An FTIR Solid-State Analysis of the Diffusion of Hindered Phenols in Low-Density Polyethylene (LDPE): The Effect of Molecular Size on the Diffusion Coefficient

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SYNOPSIS

Low-density polyethylene (LDPE) has been investigated with respect to the diffusion of hindered phenol antioxidants added to the polymer matrix. In the study, a simple method was used to measure the diffusion coefficient, with the aid of FTIR spectroscopy without any extraction or refining steps in the analysis. The diffusion coefficient, D, of five phenols containing the same 3(3,5-di-tert-butyl-4-hydroxyphenyl) structure but with different lengths of the hydrocarbon tail were obtained in the temperature range 30–60°C. The number of carbon atoms in the tail varied between 1 and 18. It was found that the logarithm of D decreased linearly with increasing molecular size. The temperature-dependence of the phenols could be described by an Arrhenius-type relationship. It was found that the activation energy, E_d, increased linearly with increasing molecular size. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

To protect polyolefins from degradation, various additives such as antioxidants are included in technical formulations.[1] To fulfill their objectives properly, the antioxidants have to be mobile to some extent. In many cases, the most severe degradation takes place at the outermost surfaces, where the need for antioxidants is therefore greatest. However, too high a mobility leads to loss of antioxidants to the environment, which, of course, reduces the protection given to the polymer. In the environment, they can also be harmful. It is, consequently, of great importance to be able to determine transport properties, i.e., diffusion within the polymer matrix and evaporation/desorption from the surface of the polymeric material, of additives such as antioxidants. It is commercially important because the use of polyolefins in different applications is extremely widespread. The use of polyolefins as wire coatings,

barrier layers, etc., in building construction implies that failure of such components affects the lifetime of large amounts of capital investment, since they are often more or less integrated into the building construction and replacement can be very costly.

It is also very important to consider physical transport processes in accelerated aging tests and lifetime prediction. In accelerated aging tests, it is of crucial importance that all factors affecting service life be accelerated to the same degree and, of course, that no new degradation mechanisms be initiated. In the past, little attention has been paid to the importance of transport processes in, e.g., service lifetime prediction. However, during the last 20–25 years, there has been a growing awareness of the importance of these factors.[2-4] Serious problems caused by migration of antioxidants were perhaps first recognized concerning insulating materials for telephone cables.[5-8]

The importance of transport processes has also been demonstrated by Calvert and Billingham[9] in a theoretical work. In their model, they considered the importance of the solubility of the additive, the rate of volatilization from the polymer surface, and the diffusion within the bulk of the polymer.

The connection between transport processes and aging, especially accelerated aging, is the main reason for this investigation. The polymer chosen in this case study is low-density polyethylene (LDPE) and the antioxidants are hindered phenols, all containing the same 3,5-di-*tert*-butylphenyl structure:
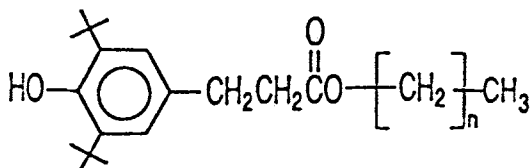
where n, the number of methylene groups, is 0, 2, 5, 11, and 17.

As can be seen, the only difference between the antioxidants is the length of the chemically inactive hydrocarbon tail. According to Scott,[10] the chemical reactivity of the antioxidants should be almost the same or at least of the same magnitude. He also showed that phenols with low molecular weight have a low stabilizing effect, owing to their ability to leave the polymer. To our knowledge, however, no detailed investigation has been undertaken to determine the diffusion coefficients of the antioxidants given above, except for the largest one.

The antioxidant with n equal to 17 is available commercially under the trade name Irganox 1076 and is manufactured by Ciba-Geigy AG. The antioxidants with $n = 0$, 2, 5, and 11 have been synthesized at our laboratory.

Dubini et al.[11] and Cicchetti et al.[12] performed diffusion measurements by obtaining concentration profiles of diffusants in a thick polymer sample, which, after a given diffusion time, was cut into thin slices. The diffusing molecules were labeled with ^{14}C. The concentration profile was obtained by measuring the radioactivity of the slices.

Roe et al.[13] described a film-stacking method, quite similar to the technique used by Dubini and Cicchetti, by which they were able to determine diffusion coefficients. Films containing an excess of the additive were placed at the top and bottom of a stack of pure films. Diffusion was then allowed to take place at an appropriate temperature and for an appropriate time. After the termination of the diffusion process, each film was examined and the content of the additive measured. By this method, both the solubility and the diffusion coefficient could be determined by regression analysis, using relevant mathematical models.

