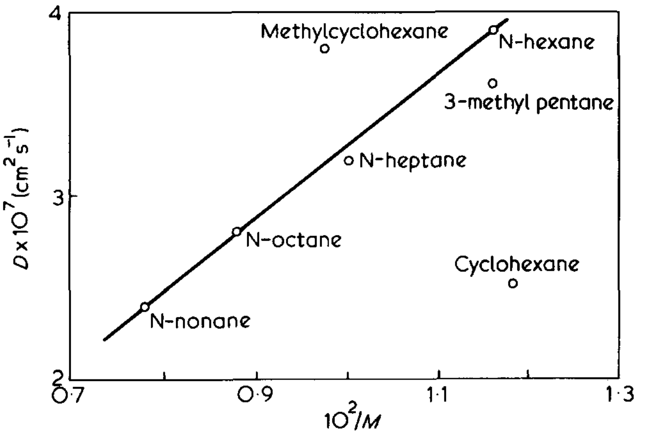


Figure 7 Diffusivities (D) of hydrocarbons in polyethylene at 25°C as a function of molecular weight (M) of the hydrocarbons

studied by Aitken and Barrer can be similarly questioned. However, definitive studies on permeation of hydrocarbons through polyethylene membranes have now become available which substantiate our hypothesis.

Peters *et al.*[30] studied the permeation of a number of linear, branched as well as cyclic hydrocarbons in polyethylene. Their data indicated that the activation energy for n-hexane, n-heptane, n-octane and n-nonane could be given as 7.15 ± 0.6 kcal mol^{-1}. However, the activation energy for a molecule such as iso-octane was approximately 10.5 kcal mol^{-1}.

Figure 7 shows a plot of diffusivity of different hydrocarbons in polyethylene plotted as a function of reciprocal molecular weight of the diffusant. It is clearly seen that the linear relationship holds good only for linear hydrocarbons (i.e. n-hexane, n-heptane, n-octane and n-nonane), but does not hold good for branched molecules (3-methyl pentane) or a cyclic molecule (e.g. cyclohexane and methyl cyclohexane). This firmly substantiates our hypothesis.

Re-examination of the two-phase concept

We have shown earlier that an analysis of Sefton and Chaing's[1] data on the basis of MB model leads to a physically improbable situation. It is interesting to examine how the parameters τ and β are affected when a linear molecule capable of diffusion by segmental motion (such as n-pentane) diffuses through a semi-crystalline polymer. In such a case, irrespective of the increase in crystallinity, the diameter of the amorphous channel will always be larger than the size of the penetrant segment. As a result, an increase in crystallinity will not affect segmental mobility and hence diffusivity, whereas if the molecule were not to undergo segmental motion, the impedance factor τ would have been a strong function of crystallinity.

Michaels and Bixler reported that for a given diffusant, β increases with increase in crystallinity. This results from the fact that with an increase in crystallinity, the channel diameters are considerably decreased. The decrease will affect the diffusivities of gases of larger diameters to a greater extent in comparison to gases of smaller diameters. This is evident from the reported data. In the case of diffusion of linear molecules, channel diameters will have no influence on crystallinity as shown previously. Consequently, β is not expected to increase with increase in crystallinity.

Another factor contributing to β is the crystallite size. As has been postulated by Sefton and Chaing[1], predicted from theoretical considerations by Klein for molecules capable of segmental motion and finally confirmed by Gardner and McNally[14], an increase in crystallite size results in a decrease in β. Thus, of the two morphological parameters, crystallinity and crystallite size, the former has no effect on either τ or β, whereas the latter leads to a decrease in β. This results in an increase in diffusivity with crystallinity (see *Figure 8*).

Co-operative segmental motion in the matrix

We have shown above how the segmental motion for a sufficiently long linear penetrant plays an important role in the diffusion process. We shall now examine the role of the co-operative segmental motion in the matrix in which diffusion occurs.

