Diffusion of Additives in Polyolefins

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Synopsis

A simple radio-tracer method based on ^{14}C is described for determining the diffusion coefficient of an additive in a polymer. Two theoretical models representing extreme cases for the diffusion system are discussed and shown to yield the same solution to within 10%. The diffusion coefficients of didodecyl 3,3'-thiodipropionate, N-octadecyldiethanolamine, and 1,1,3 - tri(2 - methyl - 4 - hydroxy - 5 - *tert* - butylphenyl)butane migrating in polyethylene, polypropylene, and poly-4-methylpentene-1 have. been measured over temperature ranges of 50–80°C., within the range 20–200°C. In each case the variation of the diffusion coefficient D with temperature T can be represented by an Arrhenius equation $D = D_0 \exp \{ -E/RT \}$, where the activation energy E is virtually independent of the size and shape of the diffusing molecule. The activation energy depends upon the polymer and is about 12.5, 21, and 14.5 kcal./mole for polyethylene, polypropylene, and poly-4-methylpentene-1, respectively.

INTRODUCTION

Reactions involving large molecules in polymers are likely to be controlled by the diffusion of one or more of the reactants. Hence a knowledge of the dependence of diffusion coefficients on temperature, molecular weight, and molecular structure of the additive and polymer will be invaluable in helping to understand reaction mechanisms. For example, the efficiency of antioxidant action will depend in part upon whether the antioxidant moves to the site of oxidation or vice versa, or whether an intermediate situation exists. For these reasons the diffusion coefficients of didodecyl 3,3'-thiodipropionate (DLTP), 1,1,3-tri(2-methyl-4-hydroxy-5-*tert*-butyl-phenyl)butane (a condensate of 3-methyl-6-*tert*-butylphenol with crotonal-dehyde) and N-octadecyldiethanolamine in polyethylene, polypropylene, and poly-4-methylpentene-1 were measured over temperature ranges of 50–80°C. between 20°C. and 200°C.

Rough calculations based on published data[1-3] showed that the diffusion coefficient was likely to be small, and consequently in any experiment involving migration from one polymer sheet to another, it would be necessary to use thin specimens, about 0.1 cm. thick, in order to complete the experiments in a reasonable time. As conventional analytical techniques are not sufficiently sensitive to follow migration of additives in these polymers at concentrations below 0.1 wt.-%, it was decided to use a radio-tracer method similar to those described by Auerbach et al.[1] and Gromov et al.[2]

EXPERIMENTAL

Materials

Didodecyl-1-[14]C 3,3'-thiodipropionate (DLTP). This was prepared by the alcoholysis of dimethyl 3,3'-thiodipropionate (0.1 mmole) with radioactive dodecyl alcohol (0.2 mmole), 1.2 wt.-% p-toluenesulfonic acid being used as catalyst. The mixture was heated at 120°C. for a total of 10 hr. and the crude product purified by chromatography in Analar benzene on deactivated Type H alumina to give a yield of 90.4% of theoretical. The radiochemical purity of this material was checked by measurement of its specific activity (found 5.01 curie/mole; calculated 5.06 curie/mole) and by reverse-phase chromatography in ethanol on acetylated paper; the position of the radioactive material was detected by autoradiography on x-ray film. The labeled DLTP gave only a single spot near the solvent front (R_f = 0.90), while in a comparative run dodecyl-1-^{14}C alcohol gave a spot near the origin, R_f = 0.02.

N-Octadecyl-1-^{14}C-diethanolamine (N-ode). Octadecyl-1-^{14}C alcohol was converted into the bromide by reaction with hydrogen bromide at 110°C. for 1 hr. The cold product was dissolved in petrol and fractionated on a column of Type H alumina by eluting with petrol, b.p. 30–40°C. Eight fractions and a final acetone purge were obtained. The bulk of the active product, 90.9% of theoretical yield, was found in fractions 1–3. With the use of inactive material, fractions 1–3 were shown to be free from OH by infrared spectroscopy. Further active material found in fractions 5–7 was known from inactive runs to be unchanged octadecanol.