Moisan[14] used this method in an extensive investigation of the diffusion of various additives in

polyethylene. Moisan used an evaluation method including extraction of the additive and UV-spectrophotometric examination of the extract.

As discussed above, we believe that the transport properties of additives are of great importance in accelerated aging tests. For this reason, there exists a need for reliable, fast, and, if possible, nondestructive methods to determine these properties.

EXPERIMENTAL

Materials

The LDPE used was produced by Neste Polyeten AB, Sweden (grade NCPE6600). The weight-average molecular weight M_w was 1.03×10^5 g/mol and the number-average M_n was 2.22×10^4 g/mol. The density, ρ, was 0.918 kg/dm^3. This value corresponds to the volume crystallinity $\alpha_v = (\rho - \rho_a)/(\rho_c - \rho_a)$ equal to 0.44 or to the mass crystallinity $\alpha_m = \rho_c(\rho - \rho_a)/\rho(\rho_c - \rho_a) = \alpha_v\rho_c/\rho$ equal to 0.48. The values[15] of ρ_a and ρ_c are equal to 0.853 and 1.000 kg/dm^3, respectively. Neste reported the polyethylene to be free from additives. The band at about 1720 cm^{-1} in Figure 1 most probably originates from ketone used as the chain-transferring agent in the polymerization process. Absorption due to oxidation
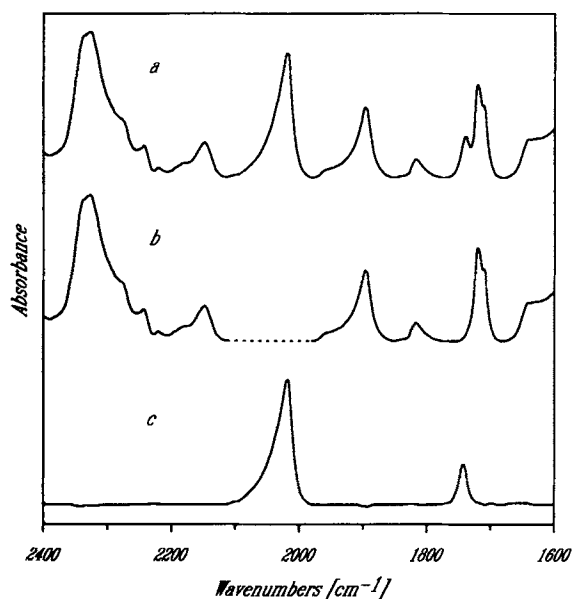
Figure 1 FTIR spectra of an antioxidant-free PE film (upper), a PE film containing antioxidant (middle), and a subtracted spectrum (bottom). The quotient in absorbance between the band at 1740 cm^{-1} and the band at 2019 cm^{-1} in the subtracted spectrum is a measure of the antioxidant concentration.

cannot be excluded, since the polymer is free from antioxidants.

The largest phenol used, Irganox 1076, was purchased from Ciba-Geigy AG, Switzerland. The other four were synthesized in-house. The syntheses of the alkyl esters of 3(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionic acid were performed starting with pentaerythrityl-3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionate, commercially available as Irganox 1010, and the alcohols: methanol, propanol, hexanol, and dodecanol. The reactions were catalyzed by *p*-toluenesulfonic acid. After the purification processes, the reaction products were analyzed and identified with LC chromatography, ^{13}C-NMR, and IR spectroscopy. The purity of the products was found to be better than 99%.

Procedure

This study describes a relatively simple method, based on the film-stacking technique described above, to determine diffusion coefficients. We have, however, used the stacking technique in a slightly modified way in this investigation. Antioxidant-doped films were placed in the middle of a stack of pure PE films instead of at the top and bottom of the stack. We have thus chosen to investigate the diffusion process only and not both diffusion and solubility. In our opinion, this will give a more accurate determination of the property investigated, because only one factor/parameter affecting the transport process is determined in a single experiment.

The additive content was determined by FTIR spectroscopy directly on the films, i.e., no extraction was used. The films can thus be stacked again and the test can continue.

