

Diffusion of Stabilizers in Polymers.

I. 2,4-Dihydroxybenzophenone in Polyolefins

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Synopsis

The diffusion of the ultraviolet stabilizer 2,4-dihydroxybenzophenone in compression-molded sheets of low-density polyethylene, high-density polyethylene, and isotactic polypropylene was investigated over the temperature range of 44–75°C. The magnitude of the diffusion coefficients for these polyolefins was found to decrease in the order low-density polyethylene > high-density polyethylene > polypropylene, the corresponding activation energies being approximately 18, 23, and 34 kcal/mole. Studies under conditions of saturation indicated that the migration of this stabilizer was confined to the more accessible amorphous regions of the polymers. The rate of loss of stabilizer from polymer samples immersed in water was also investigated at 44°C. Values of the diffusion coefficients calculated from the results of these studies were somewhat greater than those determined from the diffusion studies for the low-density polyethylene and isotactic polypropylene samples and considerably smaller in the case of high-density polyethylene. The extraction studies also permitted the quantitative evaluation of the solubilities of the stabilizer in the polymers. These were found to be 0.003, 0.03, and 0.07 wt-% for high-density polyethylene, low-density polyethylene, and polypropylene, respectively, at 44°C.

INTRODUCTION

The deterioration of the physical, chemical, and/or aesthetic properties of polymers which may occur during processing or subsequent usage has been the subject of long-standing interest and concern to polymer producers. In view of the increasing utilization of polymers in outdoor applications, protection against the detrimental effects of both heat- and light-induced degradation is frequently required. The selection of the most suitable stabilizers for a particular polymer requires consideration of a number of factors. Stabilizers must be effective from a mechanistic viewpoint (i.e., possess inherent stabilizing efficiency). The mechanisms of thermal and oxidative photodegradation, together with the corresponding mechanisms of stabilization, have been extensively reviewed in a number of recent publications.¹⁻¹⁰

In addition, the degree of compatibility of the stabilizers with the polymer, their rates of migration through, and volatility and/or extraction

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from the polymer must be taken into account. Experimental determination of these quantities, their interrelation, and their contribution to the effectiveness of various stabilizers in polymers have been the subjects of a number of recent studies.¹¹⁻³³

In view of the demonstrated significance of these parameters with respect to the efficiency of stabilizers, it was decided that a study in the areas of compatibility, mobility, volatility, and extraction of ultraviolet stabilizers in various polymers would provide information relevant to their overall effectiveness under conditions of usage. The present paper reports the results obtained for the UV stabilizer 2,4-dihydroxybenzophenone in a number of polyolefins.

EXPERIMENTAL

Materials

Ultraviolet Stabilizer

2,4-Dihydroxybenzophenone was prepared by a method similar to that reported for the preparation of 2,4-dihydroxy-4'-methoxybenzophenone.³⁴ Radioactive ¹⁴C-benzoic acid, 2.5 g, containing 1.14 mCi activity, and 2.255 g resorcinol were placed in a 30-ml two-necked flask equipped with a magnetic stirrer, gas bubbling tube, and drying tube. To this was added 5.2 ml tetrachloroethane (previously dried over molecular sieve), and the mixture was allowed to stand for a period of 2 hr in order to facilitate contact between the reactants. Gaseous boron trifluoride was bubbled via a Drechsel bottle containing dried tetrachloroethane into the mixture until the weight of the flask and contents increased by 1.8 g. The mixture was then heated on an oil bath to 100°C and stirred for approximately 4 hr. After cooling, the contents of the flask were slowly poured into 30 ml of rapidly stirred water containing 5.6 g sodium acetate. After standing overnight, the mixture was added to 70 ml petroleum ether (bp 60-80°C), giving rise to a solid precipitate which was filtered, washed repeatedly with water, and dried under vacuum at room temperature to constant weight.

The above precipitate was dissolved in 40 ml 5% caustic solution in a 100-ml conical flask. Carbon dioxide gas was bubbled through the solution until the solution became weakly alkaline, resulting in precipitation of the product which was filtered, washed with water, and dried. This precipitate was then dissolved in a solution of 200 ml water and 70 ml methanol containing 0.6 g activated charcoal and refluxed for 1/2 hr. The mixture was filtered while hot and the filtrate allowed to cool and evaporate, resulting in the precipitation of 2,4-dihydroxybenzophenone in crystalline form. The filtered and dried product was recrystallized from benzene/petroleum ether (bp 100-120°C). The final product was obtained in the form of pale-yellow, needle-like crystals (mp 144.5-147°C). The yield was 2.38 g (54%).

TABLE I
Polymer Composition and Molding Conditions

Polymer	Composition	Additives	Molding temp., °C	Molding pressure, psi	Molding substrate	Residence time, min	Cooling rate, °C/min
Polypropylene	homopolymer	small amount of phenolic anti-oxidant	200	1120	aluminum foil	10	10-20
Low-density polyethylene	as above	none	150	as above	as above	as above	as above
High-density polyethylene A	contains about 3% copolymerized propylene	as above	180	as above	as above	as above	as above
High-density polyethylene B	homopolymer	as above	180	1245	as above	—	fairly rapidly

TABLE II
Physical Properties of the Polymers

Property	Poly-propylene	Low-density polyethylene	High-density polyethylene A	High-density polyethylene B
Density, g/cm ³	0.90 ^a 0.8985 ^b	0.920 ^a 0.9190 ^b	0.955 ^a 0.9588 ^b	0.960 ^a 0.9535 ^b
Crystallinity, %	~65 ^a ~56 ^d	~40-46 ^e	~72 ^e	~80 ^a ~68 ^e
\bar{M}_n	91,700 ^{b,c}	25,600 ^{b,c}	14,000 ^{b,c}	5,500 ^a
\bar{M}_w	266,500 ^{b,c}	679,400 ^{b,c}	188,500 ^{b,c}	120,000 ^a
Intrinsic viscosity, dl/g	~2 ^a	~1.5 ^a	~2 ^a	

^a Data of supplier.