The octadecyl-1-^{14}C bromide was stirred with excess diethanolamine for about 4 hr. at 110°C. After cooling, the solid upper layer was dissolved in 30–40°C. petrol ether, absorbed on a column of alumina, and eluted with a mixture of 30–40°C. petrol and methanol (3 vol.-%) to give 10 fractions. Fractions 1 and 2 were unchanged octadecyl bromide; fractions 8 and 9 contained octadecyl-1-^{14}C-diethanolamine, yield 80.7% of theoretical. The product had an infrared spectrum identical with that of an authentic pure sample of inactive octadecyldiethanolamine. Specific activity was found to be 1.85 curie/mole (calculated 1.89 curie/mole). Radiochemical purity (isotope dilution) was 100.6%.

1,1,3-Tri[2-methyl-4-hydroxy-5-(tert-butyl-2-^{14}C)phenyl]butane. This was prepared by the condensation of crotonaldehyde with 3-methyl-6-(tert-butyl-2-^{14}C)phenol. The latter, supplied by the Radiochemical Centre, Amersham, was purified by chromatography (type H alumina, benzene followed by ether) to remove about 3% of 3-methyl-4,6-di(tert-butyl-2-^{14}C)-phenol. Crotonaldehyde was purified by fractional distillation, b.p. 103.0°C.

In the condensation reaction, 0.348 mmole crotonaldehyde was heated for 1 hr. at 80°C. under nitrogen with 1.04 mmole 3-methyl-6-(tert-butyl-2-^{14}C)-phenol in methanol using hydrochloric acid as catalyst. The product was

recrystallized twice from toluene, purified by chromatography on type H alumina (eluent 30–40°C. petrol:ethyl ether 1:1, followed by ether for the main fraction) and finally dried *in vacuo*. The yield was 42% of theoretical of 1,1,3-tri[2-methyl-4-hydroxy-5-(*tert*-butyl-2-^{14}C)phenyl]butane having a specific activity of 0.0237 curie/g., radiochemical purity of 99.2% and melting range 188–196°C. For convenience this product will be referred to as phenol A hereafter.

Polymers. These were free from additives and contained a minimum of catalyst residues. Some physical properties are summarized in Table I. The percentage crystallinity refers to the specimen after molding. Intrinsic viscosities were measured in decalin at 135°C. Carbonyl and vinyl unsaturation could not be measured for poly-4-methylpentene-1 owing to the fact that the polymer absorbs in the relevant parts of the spectrum.

TABLE I

Physical Properties of Polyethylene, Polypropylene, and Poly-4-methylpentene-1

Property	Polyethylene	Poly-propylene	Poly-4-methyl-pentene-1
Crystallinity, %	54	60	53
Carbonyl content, groups/1000 C	0.017	0.006	—
Unsaturation as —CH=CH—, groups/1000 C	0.076	—	—
Unsaturation as >C=CH$_2$, groups/1000 C	0.273	—	—
Chain branching, methyl groups/1000 C	26.5	—	—
10^{-5} × weight-average molecular weight	7.3	3.5	8.6
Intrinsic viscosity, dl./g.	1.26	2.6	2.0

Procedure

The polymers were molded under vacuum into disks about 4 cm. in diameter and 0.15 cm. thick. One side of each disk was shaped like a shallow well with walls 0.05 cm. thick and 0.025 cm. high. About 0.5 ml. of a solution consisting of 0.6 g. polyisobutylene and 4–10 mg. of radioactive additive in 100 ml. hexane was added slowly in drops to the shallow well, care being taken to cover the surface as evenly as possible. After the hexane had evaporated, a further 1.0 ml. of radioactive solution was added in two portions of 0.5 ml. as before. Ideally, the active layer should be of uniform thickness but surface tension and an uneven distribution of the active solution produced a rippled effect. The average thickness of the polyisobutylene layer was estimated to be about 10^{-3} cm. The polyisobutylene was used to prevent the active material from flaking off the surface of the disk. A thin film of polypropylene or polyethylene 10^{-4} cm. thick was put over the tacky surface to act as a dust cover. Polyethylene film

was used for disks made from polyethylene; polypropylene film for those made from polypropylene or poly-4-methylpentene-1. The presence of this film allowed the sample to be handled with little risk of contamination. The amount of active material deposited on the disk was estimated to produce an equilibrium concentration of 8×10^{-5} g./g.