Pure films were prepared from additive-free PE pellets by a molding procedure. By molding films instead of using film-blowing techniques, we believe that orientation effects in the polymer matrix may be avoided. Orientation of the polymer chains is known to affect the diffusivity.[16] The pellets were molded between two aluminum foils at 140°C for 30 s at very low pressure to melt the pellets. The pressure was then increased to 5×10^6 MPa to reach the final thickness of the film, which was 0.2 mm. The high pressure was maintained for 60 s. The films were then cooled in air between the aluminum foils. It is important that the cooling rate be the same for all the films, because the cooling rate determines the size of the spherulites.[17,18] The size of the spherulites has been reported to affect the diffusivity.[17,18]

The diameter of the disc-shaped films was approximately 10 cm.

The additive sources were prepared from master films doped with antioxidants. These were prepared from undoped ones by molding a folded, undoped film with the antioxidant smeared out on the surface. The additive concentration in the master films was about 10 times higher than in the final ones. An appropriate amount of the master film was then cut into small pieces (5 × 5 mm) and mixed with pure LDPE pellets. From this mixture, a new film was molded. This film was then cut into small pieces, which were carefully mixed and molded into a new film. This procedure was repeated six times in order to produce a homogeneous distribution of the antioxidant in the PE matrix.

Evidence for a homogeneous distribution of the additives by the procedure described above was given by spectroscopic measurement. After each mixing and molding, the concentration of the antioxidants was measured by FTIR spectroscopy at five randomly chosen points of a film. After cutting, mixing, and molding four to five times, the standard deviation reached a low and constant value, most probably corresponding to the accuracy of the measuring technique. Cutting, mixing, and molding six times was thus regarded as satisfactory in order to achieve a homogeneous distribution of the antioxidants.

In the diffusion measurements, the whole film stack was pressed between two steel plates by the use of a clamp. Next to the two outermost discs were placed aluminum foils, and outside the foils, 4 mm-thick rubber sheets. The purpose of the rubber sheets was to achieve uniform pressure over the whole disc area in order to promote maximum contact between the films and thereby avoid voids or gaps between them. We have, however, not examined the possible effects of increased resistance to diffusion at the film interfaces. Roe et al.,[13] however, performed such an examination and found no change in transport properties due to the film interfaces.

Before the diffusion process was started, all parts except the doped films were preheated in an oven to the appropriate temperature. The experiment was initiated by introducing the doped films into the disc stack. Three doped films were placed in the middle of a stack of 20 undoped ones. The reason for using three discs instead of only one was to increase the total amount of antioxidant in the stack without increasing the concentration of antioxidant in the doped films. This procedure is believed not to exceed the solubility of the antioxidants in the polymer matrix. A larger amount of antioxidant in the stack gives a higher concentration in each film and, con-

sequently, better accuracy in the determination of the diffusion coefficients.

The total height of a stack was approximately 4 mm. The temperatures chosen were 30, 40, 50, and 60°C, respectively. The true temperature was measured with a carefully calibrated thermocouple. The temperature was also continuously recorded. The deviation in temperature from the set values given above was ±0.3°C. The mol concentration in the doped films was the same for all five antioxidants. The weight concentration for the octadecylester (Irganox 1076) was 0.1%, which corresponds to the concentration commonly used in practical applications.

The concentration of the antioxidant in each film in a stack was calculated from absorbance spectra obtained by an FTIR spectrophotometer (Mattson Cygnus 100). The ester band at 1740 cm^{-1} was used as a measure of the antioxidant concentration. The polyethylene band at 2019 cm^{-1} was removed in a spectrum from a pure PE film by the use of the FTIR computer software. This "reduced" spectrum was then subtracted from spectra from the films in the stack, i.e., the band at 2019 cm^{-1} was not influenced by the subtraction and was, consequently, present in an "undisturbed state" in the subtraction spectra from the films. The absorbance band at 2019 cm^{-1} could thus be used as an internal standard (see Fig. 1). The quotient A_{1740}/A_{2019} is a measure of the antioxidant concentration. A_{1740} and A_{2019} are the absorbance of the respective bands. As pointed out above, spectra from pure polyethylene contain bands at about 1720 cm^{-1}. The spectral subtraction technique eliminates, however, the contribution from these bands.

It was assumed that the concentration gradient within a film could be approximated by a straight line and that the measured value corresponds to the concentration in the middle of a film. The actual gradient is, of course, better represented by eq. (1) below, but the errors introduced by the approximation are believed to be quite small.

