Diffusion and Solution of Gases into Thermally Softened or Molten Polymers:

Part II. Relation of Diffusivities and Solubilities with Temperature Pressure and Structural Characteristics

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Solubilities and diffusivities of various gases (helium, nitrogen, carbon dioxide, argon, neon, krypton, and monochlorodifluoromethane) in molten or thermally softened polymers (polyethylene, polypropylene, polyisobutylene, polystyrene, and polymethylmethacrylate) have been correlated with structural characteristics, temperature, and pressure. Temperature dependence of both Henry's Law constants and diffusivities were of the Arrhenius equation form. No appreciable effect of pressure was found for either Henry's Law constants or diffusivities up to 300 atm. Earlier correlations for Henry's Law constants in solid polymer systems were found to be inapplicable for molten and thermally softened polymers. New correlations were developed individually for the latter systems. The correlating factor used was the gas Lennard-Jones force constant. Existing correlations for diffusivities were also found not to apply to molten and thermally softened systems. New correlations were again developed on an individual polymer basis. These related diffusivity to gas Lennard-Jones collision diameter or molecular diameter. Generalized correlations were also developed that held for a number of polymers. These were for both Henry's Law constants and diffusivities.

In an earlier paper (*1*) solubility and diffusivity data were presented for gases absorbed into molten or thermally softened polymer systems. The intent of this paper is to use these data together with other literature information (*2* to *10*) to correlate solubilities and diffusivities with temperature, pressure, and gas and polymer structural characteristics for molten or thermally softened polymer systems.

EFFECT OF PRESSURE ON GAS SOLUBILITIES AND DIFFUSIVITIES

It was shown previously (*1*) that Henry's Law held for pressures up to 20 atm. for a large number of gas-molten polymer or gas-thermally softened polymer systems. Included were data for sorption of carbon dioxide, nitrogen, helium, and argon in polyethylene, polypropylene, polyisobutylene, polstyrene, and polymethylmethacrylate. Additional data for monochlorodifluoromethane in polyethylene, polypropylene and polystyrene as well as krypton and neon in polyisobutylene and polymethylmethacrylate showed an adherence to Henry's Law up to 20 atm. Other investigators (*2* to *4*) found that Henry's Law held up to at least 100 atm. (nitrogen, methane with polyethylene) and possibly (*5*) up to 300 atm. (nitrogen, hydrogen with polystyrene). Likewise, no appreciable effect of pressure on diffusivities was found for the foregoing systems up to 300 atm.

EFFECT OF TEMPERATURE ON SOLUBILITIES AND DIFFUSIVITIES

Previous work on sorption of gases into solid polymer systems (*6* to *10*) had shown that both solubilities and diffusivities followed the Arrhenius behavior with temperature.

The same result was found for gas sorption into molten polymer systems. In Figure 1 the logarithms of experimental Henry's Law constant are plotted versus the reciprocal of temperature for two systems (*1*), carbon dioxide-polyethylene and carbon dioxide-polypropylene. As can be seen the following relation holds:

$$H = H_o \exp\left(-\frac{E_s}{RT}\right) \tag{1}$$

Values of E_s, the heat of solution, are compared to those found for other gas-molten polymer or thermally softened polymer systems (*1* to *5*) in Table 1. Values for helium, nitrogen, carbon monoxide, argon, methane, and carbon dioxide in solid amorphous polyethylene (*7*) were 1.4, 0.5, 0.5, —0.3, —0.7 and —1.3 k.cal./mole. In addition, values of 1.8, 0.1, —0.8, —2.8 and —2.2 k.cal./mole were found for helium, nitrogen, oxygen, carbon dioxide, and ethylene respectively in solid natural rubber (*12*).

From these data it can be seen that the values and signs of E_s change with the gas-polymer system. In gas-solid polymer systems the heat of solution of a gas in a given polymer moved from endothermic to exothermic as the gas Lennard-Jones collision diameter increased. The same type of behavior is seen for the solution of nitrogen and carbon dioxide in molten polyethylene (Table 1). In solid polymer systems the endothermic behavior at the lower Lennard-Jones collision diameters indicates the possibility of a free volume solution model while the exo-