Each sample was next held under slight compression at the bottom of a small aluminum can, the base of which had been cut away to leave a hole 3 cm. in diameter. The can was kept under nitrogen at the required temperature in a vapor thermostat. From time to time the can was removed and the diffusion followed by measuring the activity of the surface exposed at the base of the can. As the diffusion equations described below are applicable only to the axial movement of the additive, edge effects due to diffusion into the well walls were reduced to a minimum by using the base of the can as a mask. In most of the experiments the surface initially non-active was the one exposed for counting.

Measurement of surface activity has been followed in two ways: (1) up to run 38 the sample was placed in contact with a piece of plastic scintillator (Naton 136, dissolved in polystyrene, made by Nash and Thompson) and the light pulses counted by means of an Ekco scintillation counter; (2) from run 38 a Geiger-Müller tube with a thin end window (thickness 2.1 mg./cm.[2]) was used. The first method was found to be slightly less reliable than the second because the presence of active material initiated a small amount of polymer oxidation (the sample had to be exposed to air during counting), which produced light pulses that were also counted.[4] The effects of oxyluminescence were observed only in the very early stages of a diffusion experiment, that is before the additive had time to reach the surface in contact with the scintillator. Once the active material was sufficiently close to the scintillator for β-rays to produce light pulses in the scintillator, they rapidly outweighed those due to oxidation. As light pulses due to oxidation required time to reach their maximum value, they were most noticeable for systems involving low diffusion coefficients, e.g., phenol A in polypropylene, and produced plots of counting rate against time similar in shape but lower in magnitude than those expected for diffusion. To avoid confusing oxyluminescence effects with diffusion, it was decided to use Geiger-Müller counting.

THEORETICAL TREATMENT

The results can be analyzed in different ways depending upon the assumptions used to describe the system. Five assumptions are common to all the treatments. These are (1) the layers of polymer, polyisobutylene, and film cover are of uniform thickness; (2) the volume of the well walls surrounding the active layer is sufficiently small in comparison with the rest of the polymer to have a negligible effect on the diffusion behavior; (3) the small amount of forward scattering[5] of the β-rays can be neglected; (4) destruction of the additive due to oxidation initiated by β-rays is small

and can be neglected; and (5) runs where scintillation counting was employed are unaffected by light pulses due to polymer oxidation. Assumptions 3 and 5 are likely to be important only in the early stages of an experiment when the diffusion is being followed from the side initially non-active, since under these conditions the counting rate is small.

Solutions of the diffusion equation, eq. (1), applicable to the current system have been published only for a few simplified cases in which the diffusion coefficient D is constant throughout the sample. In practice the diffusion coefficient of an additive in polyisobutylene is likely to be larger than that in polyethylene, polypropylene, or poly-4-methylpentene-1 because polyisobutylene is more amorphous. Consequently further assumptions have to be made about diffusion in polyisobutylene.

$$\delta c/\delta t = D\delta^2 c/\delta x^2 \tag{1}$$

Here c is the concentration of additive (in grams per milliliter), t is time (in seconds), D is the diffusion coefficient (in centimeters per second), and x is the distance (in centimeters).

Model A

The solubility and diffusion coefficient of an additive in polyisobutylene are assumed to be the same as those in the polymer being studied.

The source is defined to occupy the region $h < x < k$ with diffusion taking place into the polymer sheet $k < x < L$ and into the thin film cover $0 < x < h$. Here h is the thickness of the film cover, k is that of the film cover plus polyisobutylene layer, and L that of the entire specimen. For this model Crank[6] has given the following solution of the basic diffusion equation:

$$c/c_E = 1 + [2L/\pi(k - h)] \sum_1^{\infty} 1/n [\sin (n\pi k/L)$$

$$- \sin (n\pi h/L)] \cos (n\pi x/L) \exp \{-n^2 V\} \tag{2}$$

where V is given by $V = D\pi^2 t/L^2$ and the subscript E refers to equilibrium conditions. The counting rate R_0 at the surface $x = 0$, corresponding to the initially active side of the sample, depends upon the attenuation of the β-rays by the polymer, e.g.,