The subtracted spectra contain not only the ester band but also a band at 3650 cm^{-1}, originating from the phenolic hydroxyl group in the antioxidant. Since the hydroxyl group is the active group in the antioxidant, the presence of the hydroxyl band makes it possible to follow not only diffusion processes but also chemical reactions involving the antioxidant. This is, however, beyond the scope of this investigation, but will be reported on in a study in progress, which also includes the effect of desorption/evaporation.

The large diameter of the stacks compared to the height leads to a more-or-less one-dimensional diffusion perpendicular to the films. Moreover, the diffusion was terminated, by cooling and separating the films, before the diffusing molecules reached the outermost films. These simple boundary conditions fulfill the requirements for using the expression[19]

$$c = \frac{1}{2} c_0 \left(\text{erf} \ \frac{h - x}{2(Dt)^{1/2}} + \text{erf} \ \frac{h + x}{2(Dt)^{1/2}} \right) \quad (1)$$

where c is the concentration; c_0, the initial concentration; D, the diffusion coefficient; $2h$, the total thickness of the doped films; x, the distance; t, the time; and erf, the error function.

Equation (1) is the solution of Fick's second law of diffusion $[(\delta c)/(\delta t)] = D[(\delta^2 c)/(\delta x^2)]$ for the boundary condition given above, where the diffusion coefficient is a constant, i.e., independent of the concentration of the diffusing molecules. The diffusion coefficients were determined by using a least-square curve-fitting procedure for best fit between the experimental results and eq. (1).

RESULTS AND DISCUSSION

Figure 2 exemplifies the concentration profiles of antioxidant in a film stack after heat treatment at 50°C for 36 and 72 h, respectively. The antioxidant in this case was the octadecyl ester, i.e., n equals 11 in the chemical formula above. As can be seen, there is a very good fit between the experimental data and the theoretical curve obtained from eq. (1). Moreover, the calculated diffusion coefficients also agree very well for the two different times investigated. The difference in the value of the diffusion coefficients is less than 4%. The results above indicate that the diffusion process is very well described by Fick's laws of diffusion with constant diffusion coefficients. This is in agreement with results presented by Chiou et al.[20] for semicrystalline polymers.

The diffusion coefficients for the five antioxidants at the four different temperatures are collected in Table I. As can be seen from Table I, the ratio in diffusivity between the smallest and largest antioxidant is about 4 at 30°C and only about 2 at 60°C. These values are too small to explain the difference in the loss rate of additives, measured by Scott,[10] on the basis of a difference in diffusitivity. Instead, the results are in agreement with the discussion given by Scott, who attributed the difference in loss rate to different volatilities.
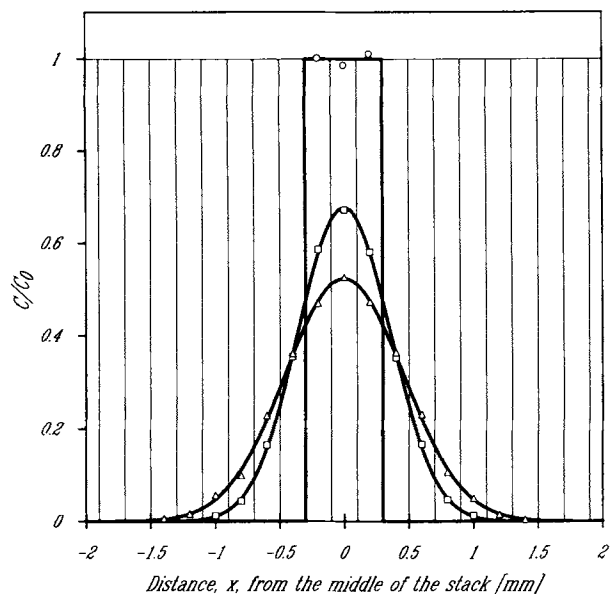
Figure 2 The figure exemplifies the concentration profiles of an antioxidant in a film stack of polyethylene (LDPE) after heat treatment at 50°C for 0, 36, and 72 h, respectively. The antioxidant in this case was the dodecylester. The solid curves represent theoretical values according to eq. (1). The circles, squares, and triangles represent experimental values.

The temperature-dependence of the diffusion coefficient can be expressed by an Arrhenius expression:

$$D = D_0 \exp(-E_d/RT) \qquad (2)$$

where D_0 is the preexponential factor; E_d, the activation energy; R, the universal gas constant; and T, the temperature.