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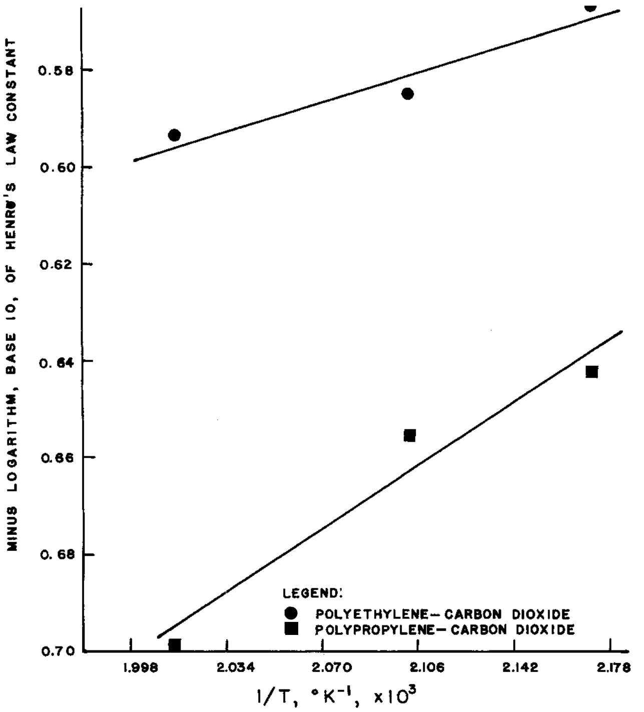

Fig. 1. Logarithm Henry's Law constant versus reciprocal of temperature.

thermic behavior for the larger Lennard-Jones collision diameters indicates a substitutional lattice solution model.

Figure 2 is a plot of the logarithm of diffusivity vs. the reciprocal of temperature for two systems studied in the present work. Once again an Arrhenius type of relation is found as with gas-solid polymer systems.

$$D = D_0 \exp\left(-E_d/RT\right) \tag{2}$$

TABLE 1. HEATS OF SOLUTION AND ENERGIES OF ACTIVATION FOR VARIOUS STUDIES

Gas	Polymer	Reference	Temperature range °C.	E_s k.cal./mole	E_d k.cal./mole
CO_2	molten polyethylene	present	188-224	—0.80	4.4
N_2	molten polyethylene	(*2* to *4*)	125-188	0.95	2.0
CO_2	molten polypropylene	present	188-224	—1.7	3.0
N_2	thermally softened polystyrene	(*5*)	120-188		10.1
H_2	thermally softened polystyrene	(*5*)	119-188		9.6
N_2	thermally softened polystyrene	(*5*)	136-188	—1.7	
H_2	thermally softened polystyrene	(*5*)	126-188	—1.9	
CH_4	thermally softened polystyrene	(*2* to *4*)	125-188	1.05	3.6

Values of E_d for gas-molten polymer systems are given in Table 1. In solid polyethylene systems E_d values for helium, nitrogen, carbon monoxide, argon, methane, and carbon dioxide were 5.6, 9.0, 8.8, 9.3, 10.4, and 8.5 k.cal./mole. Likewise, E_d values for solid natural rubber were 4.3, 8.7, 8.3, 8.9, and 9.5 for helium, nitrogen, oxygen, carbon dioxide, and ethylene. The gas-solid polymer data show that the energies of activation for diffusivities increase with increasing Lennard-Jones collision diameters. The same behavior is noted for gas-molten polymer systems.

EFFECT OF GAS AND POLYMER STRUCTURE ON SOLUBILITY

Michaels and co-workers (*6* to *8*) studied the relation of gas structure to solubility in solid polymers. They found that a solution essentially takes place in amorphous regions and that solubility could be related to gas structure. A relationship was developed for the solubility constant in the amorphous phase of polyethylene and the Lennard-Jones force constant (ϵ/K) of the sorbed gas. The relation resulted in a linear plot when the logarithm of the solubility constant was plotted against ϵ/K. Michaels