Diffusion in polymers consists of two steps (1) creation of free volume or a hole in which the diffusing molecule can be accommodated and (2) jump of the diffusing molecule into the hole formed in the earlier step. The hole formation is a result of thermal motion of the polymer segments, where a number of segments undergo a co-operative motion due to the localization of thermal energy. The larger the size of the diffusing molecule, the larger is the hole size required for diffusion to take place. Consequently, a larger number of chain segments will have to contribute to the hole formation step. However, diffusion of linear diffusants takes place as a result of motion of individual segments. As a result, as opposed to the case of diffusion of gases, the number of segments contributing to hole formation is not expected to increase with increasing size of the diffusant. In what follows, we will substantiate this idea by calculating the number of segments involved in the hole formation step. On the basis of Bueche's theory we shall analyse the data reported by Chen and Ferry[10] for diffusivity of hexadecane in natural rubber.

Bueche's theory[27] postulates that polymer segments will be able to move when a group of segments, normally

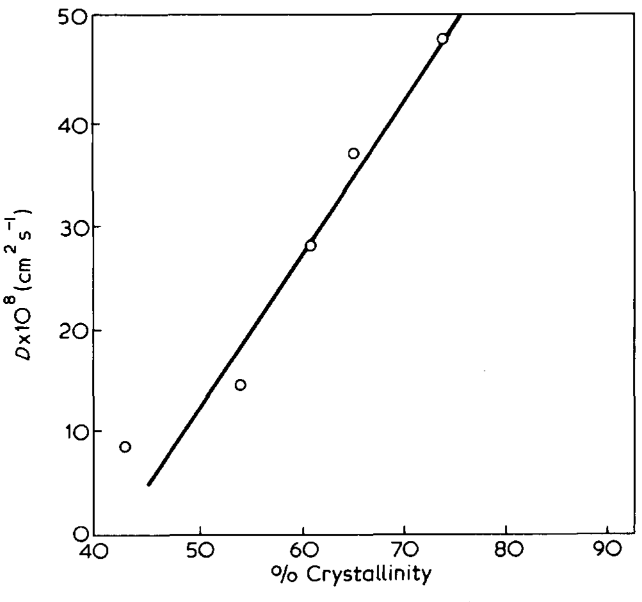


Figure 8 Effect of crystallinity on diffusivity (D) of iso-octane in sclair polyethylenes (Data: reference 1)

Table 5 Evaluation of number of $-CH_2-$ units involved in diffusion of hexadecane in natural rubber as a function of increasing crosslinking (Data in reference 10)

Sample code	$\nu \times 10^4$ mol/cc	$D_{25} \times 10^8$ cm^2 s^{-1}	T_g (K)	$D_g \times 10^{11}$ cm^2 s^{-1}	N	Number of $-CH_2-$ units
98 F	0.46	7.4131	201.95	2.3403	2.9536	4.0165
98 G	0.62	7.4131	202.63	2.5452	2.9228	4.0588
98 H	0.80	7.4131	203.39	2.7937	2.8876	4.1083
98 I	1.20	7.0794	205.09	3.2776	2.8134	4.2166
98 J	1.69	6.4565	207.16	3.8231	2.7233	4.3562
109–A_1–20	0.47	7.5857	202.00	2.4096	2.9513	4.0196
109–A_1–40	0.75	7.0794	203.18	2.6000	2.8982	4.0933
109–A_2–40	0.81	7.4131	203.43	2.8075	2.8869	4.1093
109–A_2–75	1.27	6.9183	205.38	3.3164	2.8006	4.2359
109–A_2–150	1.86	6.1659	207.88	3.9729	2.6923	4.4063
109–B_1–20	0.29	7.4131	201.23	2.1401	2.9863	3.9725
109–B_1–40	0.58	7.0794	202.46	2.3802	2.9617	4.0055
109–B_2–40	0.54	7.4131	202.29	2.4410	2.9381	4.0377
109–B_2–75	0.88	7.0794	203.73	2.7807	2.8736	4.1283
109–B_2–150	1.52	6.4565	206.44	3.5115	2.7544	4.3069

occupying a volume V_0 has its volume increased to Q_{00}, as a result of volume fluctuations. The frequency of segmental motion P, is given by