$$R_0 = H \int_0^L cf(x)dx \tag{3}$$

where $f(x)$ is the fraction of β-rays reaching the surface from nuclei disintegrating at distance x. The constant H embodies terms for the counting efficiency, the cross-sectional area of the sample surface exposed to the counter, and the specific activity of the additive. If forward scattering[5] is neglected, then to a good approximation:
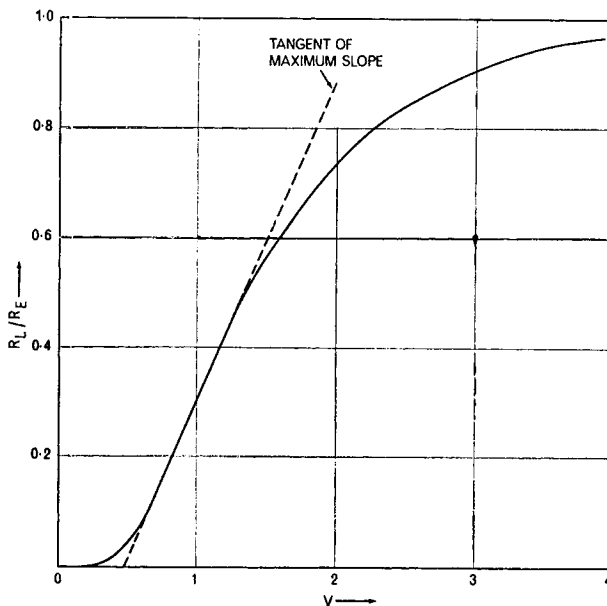
$$f(x) = \exp \{-ux\} \tag{4}$$

Fig. 1. Theoretical variation of R_L/R_E with V for model A.

where u is the absorption coefficient and falls in the range 250–270 cm.$^{-1}$
for the polymers under test.[2,7]   Substituting for $f(x)$ and c in eq. (3) and
integrating gives:

$$R_0/R_E = 1 + [2Lu^2/\pi(k - h)] \sum_1^\infty A(n)[\sin(n\pi k/L) \sin(n\pi h/L)]$$

$$\times \exp\{-n^2V\} \quad (5)$$

where the subscript 0 refers to surface $x = 0$, and the function $A(n)$ is
given by:

$$A(n) = (1 - \exp\{-uL\})/(u^2n + n^3\pi^2/L^2) \quad (6)$$

If the diffusion is followed from the surface initially non-active, i.e., at
$x = L$, eq. (5) is again obtained, with R_L replacing R_0 but $A(n)$ is now
changed to:

$$A(n) = (\cos n\pi - \exp\{-uL\})/(u^2n + n^3\pi^2/L^2) \quad (7)$$

The values of R_0/R_E and R_L/R_E have been calculated from eqs. (5), (6),
and (7) for a number of values of V by means of a computer.   A graph of
R_L/R_E against V is shown in Figure 1, from which it can be seen that the
plot is approximately linear from $R_L/R_E = 0.1$–0.5.   A straight line drawn
through this section, i.e., the tangent of maximum slope, intercepts the V
axis at 0.487.   Provided $1 \gg k/L$ and $u > 10\pi/L$, this intercept is virtually
independent of the dimensions of the sample, the quantity of antioxidant
and the absorption coefficient u.   The dimensions of the layers were set so
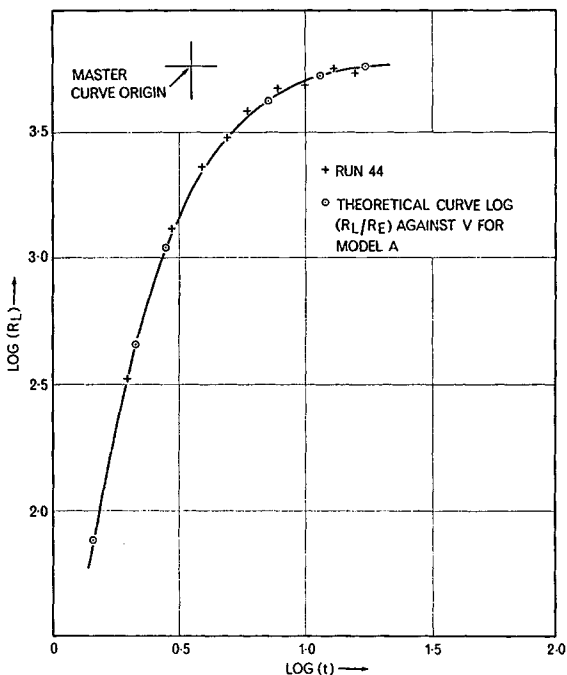
Fig. 2. Comparison of experimental and theoretical variation of the surface counting rate R_L with time t for the diffusion of DLTP in poly-4-methylpentene-1 at 200°C.