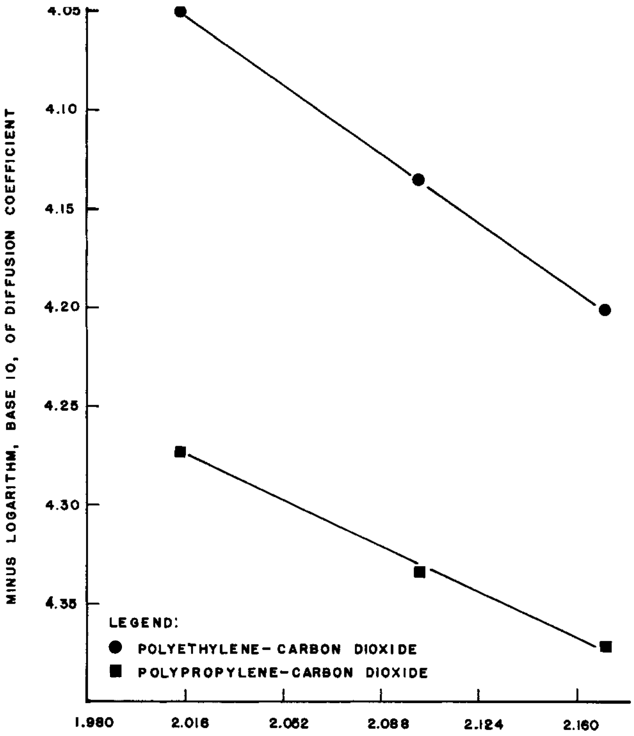

Fig. 2. Logarithm diffusivity versus reciprocal of temperature.

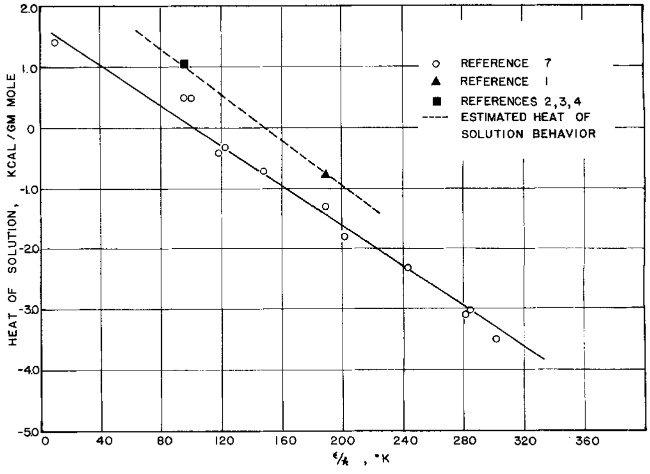

Fig. 3. Heat of solution versus Lennard-Jones force constants for solid amorphous and molten polyethylene.

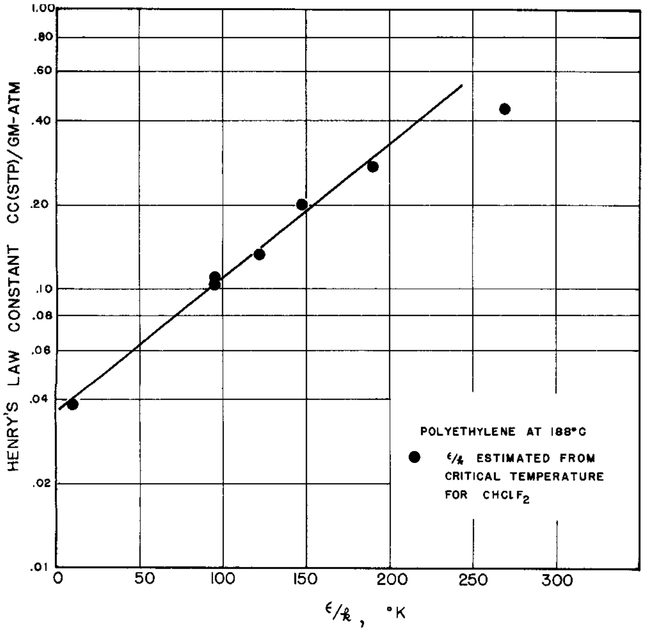

Fig. 4. Logarithm Henry's Law constants versus Lennard-Jones force constants for molten polyethylene at 188°C.

(7) also presented a correlation of the heat of solution with the Lennard-Jones force constant (see Figure 3).

It was decided to use these existing correlations and determine if they could represent the solubility data (*1* to *4*) for gases in molten polyethylene since the melt should have been completely amorphous in nature. The average percent deviation was 31.3% for polyethylene and 44% for the other polymers (polystyrene, polypropylene, polyisobutylene, and polymethylmethacrylate).

It was obvious that a routine extension of Michaels' work would not correlate the data for molten or thermally softened polymer systems. New correlations (Figures 4 and 5) were then developed. Average percent deviations were 13% for polyethylene and 24.8% for the remaining polymers.