$$P = P_0/2\left[1 - \mathrm{erf}[A/B\sqrt{T} - B\sqrt{T}]\right] \quad (5)$$

Here P_0 denotes the proportionality constant and A and B are defined as follows:

$$A = \frac{\alpha_2(Q_{00} - V_{00})}{2\beta R} \quad (6)$$

$$B = \alpha_2(V_{00}/2\beta R)^{1/2} \quad (7)$$

Here α_2 is the difference in volume expansion coefficient in the liquid and glassy phases, Q_{00} is the volume required for segmental rotataion, V_{00} is the occupied volume for a polymer segment and β is the compressibility coefficient. A and B can be calculated such that the plot log D vs. log T is superimposed on log $\frac{P_0}{2P}$ vs log (B^2T) plot. Q_{00} and V_{00} can then be calculated from the knowledge of α_2 and β.

Bueche[28] also arrived at the WLF equation on the basis of the free volume theory, which was expressed as follows:

$$\ln a_T = -\frac{[Nf_c/\langle f_g \rangle][T - T_g]}{T - T_g + [\langle f_g \rangle/\alpha]} = \ln\frac{P_g}{P_T} \quad (8)$$

Here, N denotes the number of free segments undergoing segmental motion, f_c is the critical fractional free volume at temperature T and f_g is the fractional free volume for the diffusion step at glass transition temperature. Substituting $\frac{D_g}{D_T}$ for $\frac{P_g}{P_T}$ we obtain:

$$-N = \frac{f_g}{f_c}\ln\frac{D_g}{D_T} + \frac{f_g^2 \ln\frac{D_g}{D_T}}{f_c(T - T_g)} \quad (9)$$

We shall now evaluate N for the data reported by Chen and Ferry on the diffusion of n-hexadecane in natural rubber. The relevant approximation made as well as the details of a typical calculation are shown in the Appendix.

The calculations show that for a wide range of systems summarized in *Table 5*, the number of $-CH_2-$ units involved in the diffusion process of n-hexadecane turns out to be 5. This is practically the same as that involved in diffusion of carbon dioxide in polyvinylchloride–polyvinyl acetate copolymer films[29], which conclusively proves that the number of $-CH_2-$ units involved in the diffusion step remains constant.

CONCLUSIONS

Although extensive experimental data and theories on diffusion in polymers are available in the literature, our understanding of the phenomenon is far from complete. This is due to the fact that diffusivity is affected by a number of parameters, whose influence cannot be singled out in each case. For instance, it is not clear as to which of the two factors, viz. crystallinity or crystallite size will have a more dominant influence on the chain immobilization parameter β. In the latter case, one would anticipate an increase in diffusivity with crystallinity even for molecules such as nitrogen, oxygen or neon diffusing in systems such as sclair polyethylenes. A systematic quantitative investigation of the influence of crystallization conditions on crystalline structure, intercrystalline tie molecules and diffusivity of non-reacting gases and that of linear molecules are required to evaluate the influence of each parameter. Possibilities should be explored to extend the Klein model to account for diffusion behaviour of C_5–C_{20} hydrocarbons.

Apart from the fundamental aspects of the phenomena discussed above, the concept of diffusion by segmental motion appears to have far reaching consequences of technological importance. Some of these are mentioned below.

Migration of extender oils from rubbers and of paraffin oils (used as tertiary plasticizers) in PVC formulations can be attributed to the fact that such linear molecules are able to diffuse out as a result of segmental motion. Deliberate introduction of more complex structures, e.g. pentaerythritol esters of long chain fatty acids would at least partly overcome the problem.

One is faced with a problem of exactly opposite nature in the field of stabilization of rubbers. Compared to liquids, diffusivity of antioxidants is much lower in rubbers, which accounts for their lower efficiency. Further, with an increase in crosslinking, the diffusivity of antioxidants decreases more rapidly than that of oxygen.