that these conditions held. The diffusion coefficient is then given by $D = 0.487\ L^2/\pi^2 t_m$, where t_m is the intercept on the time axis of the tangent of maximum slope to the experimental graph of R_L against t. This method of obtaining D will be referred to as the intercept method.

The diffusion coefficient can also be obtained by superimposing experimental plots of log R_0 or log R_L against log t on top of the corresponding master curve of log (R_0/R_E) or log (R_L/R_E) against log V. The values of R_E and $D\pi^2/L^2$ are derived from the position of the master curve origin on the experimental plot (Fig. 2). This approach will be termed the master curve method.

The intercept method can be terminated when R_L/R_E is about 0.7 and is therefore particularly useful at low temperatures where the diffusion is slow. To obtain a good fit by the master curve method, the diffusion cannot be terminated before R_L/R_E is about 0.95 or R_0/R_E is about 0.98, and as a result requires roughly twice as long as the intercept method.

Model B

Here it is assumed that (1) the polyisobutylene behaves as a perfectly stirred liquid, (2) the additive concentration just inside the polypropylene layer at the interface of the two polymers is K times that in the polyisobutylene, and (3) the cover film at the surface $x = 0$ is of zero thickness. Be-

cause of assumption *3*, the theoretical treatment is only valid for the surface $x = L$.

Experimentally K can only be obtained very approximately, by measuring the counting rates on both sides of a specimen when equilibrium has been reached. This can be done satisfactorily only for large diffusion coefficients which limits measurement to the upper end of the temperature range over which the diffusion is followed. In the case of DLTP diffusing into polypropylene for example, K could be determined only at 100 and 135°C. All the systems studied had a K value of about 0.5. It was assumed that the same value of K applied at all temperatures.

Solutions to this model have been described by Crank[6] and for the current case the variation of additive concentration with distance and time is given by:

$$c/c_E = 1 + 2(1 + a) \sum_1^{\infty} B(n) \sec q_n \cos [q_n(x - L)/(L - k)] \exp \{-q_n^2 Y\}$$

(8)

where q_n are the nonzero positive roots of the transcendental equation

$$\tan q_n = -a q_n$$

$$a = k/KL$$

$$Y = Dt/(L - k)^2$$

and

$$B(n) = (1 + a + a^2 q^2_n)^{-1}$$

Substituting for c and $f(x)$ in eq. (3) and integrating gives:

$$R_L/R_E = 1 + 2u^2(1 + a) \sum_1^{\infty} B(n) [u^2 + q_n^2/(L - k)^2]^{-1} \sec q_n$$

$$\times \exp \{-q_n^2 Y\} \quad (9)$$

It can be shown that in the limit as k approaches zero, models A and B become identical.

Equation (9) has been solved on a computer to give values of R_L/R_E for a range of values of $Dt/(L - k)^2$ and K. These calculations show that for K less than 1, the diffusion coefficient obtained with model B is always greater than that from model A, the difference increasing with decreasing K. For example, the ratio of the diffusion coefficient obtained with model B to that for model A is 1.00, 1.02, 1.07, and 1.11 for K equal to 1.0, 0.5, 0.2, and 0.1, respectively. Qualitatively, the real life situation is expected to lie somewhere between the two extremes represented by models A and B, so provided $K > 0.1$, neither should introduce more than a 10% error in D. As K was found to be about 0.5 in all cases, the results summarized in the following section were analyzed by model A because this could be used to follow diffusion from either surface.