The correlations of Figures 4 and 5, therefore, appear to more satisfactorily describe the solubility behavior of gases in molten or thermally softened polymer systems than the existing correlations of Michaels. There was, however, a difficulty in that the type of correlations shown in Figures 4 and 5 require experimental data for a variety of gases interacting with a given molten or thermally softened polymer. (The same defect applied to Michaels' correlations.) The result was that solubility data could not be estimated for systems for which no experimental data were available.

As a consequence of this shortcoming, attempts were made to develop a generalized solubility correlation. The most successful of these is shown in Figure 6. Data calculated for the correlation polymers (polystyrene, polyisobutylene, and polymethylmethacrylate) deviated by 42.6% on the average from experimental data. If the data of Newitt and Weale (*5*) were not considered [these data were pointed out to be in question (*1*) earlier], the average error dropped to 24.4%.

On the basis of the preceding it is recommended that:

1. The correlations of the present work (Figures 4 and 5) be used to estimate Henry's Law constants in molten or thermally softened polymer systems rather than existing correlations for solid systems (*6* to *8*).
2. Henry's Law constants for which no experimental data are available be estimated from Figure 6. This technique is limited to polymers which are essentially amorphous in the solid state.

EFFECT OF GAS AND POLYMER STRUCTURE ON DIFFUSIVITY

Michaels, et al. (*9*, *10*) have developed a correlation for diffusivities of gases in solid polymer systems. Their technique established a relation between the logarithm of the diffusivity divided by the square of the gas molecule diameter and the gas molecule diameter itself. Data for solid, amorphous polyethylene were successfully correlated with this method.

A routine extension of this correlation to molten and thermally softened polymers was unsuccessful since the average percent deviations were 89% for polyethylene and 82% for the other polymers (polypropylene, polystyrene, and polyisobutylene).

New correlations (Figures 7 and 8) for diffusivity of gases into molten and thermally softened polymers were then developed since a routine extension of Michaels' work was unacceptable. These correlations yielded the following average percent deviations: polyethylene (30%), polypropylene (29.9%), polystyrene (41.3%) and polyisobutylene (48.3%). The overall average deviation was 35.4%.

The correlations shown in Figures 7 and 8 appear then to be superior to Michaels' work. However, both these and Michaels' earlier work share a common defect. The shortcoming is that they cannot be used to estimate diffusivity behavior for polymers for which no experimental data is available. As a result, a generalized correlation of diffusivity behavior was developed (*11*) as per Figure 9. This correlation was combined with the dependence of diffusivity on Lennard-Jones collision diameter to yield

$$D = \frac{K_1 \exp(-K_2 M)}{(\sigma)^{3.3}} \tag{3}$$

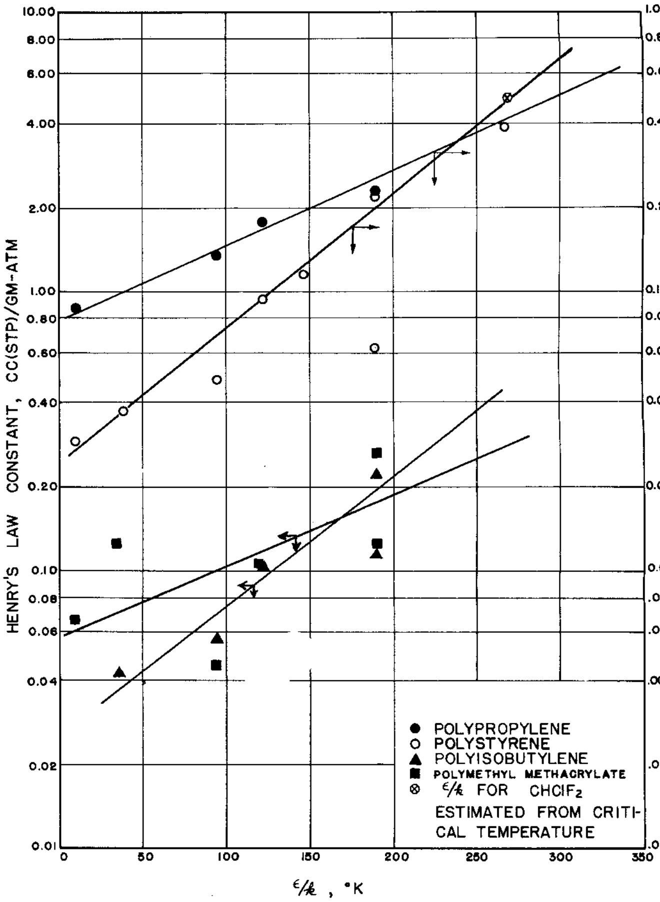

Fig. 5. Logarithm Henry's Law constants versus Lennard-Jones force constants for molten polypropylene, thermally softened polymethylmethacrylate, polystyrene, and polyisobutylene at 188°C.