In Figure 3, Arrhenius plots are shown for the five antioxidants. As can be seen, there is a good linear correlation between $\ln D$ and $1/T$ within the chosen temperature range. The activation energies, E_d, and preexponential factors, D_0, for all five antioxidants are calculated from best-fitted straight lines. The values of D_0 and E_d are given in Table II.

An interesting result is obtained when the activation energies are plotted as a function of the number of methylene groups, n, in the tail or the molar mass of the antioxidants, M. As can be seen in Figure 4, the correlation is almost linear. A similar result is obtained when the logarithm of the preexponential factor, $\ln D_0$, is plotted vs. n or M (see Fig. 5).

The results from Figures 4 and 5 suggest that the activation energies, E_d, could be expressed as a linear function of n (the number of methylene groups in the hydrocarbon chain):

$$E_d(n) = E_0 + k_1 n \qquad (3)$$

and the preexponential factors D_0 as

$$\ln D_0(n) = A + k_2 n \qquad (4)$$

or

$$D_0(n) = \exp(A + k_2 n) \qquad (5)$$

Substituting eqs. (3) and (5) into eq. (2), we get

$$D(T, n) = B(T) \exp[k(T)n] \qquad (6)$$

where $B(T) = \exp(A - E_0/RT)$ and $k(T) = k_2 - k_1/RT$.

Table I   Diffusion Coefficients, D, of Hindered Phenols[a] in LDPE

Diffusant[a]	No. Methylene Groups (n)	Molar Mass (M) (g/mol)	$D \times 10^{14}$ m^2/s (Temperature, °C)			
			30	40	50	60
Methylester	0	292	5.72	21.7	51.2	135
Propylester	2	320	4.78	19.1	44.8	125
Hexylester	5	362	4.09	16.1	41.9	114
Dodecylester	11	446	2.97	11.6	34.3	89.7
Octadecylester[b]	17	530	1.43	8.57	19.0	66.6

[a] Alkyl esters of 3-(3,5-di-tert-butyl-4-hydroxy-phenyl)propionic acid.
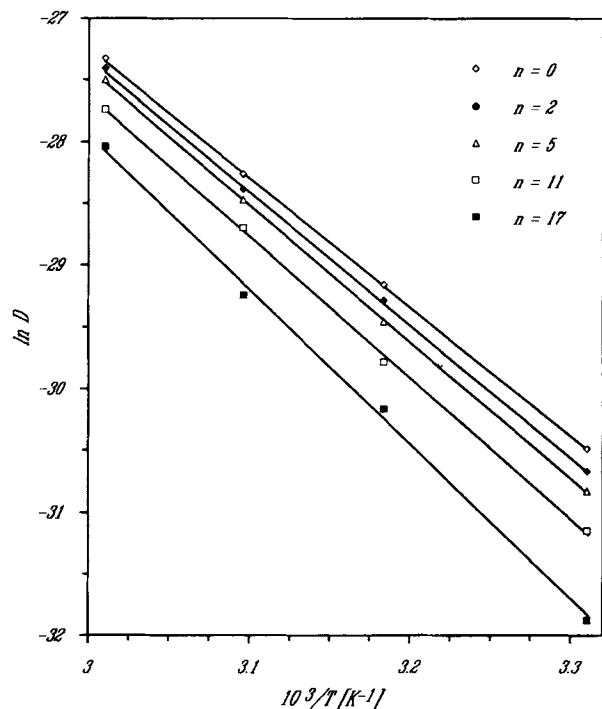[b] Irganox 1076.

Figure 3 Plots of ln D vs. $1/T$ for the five antioxidants.

According to eq. (6), there is an exponential relation between the diffusion coefficient and the length of the hydrocarbon tail or, in this case, the molar mass of the antioxidants, since the mass is proportional to the number of methylene groups in the tail.

In Figure 6, ln D is plotted against n, i.e., the length of the hydrocarbon tail, for the four temperatures. As can be seen, the correlation between the diffusion coefficient, D, and the number of methylene groups, n, can, as a good approximation, be represented by eq. (6).

The results and the discussion above are in agreement with the observation presented by Asfour et al.,[21] who studied the diffusion of saturated linear hydrocarbons (n-alkanes) in LDPE, and Moisan,[22] who investigated the diffusion of a series of linear methylesters in LDPE. The common property in the three investigations is that the different diffusants belong to linear homologous series. A similar result was also found by Dubinin et al.,[11] who studied the diffusion of a series of esters and benzophenones in isotactic polypropylene.