RESULTS AND DISCUSSION

From the theoretical point of view, it is advantageous to follow the diffusion from the surface $x = L$ because the results can then be analyzed by both the intercept and master curve methods and an average taken. In addition, a run followed from the surface $x = L$ can be terminated sooner than the corresponding one followed from $x = 0$, so that any effects due to oxidation or decomposition of the additive will be kept to a minimum. For these reasons virtually all the runs were carried out with the diffusion followed from the surface $x = L$. Results for typical experiments are shown in Figures 2 and 3 and the values of diffusion coefficients at a number of temperatures given in Table II. In runs, 5, 6, and 9 the diffusion was followed from the surface $x = 0$ in order to provide checks. From a comparison of runs 6 and 7, it can be seen that the value of the diffusion coefficient based on measuring R_0 is slightly smaller than that based on R_L but is almost within the experimental error of about 5–10%.
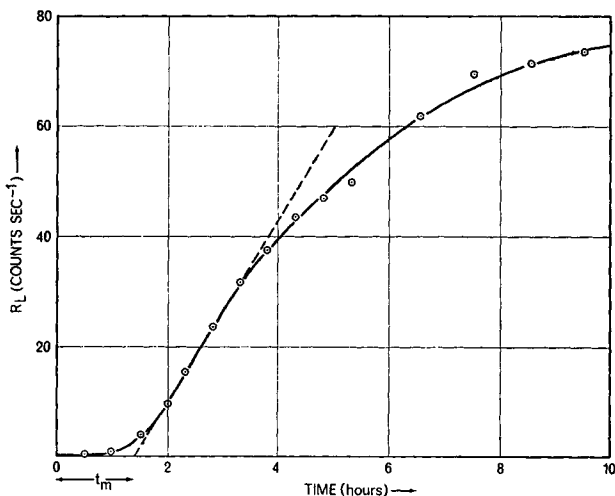
Fig. 3. Variation of surface counting rate R_L with time for the diffusion of DLTP in polypropylene at 135°C.

The diffusion of DLTP in poly-4-methylpentene-1 at 200°C. run 44, was followed by both Geiger-Müller and scintillation counting. Analyzing the results by the master curve method gave diffusion coefficients of $(1.59 \pm 0.15) \times 10^{-7}$ and $(1.68 \pm 0.15) \times 10^{-7}$ cm.²/sec. for Geiger-Müller and scintillation counting respectively, while the intercept method gave $(1.66 \pm 0.1) \times 10^{-7}$ cm.²/sec. for both counting techniques. As these results are all very close together, our assumption that oxyluminescence is not important in any of the runs followed by scintillation counting is reasonable.

The diffusion of N-octadecyldiethanolamine in polyethylene and polypropylene has produced some unusual results. Runs with polyethylene at

TABLE II
Dependence of Diffusion Coefficient on Temperature, Polymer, and Additive

Run	Polymer	Additive	Temperature, °C.	D, cm.^{2}/sec.
5	Polypropylene	DLTP	96	$(1.9 \pm 0.2) \times 10^{-8}$
6	Polypropylene	DLTP	78	$(4.1 \pm 0.2) \times 10^{-9}$
7	Polypropylene	DLTP	78	$(4.9 \pm 0.3) \times 10^{-9}$
8	Polypropylene	DLTP	135	$(1.89 \pm 0.15) \times 10^{-7}$
9	Polypropylene	DLTP	100	$(2.1 \pm 0.2) \times 10^{-8}$
10	Polypropylene	DLTP	56	$(5.4 \pm 0.4) \times 10^{-10}$
11	Polypropylene	N-ode	100	$(2.6 \pm 0.3) \times 10^{-8}$
25	Polypropylene	N-ode	78	$(6.5 \pm 0.7) \times 10^{-9}$
27	Polypropylene	N-ode	135	$(3.8 \pm 0.4) \times 10^{-7}$
14	Polyethylene	N-ode	100	$(1.1 \pm 0.1) \times 10^{-7}$
15	Polyethylene	N-ode	78	$(6.1 \pm 0.5) \times 10^{-8}$
16	Polyethylene	N-ode	56	$(2.8 \pm 0.3) \times 10^{-8}$
17	Polyethylene	N-ode	20	$(1-2) \times 10^{-9}$
19	Polyethylene	DLTP	100	$(2.4 \pm 0.2) \times 10^{-7}$
28	Polyethylene	DLTP	56	$(2.3 \pm 0.3) \times 10^{-8}$
30	Polyethylene	DLTP	78	$(7.5 \pm 0.8) \times 10^{-8}$
49	Polyethylene	Phenol A	100	$(3.5 \pm 0.2) \times 10^{-8}$
50	Polyethylene	Phenol A	78	$(1.34 \pm 0.1) \times 10^{-8}$
52	Polyethylene	Phenol A	56	$(4.3 \pm 0.4) \times 10^{-9}$
40	Poly(4MP)[a]	Phenol A	140	$(2.5 \pm 1.0) \times 10^{-9}$
47	Poly(4MP)	Phenol A	173	$(9.0 \pm 1.5) \times 10^{-9}$
43	Poly(4MP)	Phenol A	200	$(2.1 \pm 0.2) \times 10^{-8}$
44	Poly(4MP)	DLTP	200	$(1.65 \pm 0.15) \times 10^{-7}$
46	Poly(4MP)	DLTP	173	$(5.5 \pm 1.0) \times 10^{-8}$
45	Poly(4MP)	DLTP	150	$(3.8 \pm 0.7) \times 10^{-8}$
38	Polypropylene	Phenol A	140	$(2.6 \pm 0.2) \times 10^{-8}$
51	Polypropylene	Phenol A	150	$(3.7 \pm 0.3) \times 10^{-8}$
53	Polypropylene[b]	Phenol A	100	$(9 \pm 2) \times 10^{-10}$