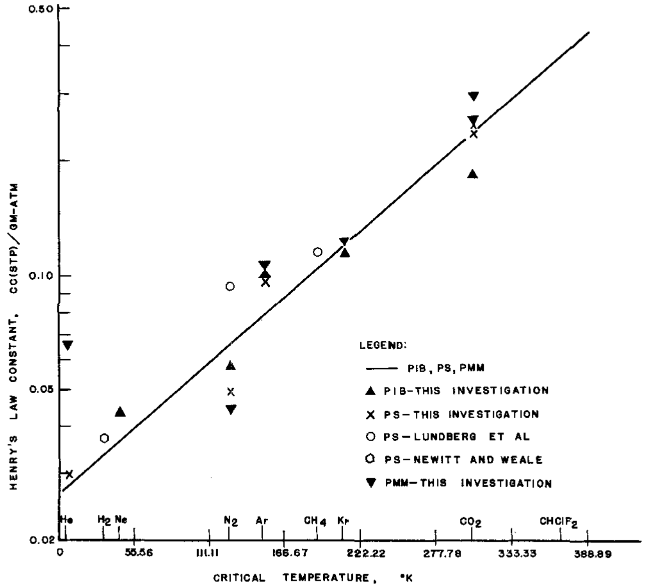

Fig. 6. Logarithm Henry's Law constant versus gas critical temperature for various polymers at 188°C.

At 188°C., K_1 and K_2 were 0.016 and 0.034 respectively. Values of diffusivity calculated from Equation (3) deviated by 41.5% from the experimental values. Individual average deviations for the polymers were polyethylene (44.1%), polypropylene (34.6%), polyisobutylene (38%), and polystyrene (41%).

It should be noted that Equation (3) and Figures 7 and 8 do not indicate two different dependencies of D on molecular diameter or Lennard-Jones collision diameter. In the one case (Figures 7 and 8) the log of D/d^2 is a function of d while in Equation (3) D is related to $(\sigma)^{-3.3}$ [or $(d)^{-3.3}$]. These are not inconsistent since they merely show D can be related to d by two different methods. Furthermore, the treatment of Figures 7 and 8 is not the same as that of Michaels (*6* to *8*) since the slope of the correlation lines differ.

Analysis of the diffusivity correlations indicates

1. Individual polymer data can be correlated as per Figures 7 and 8. Such a technique will yield estimated diffusivity values within 35% of experimental values.
2. Data for polymers for which no data are available can be estimated by using Equation (3). Such estimations should be confined to materials which have basically the polyethylene chain with various pendant groups such as polypropylene, polystyrene and polyisobutylene.

DISCUSSION

The present study has developed correlations for solution and diffusion of gases into molten or thermally softened polymers. It has been found possible to generally correlate such data for groups of polymers. In the case of Henry's Law constants the correlation applied to polystyrene, polymethylmethacrylate, and polyisobutylene. The diffusivity correlation held for polymers which had the basic polyethylene chain structure.

Reasons for these general correlations are not complenely clear. A possible factor in the case of Henry's Law constants could be the polymer chain flexibility. This does not, however, seem to be the case. Polymer chain flexibility is related to the polymer glass transition temperature (*13*). Hence, the polymer glass temperatures can be used as an index of chain flexibility. On this basis the polymers would be ordered as follows. Polyethylene (lowest glass temperature), polyisobutylene, polypropylene, polystyrene, and polymethylmethacrylate (*14*). However, in Figure 6, polyethylene and polypropylene deviate from