It is of interest to note the increase in activation energy for each —CH_2— group. Asfour et al. reported a value about 7.5 kJ/mol. We found a value about 1.0 kJ/mol. Moisan did not report any value. It is, however, possible to make an estimate by using the values of the activation energies given in Table 6 in Ref. 22. The low-temperature values are used, since they correspond to the temperatures used in our investigation. Our calculation gives a value of about 3.5 kJ/mol per methylene group. In all of the three cases above, we have a saturated linear hydrocarbon chain attached to another group. In the investigation of Asfour et al., this group is simply a small methyl group. In Moisan's investigation, it is a relatively small ester group, whereas in our investigation, it is a relatively large bulky group. As seen from the figures above, the increase in activation energy for adding a —CH_2— group is reduced when the attached group increases in size.

Typically,[13] the correlation between the diffusion coefficient and the molar mass of the diffusant is represented by an expression of the form

$$D = bM^{-a} \qquad (7)$$
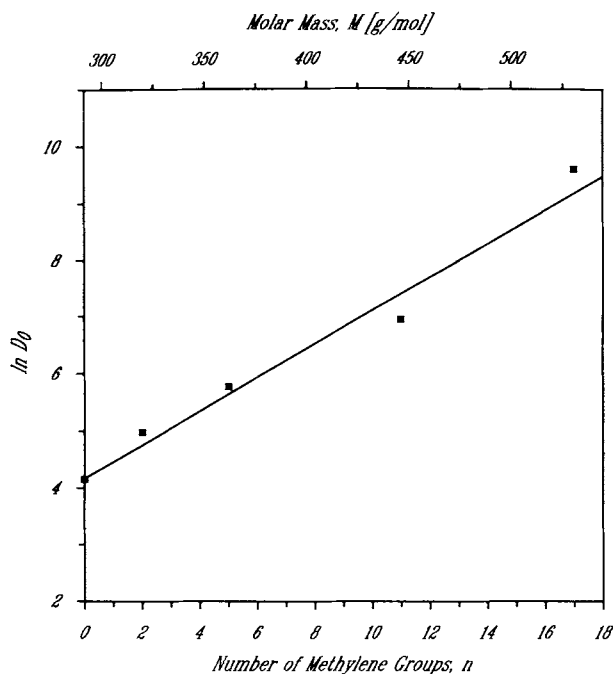
In Figure 7, a curve representing eq. (7) is included

Table II   Activation Energies, E_d, and Preexponential Factors, D_0, for Diffusion of Hindered Phenols[a] in LDPE

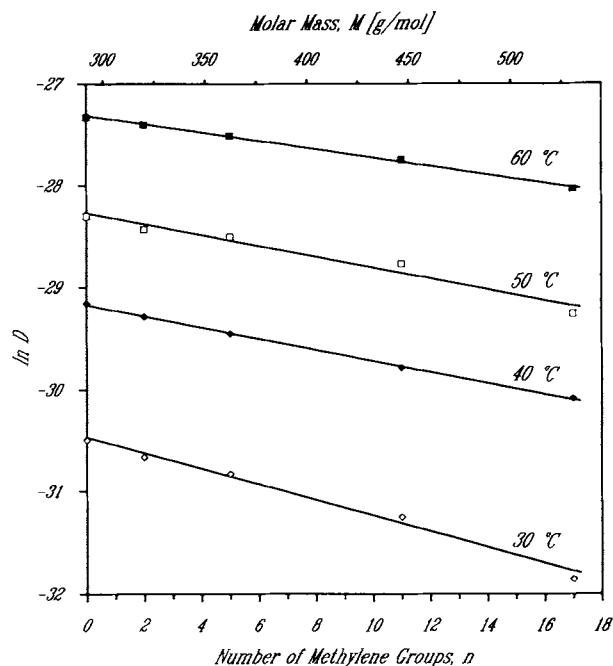| Diffusant[a]	No. Methylene Groups (n)	Molar Mass (M) (g/mol)	Activation Energy (E_d) (kJ/mol)	Preexponential Factor (D_0) (m²/s)
Methylester	0	292	87.0	63.6
Propylester	2	320	89.6	147
Hexylester	5	362	92.0	323
Dodecylester	11	446	95.5	776
Octadecylester–Irganox 1076	17	530	104	14,800

[a] Alkyl esters of 3-(3,5-di-*tert*-butyl-4-hydroxy-phenyl)propionic acid.