[a] Poly-4-methylpentene-1.
[b] From experiments based on extraction by vegetable oils.

78°C. and above behaved normally, in that the variation of counting rate with time was similar to that observed for both phenol A and DLTP in polyethylene, polypropylene, and poly-4-methylpentene-1. However, at 56°C. and below, the counting rate at equilibrium for the surface initially non-active decreases with decreasing temperature, being only about twice background at room temperature and much lower than expected from experiments at 100°C. The most likely explanation for this behavior is that the amount of N-octadecyldiethanolamine deposited on the polyethylene is sufficient to exceed the solubility at 56°C. and below. Further evidence to support this hypothesis comes from runs with polyethylene which have reached equilibrium at 78°C. and 100°C., where it was found that when these specimens were allowed subsequently to stand for 3–4 weeks at room temperature, the counting rate on both sides went up by a factor of about 1.5 from the equilibrium value, indicating that the additive

was concentrating on the polymer surface.   In addition a sample of poly-ethylene, originally containing 600 ppm of active N-octadecyldiethanol-amine, which had been stored for 12 months at room temperature was wiped with cotton wool to see if the additive was present on the surface. The cotton wool was placed in a scintillation fluid and counted.   About 15% of the additive was removed in this way, showing that it was accumulating on the surface.

If the amount of additive in the polyisobutylene layer exceeds the solubility at all times during a diffusion experiment, then the concentration at the polyethylene surface adjacent to the polyisobutylene layer will remain constant.   For these conditions the diffusion coefficient should be calculated by means of a model based on a constant surface concentration.   Such a model has been described by Auerbach[8] and Crank[6] and in fact corresponds to absorption by a membrane.   Examination of this model leads to the conclusion that the diffusion coefficient can be obtained by the intercept method but the relation $D = 0.75\ L^2/\pi^2 t_m$ should be used instead of $D = 0.487\ L^2/\pi^2 t_m$.   Runs at 78°C. in the case of polypropylene and at 56°C., and 20°C. for polyethylene were analyzed this way.   It is possible that some runs will initially correspond to the membrane model but will later approximate to models A or B.   As a result, diffusion coefficients for N-octadecyldiethanolamine may be in error by up to a factor of 1.6.

The diffusion coefficients are summarized in Table II.   In each case the variation of diffusion coefficient with temperature can be represented by:

$$D = D_0 \exp\left\{-E/RT\right\} \tag{10}$$

where E is the activation energy and D_0 is a constant related to the entropy of activation.   Values of E and log D_0 are given in Table III which also contains data taken from the literature for the diffusion of 2,6-di-*tert*-butyl-*p*-cresol[9] and *n*-octadecane[7] in polyethylene, and 2,6-di-*tert*-butyl-*p*-cresol,[2] di-2-ethylhexyl phthalate,[10] phenothiazine,[2] and substituted benzophenones[12] in polypropylene.