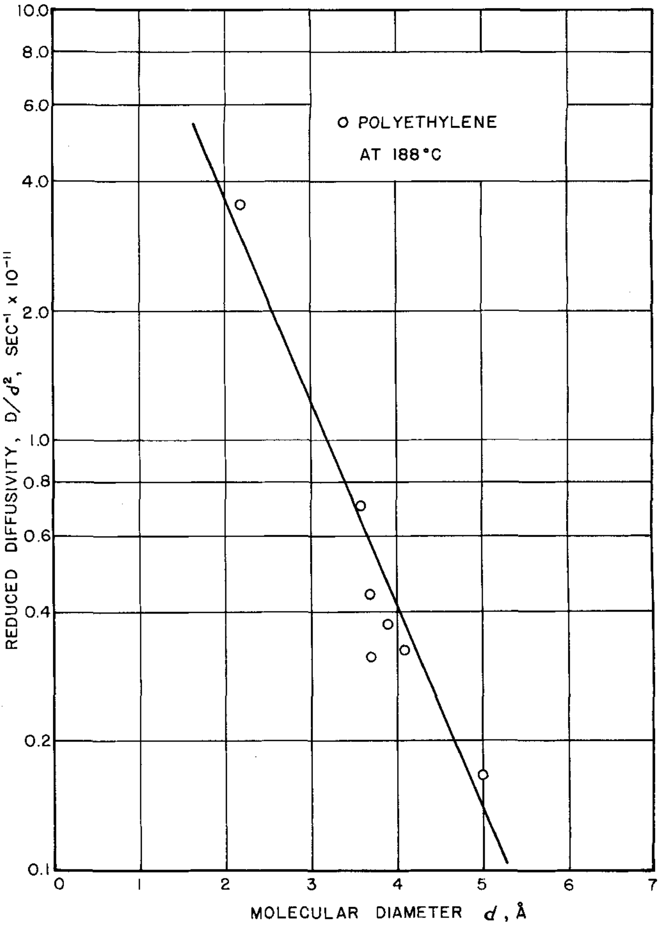

Fig. 7. Logarithm (diffusivity divided by square of gas molecular diameter) vs. molecular diameter molten polyethylene at 188°C.

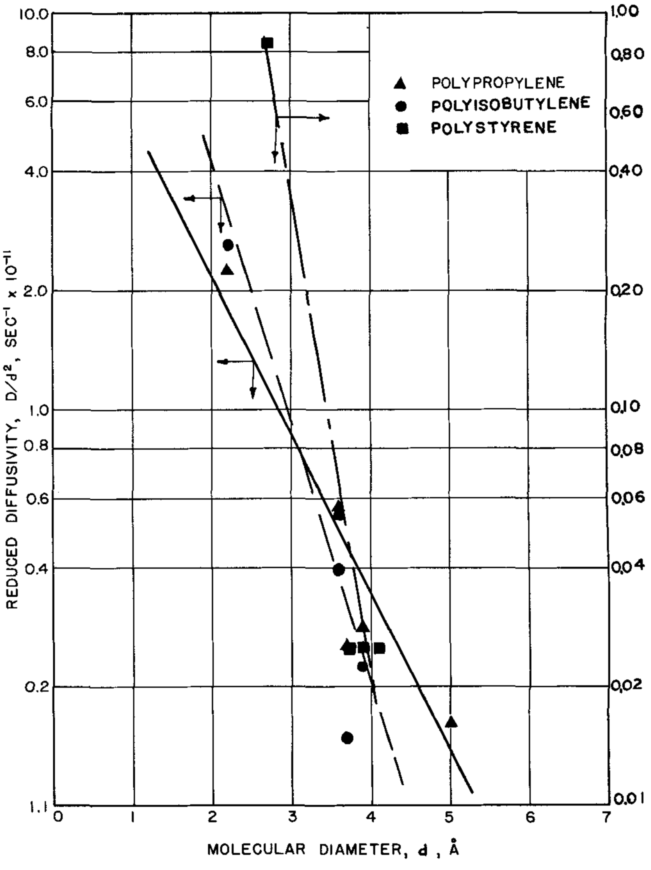

Fig. 8. Logarithm (diffusivity divided by square of gas molecule diameter) vs. molten polypropylene and thermally softened polyisobutylene and polystyrene at 188°C.

the correlation line while polyisobutylene agrees with the line. This then would seem to eliminate the possibility of chain flexibility as an explanation for Figure 6. In a similar manner polymer cohesive energy density would not seem to be a factor since the values for polyetheylene and polyisobutylene are almost identical (*15*).