Molar Mass, M [g/mol]
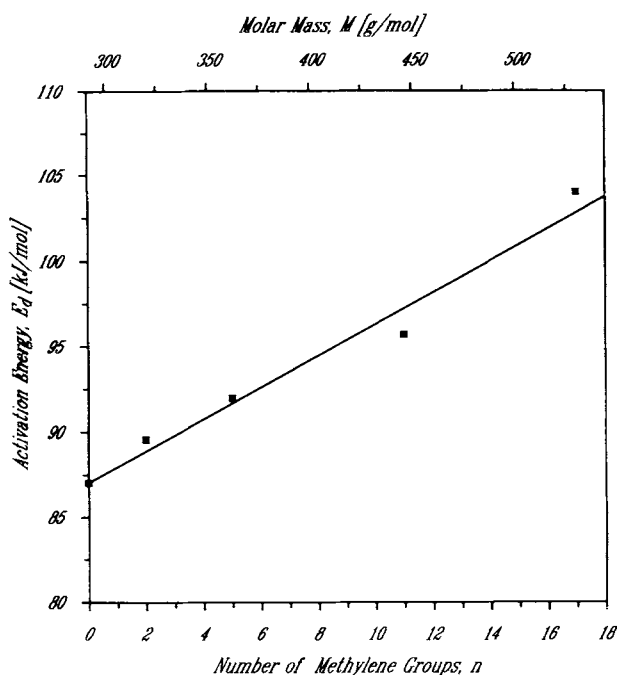
Figure 4 The activation energy, $E_d(n)$, as a function of the number of methylene groups, n, in the hydrocarbon tail of the antioxidants $[E_d(n) = E_0 + k_1 n]$. $E_0 = 87.0$ kJ/mol and $k_1 = 0.927$ kJ/mol per — CH_2 — group.

Molar Mass, M [g/mol]

Figure 6 Ln D plotted vs. the number of methylene groups, n, in the hydrocarbon tail of the antioxidants for 30, 40, 50, and 60°C, respectively. The solid lines represent eq. (6) $[D(T, n) = B(T)\exp[k(T)n]$ using the values given in Figures 4 and 5.

for the best fit of a and b to the experimental points. A curve representing eq. (6) is also included. As can be seen, in Figure 7, eq. (6) gives better agreement with the experimental points than does eq. (7).

An interesting result is obtained when eq. (3) is rewritten:

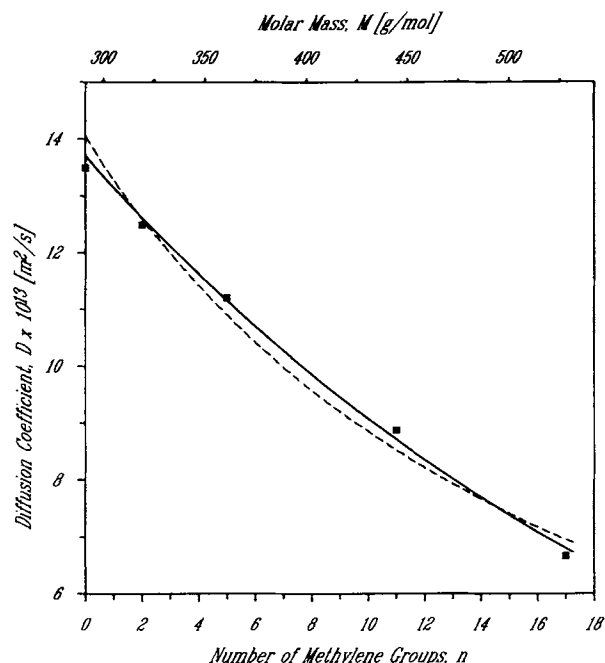$$n = [E_d(n) - E_0]/k_1 \qquad (8)$$

This holds, of course, only for linear homologous series or for diffusants differing only in the number of repeating units in a linear chain.

Substitution of eq. (8) in eq. (4) gives

$$\ln D_0(n) = A - (k_2/k_1)E_0 + (k_2/k_1)E_d(n) \qquad (9)$$

or, after insertion of the values of k_1, k_2, A, and E_0, which could be obtained from the straight lines in Figures 4 and 5 (the values are given in the figure legends),

$$\ln D_0(n) = 0.32 E_d(n) - 24 \qquad (10)$$

Molar Mass, M [g/mol]

Figure 5 The preexponential factor, D_0, as a function of the number of methylene groups, n, in the hydrocarbon tail of the antioxidants $[\ln D_0(n) = A + k_2 n]$. $A = 4.17$ and $k_2 = 0.295$ per — CH_2 — group.