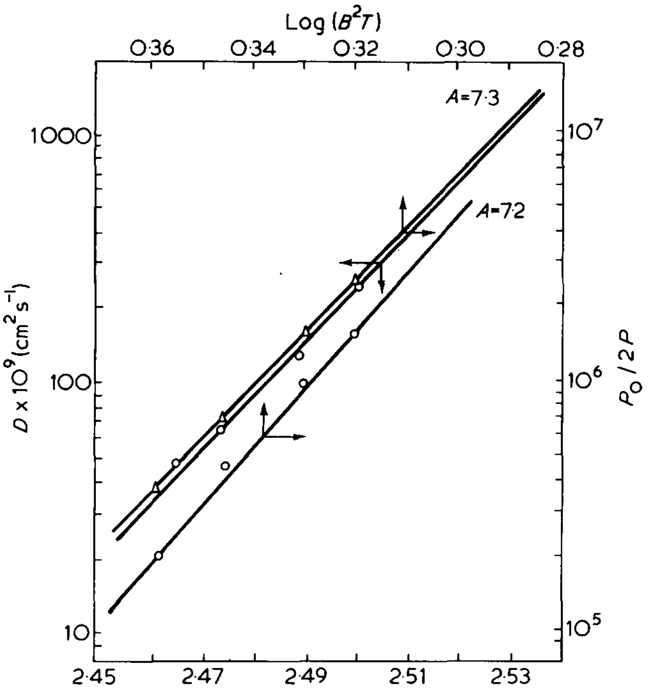


Figure 9 Plots for best fits of A and B in Bueche's equation (Data: reference 10)

Consequently, antioxidant efficiency decreases with increase in crosslink density. Diffusivity of an antioxidant whose structure is so modified that it is capable of diffusing by segmental motion, would be less affected than that of oxygen (see *Figure 4*). As a result, antioxidant efficiency is expected to increase with increased crosslink density.

In the field of polyester dyeing, diffusion of a disperse dye into the semicrystalline polymer is the rate controlling step. Diffusivity of the dye decreases with increase in crystallinity and draw ratio, which retards the rate of dyeing. Deliberate introduction of a linear chain into the dye structure would enable it to diffuse by segmental motion. In such an event, diffusivity would indeed increase with crystallinity and enhance dyeing rates.

In summary, the concept of diffusion of linear molecules by segmental motion proposed in this paper provides guidelines for further research in this field, which would lead to a better understanding of the phenomenon. The paper also proposes the use of diagnostic plots of the kind used in *Figure 3* to distinguish the nature of behaviour of isomers of pentane in the framework of MM model. Further, it also suggests a potential approach for manipulation of molecular architecture of plasticizers, antioxidants and dyes so as to enhance their efficiency.

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APPENDIX

Kumins and Kwei[29] assumed that each $-CH_2-$ unit in the polymer occupies a volume of 30 Å^3. The number of units involved in the diffusion step is then obtained by dividing V_{00} by 30. This value, when divided by N, gives the number of $-CH_2-$ units in the segment which will contribute to hole formation step.

Figure 9 shows plots of log D vs. log T and of log $\frac{P_0}{2P}$ vs. log B^2T. The best fit was obtained for $A=7.3$ and $B=8.48\times10^{-2}$.

The coefficient of compressibility, β was calculated from the relationship

$$S=[\alpha T/\beta]^{1/2}$$

where S denotes the solubility parameter and α, the coefficient of expansion above T_g. It was found to be 2.689×10^{-11} dyne^{-1}.

From these data we have

$$Q_{00}=536\ \text{Å}^3/\text{molecule and } V_{00}=356\ \text{Å}^3/\text{molecule}$$

For the calculation of N in equation 3, the glass transition temperature was calculated using the relationship

$$T_g=T_{g0}+\frac{3.9\times10^4}{M_c}$$

where T_{g0} denotes the glass transition temperature of the uncrosslinked polymer and M_c, the molecular weight between the crosslinks. Diffusivity of hexadecane at T_g was calculated from the knowledge of the temperature dependence of diffusivity. It was further assumed that $f_g=0.11$ and $f_c=0.30$. Substitution of above values gives $N=2.8$ for the vulcanizate number $109-A_2-150$. From this value of N, number of $-CH_2-$ units involved in the diffusion process of hexadecane, was calculated by dividing V_{00} by 30 N and was found to be 4.40, i.e. 5.