It is interesting to observe that although the shape and molecular weight of the diffusing molecules vary considerably from *n*-octadecane to phenol A, the activation energy for diffusion in polythene remains virtually unaltered. Similar results have been obtained by Auerbach et al.[1] for *n*-octadecane and related compounds in rubbers.   Behavior of this type suggests that the energy required for diffusion is used primarily in overcoming polymer–polymer interactions.   However, in the case of polypropylene where more data are available, the activation energy covers the range 20–33.4 kcal./mole, indicating that the structure of the diffusing molecule can have a profound effect on the activation energy but there is no simple correlation between them.

As these polymers are nonpolar and have roughly the same crystallinity, it might be expected qualitatively that the activation energy for a given penetrant would depend upon polymer properties in a manner analogous to that described by van Amerongen for rubbers;[12] that is, the activation

TABLE III
Arrhenius Parameters for Diffusion

Polymer	Additive	Activation energy, kcal./mole	log D_0
Polyethylene	n-Octadecane	12.4	1.3
Polyethylene	DLTP	12.4	0.5
Polyethylene	N-ode	12.3	0.5
Polyethylene	Phenol A	12.2	−0.3
Polyethylene	2,6-Di-tert-butyl-p-cresol	13.1	0.8
Polypropylene	N-ode	20.5	4.6
Polypropylene	DLTP	19.8	3.9
Polypropylene	Phenol A	22.3	4.2
Polypropylene	2,6-Di-tert-butyl-p-cresol	23.0	6.6
Polypropylene	Di-2-ethylhexyl phthalate	24.8	—
Polypropylene	Phenothiazine	33.4	12
Polypropylene	2-Hydroxy-4-methoxy-benzophenone	19	—
Polypropylene	2-Hydroxy-4-octyloxy-benzophenone	24	—
Polypropylene	2-Hydroxy-4-dodecyloxy-benzophenone	27	—
Poly-4-methylpentene-1	DLTP	14.5	0.1
Poly-4-methylpentene-1	Phenol A	14.2	−1.1

TABLE IV
Comparison of Polymer Properties with Activation Energy for Diffusion

Polymer	Poly-ethylene	Poly-propylene	Poly-4-methyl-pentene-1
Glass transition temperature, °C.	−125	−20	30
Cohesive energy density, cal./cc.	58–68	85–89	—
Activation energy for Newtonian viscous flow, kcal./mole[a]	11.5	15.2	26
Activation energy for diffusion of DLTP, kcal./mole	12.4	19.8	14.5

[a] Measurements carried out in this laboratory by E. C. Clark at constant shear stress of 10^3 dynes/cm.^{2}.

energy would be expected to increase with increasing glass transition temperature and cohesive energy density and be of the same magnitude as the activation energy for viscous flow. On this basis, the activation energies should be in the order poly-4-methylpentene-1 > polypropylene > polyethylene, but this is not observed experimentally (Table IV).

The high activation energy for diffusion in polyethylene and polypropylene compared with that for viscous flow can be attributed partly to

diffusion being restricted to a tortuous path through the amorphous region and partly to a variation of activation energy for viscous flow with temperature. The latter, for example in the case of poly(vinyl acetate), changes from 15 kcal./mole at 200°C. to 42 kcal./mole at 60°C.[13] A similar behavior has been observed for other polymers.[14] As the diffusion runs were carried out below the melting point and roughly 100–150°C. below the average temperature for melt viscosity measurements, the activation energy for viscous flow in the amorphous regions might be much greater than that expected from the melt viscosity data. The presence of lamellar crystallites not only reduces the mobility of polymer chains in the amorphous regions because the crystallites act as crosslinks but also imposes a tortuous diffusion path. The closer the crystallites become the more tortuous the diffusion path and the lower the mobility of polymer molecules. Michaels and Bixler[15] have shown that both chain mobility and tortuosity can increase the activation energy compared with that for a completely amorphous polymer.

The anomalously low activation energy for diffusion in poly-4-methylpentene-1 cannot be explained satisfactorily, though it might be related to the low density of the crystallites compared with that for the amorphous polymer.

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