Figure 7 The diffusion coefficient plotted vs. the number of methylene groups, n, in the hydrocarbon tail of the antioxidants for 60°C. The solid line represents eq. (6), whereas the broken line represents eq. (7).

or in common logarithms,

$$\log D_0(n) = 0.14 E_d(n) - 10.4 \qquad (11)$$

This expression should be compared with the empirical expression[23]:

$$\log D_0 = 0.5(E_d/1000 - 8.0) \qquad (12)$$

correlating D_0 and E_d for elastomers, or after using the same units for D_0 (m^2/s) and E_d (kJ/mol) as in eq. (11):

$$\log D_0 = 0.12 E_d - 8 \qquad (13)$$

In a semicrystalline polymer such as LDPE, diffusion is thought to be confined to the amorphous regions, where the diffusion is regarded to be Fickian in a rubbery matrix.[20] As is seen, eqs. (11) and (13) are of the same form, i.e., there is a logarithmic or an exponential relation between D_0 and E_d. There are, however, some differences between the corresponding constants in eqs. (11) and (13). When the equations are expressed in an exponential form, the differences are quite large.
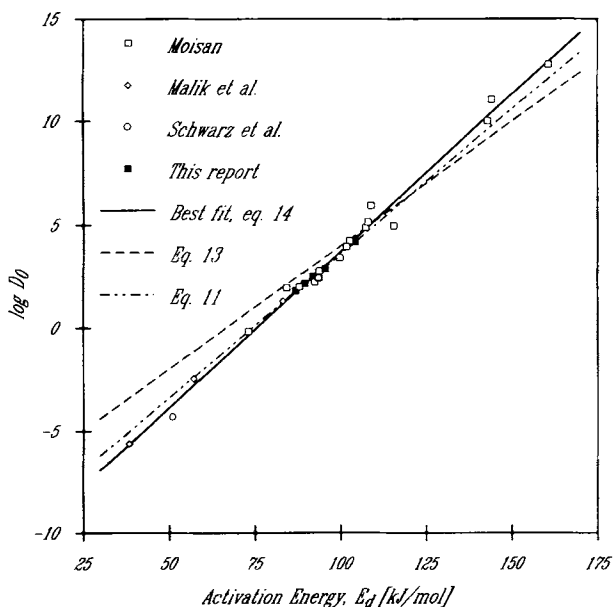
In Figure 8, log D_0 is plotted vs. E_d for a number of additives in LDPE,[24,25] including hindered amine stabilizers (HALS) and the antioxidants investigated in this report. Most of the data were obtained by Moisan.[14] The line representing the best least-square curve fit is given in the figure, together with the line representing eq. (13). As is seen, the deviation from a straight line is small. The equation for the line could be expressed as

$$\log D_0 = 0.15 E_d - 11.4 \qquad (14)$$

As is seen, there is a better agreement between eqs. (11) and (14) than between eqs. (13) and (14).

CONCLUSIONS

1. Solid-state FTIR spectroscopy combined with spectral subtraction is demonstrated to be a fast, sensitive, and non-destructive technique in the determination of transport properties of carbonyl containing diffusants in polyolefins.
2. The diffusion of the five antioxidants is Fickian with no concentration-dependent diffusion coefficient in the concentration range studied.

Figure 8 Log D_0 plotted vs. E_d for a number of additives in LDPE, including hindered amine stabilizers (HALS) and the antioxidants investigated in this report.

3. Linear Arrhenius plots were obtained in the temperature range 30–60°C, which indicates constant activation energies.

4. A linear relationship was found between the activation energy, E_d, and the number of methylene (— CH_2 —) groups in the hydrocarbon chain of the antioxidants.

5. A linear relationship was also found between the logarithm of the preexponential factor, D_0, and the number of methylene (— CH_2 —) groups in the hydrocarbon chain of the antioxidants.

6. The findings above demonstrate an observed exponential correlation between the diffusion coefficient, D, and the number of methylene groups in the hydrocarbon tail of the antioxidant, or between D and the molar mass of the antioxidant.

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