However, further examination of the correlation of Figure 6 shows one factor common to polystyrene, polyisobutylene, and polymethylmethacrylate, namely, that they are mainly amorphous in the solid state. Furthermore, the data for both polyethylene and polypropylene (semicrystalline in the solid state) deviated badly from both the correlation line and data of Figure 6. These results taken with those of Foster and Griskey (*16*), who found that compressibilities of molten polymers are not independent of solid polymer morphology, indicate a possible reason for the behavior of Figure 6. This is not to say that crystallites exist in molten or thermally softened systems but rather that the factors which influence the morphological behavior of the solid state still can prevail in molten or thermally softened systems. In particular, the effect of the pendant groups in polystyrene, polymethylmethacrylate and polyisobutylene appear to continue to influence polymer behavior.

Obvious explanations for Equation (3) and Figure 9, the generalized diffusivity correlation, also do not hold. Chain flexibility is not an appropriate explanation since as before the glass temperature of polyisobutylene lies between those for polyethylene and polypropylene while the correlation shows the polyisobutylene diffusivity data to be lower than either of the other two polymers. The same holds true for cohesive energy density since the values for polyethylene and polyisobutylene are nearly the same. Upon consideration of existing theories of diffusion (*17* to *20*) in liquids a pattern for the correlation does become discernible. All of these theories share one factor in common, namely, diffusivity is inversely proportional to a viscosity. One cannot properly speak of a viscosity in describing the four polymers of Figure 9 at 188°C. One reason is that polystyrene and polyisobutylene form thermally softened masses rather than melts (as with polyethylene and polypropylene). Furthermore, in polymeric melts one cannot speak of a viscosity because of the non-Newtonian nature of these materials.

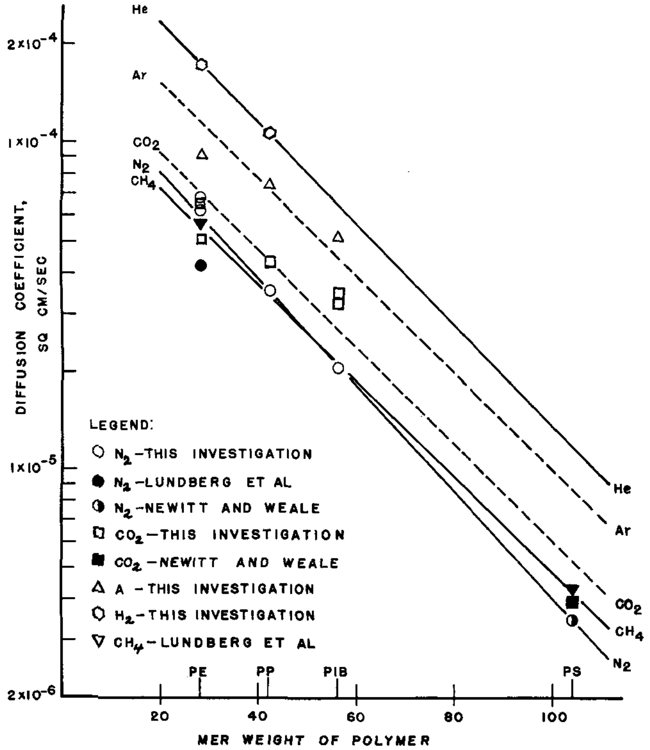

Fig. 9. Logarithm diffusivity versus polymer mer weight at 188°C.

It is possible, however, to speak of relative consistencies of the polymers of Figure 9 or, in another sense, of the relative mobilities of diffusing species in them. If such a distinction is made, the materials could be arranged (in order of increasing consistency or decreasing diffusing species mobility) as polyethylene, polypropylene, polyisobutylene, and polystyrene. This fact checks with Einstein's original relation which showed diffusivity to be related directly to the mobility of the diffusing species.

Hence, it would seem that the relation indicated in Figure 9 between diffusivity and mer weight actually is between diffusivity and mobility of the diffusing species since these polymers differ structurally in the pendant groups attached to the basic polyethylene chain. For this reason, it is recommended that Equation (3) be used only to estimate data for polymers whose basic chain structure corresponds to polyethylene.

NOTATION

D = diffusivity, sq.cm./sec.
D_o = constant, sq.cm./sec.
E_d = energy of activation for diffusion k. cal./g. mole
E_s = heat of solution, k. cal./g. mole
H = Henry's Law constant, cc.(STP)/g. atm.
H_o = constant, cc.(STP)/g. atm.
K_1, K_2 = constants
M = polymer mer weight
R = gas constant, cal./g. mole °K.
T = temperature, °K.
K = Boltzmann constant
ϵ/K = Lennard-Jones force constant
σ = Lennard-Jones collision diameter
d = molecular diameter

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