^b Data provided by RAPRA.

^c See Appendix for MWD data.

^d Calculated from density measurements (ref. 39).

^e Calculated from density measurements (refs. 40-42).

Polymers

The polymers used in the present study were commercial samples in the form of 1.5-mm-thick compression-molded sheets. Data concerning the composition and conditions of molding, as provided by the suppliers, may be found in Table I. Some of the physical properties of the polymers are listed in Table II.

Procedure

Diffusion Studies

Diffusion experiments were performed using 3.5-cm-diameter discs cut from the original sheets on a press using a circular cutter. The rate of migration of the radioactive 2,4-dihydroxybenzophenone was measured by depositing a thin layer of stabilizer on one side of a polymer disc and monitoring the increase in the counting rate at the initially stabilizer-free surface by means of a Geiger-Müller tube (end window thickness ~2.7 mg/cm²). The stabilizer was applied to the disc in the form of an acetone solution. In order to ensure uniform spreading of the solution, a piece of circular lens tissue of diameter slightly less than that of the disc was placed on the disc prior to application of the solution. The stabilizer was then applied using a syringe in one 0.04-ml quantity. Microscopic examination indicated a quite uniform distribution of stabilizer on both the lens tissue and underlying polymer over substantially the entire surface. There was, however, a noticeable accumulation at the circumference of the lens tissue and polymer disc. Possible detrimental effects that might be incurred as a result of this were eliminated by the design of the diffusion cell.

The polymer disc was then placed on an aluminum disc (covered with aluminum foil) with a disc of 0.009-mm aluminum foil placed on the stabilizer-free surface. The assembly was then wrapped at the edges with foil and placed in a brass diffusion cell (see Fig. 1). The insert was posi-

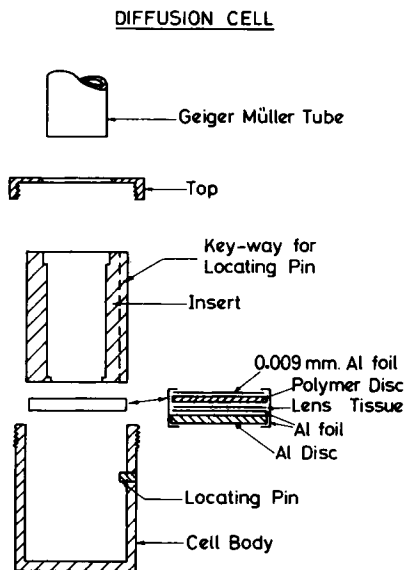


Fig. 1. Diagram of diffusion apparatus.

tioned on top of the "disc" assembly and the top screwed on until "finger tight." Rotation of the insert during tightening was prevented by a locating pin and key-way arrangement and reproducible positioning of the Geiger-Müller tube by an internal diameter-counter bore design. The cell design restricted measurements to a central circular area with a diameter of 1.9 cm, thus precluding the possibility of "edge effects" resulting from either the cutting of the discs from the sheets or the above-noted accumulation of stabilizer. Temperature control was achieved by placing the cell assembly in a water bath ($\sim 70\%$ immersed) maintained within $\pm 0.05^\circ\text{C}$ of the desired temperature. Readings were taken at appropriate intervals, ranging from 30 min to a number of days, depending upon the rate of diffusion.

Preliminary studies were made using discs whose thickness corresponded to that of the original material (i.e., 1.5 mm). It soon became evident, that the values of the diffusion coefficients over the temperature range of interest were quite low, particularly in the case of polypropylene; and in order that meaningful measurements might be made within a reasonable period of time, a reduction of the thickness of the discs would be required. This was achieved by carefully facing on both surfaces on a lathe, the disc being attached to the facing plate by means of two-sided adhesive tape. This method yielded discs having macroscopically smooth surfaces with a maximum variation of 0.004 mm in thickness over the entire disc (i.e., a maximum of 1.5% in the case of the thinnest disc used).

Extraction Studies

The rate of loss of stabilizer from the polyolefins immersed in water was studied at 44°C . Stabilizer was incorporated into the polymer disc at

44°C by the method outlined above or diffused into the polymer at a higher temperature and the stabilizer allowed to "bloom out" of the disc at 44°C. Once an equilibrium counting rate was attained, the disc was removed from the cell, the surface sparingly wiped with cotton wool and acetone to remove any excess stabilizer, and then immersed in approximately 10 ml water in a round-bottomed tube, ensuring that both surfaces of the disc were in contact with water. Temperature control was maintained by placing the tube in a temperature control bath.

The amount of stabilizer lost from the disc as a function of time may be calculated by determining the volume of water in which the sample was immersed and the concentration of stabilizer in this volume. In the present study, the total volume of water was replaced at appropriate intervals and the activity of this sample, resulting from the presence of radioactive stabilizer, was measured by liquid scintillation counting using an Isotope Development Limited Scintillation unit (liquid measuring head 2022; coincidence control unit 2032B; scaler 1700 series II). The background was determined for 3 ml scintillation solution (NE 240, Nuclear Enterprises Ltd). The counting rate of the water samples was then determined by the addition of 0.6 ml solution in four aliquots. The values of the counting rates (c/sec/ml) used in subsequent calculations were the average of those obtained for at least two 1000-sec counting intervals. No effect of quenching was observed for the concentrations of stabilizer encountered during the course of the experiments, and hence an average value of those obtained for the four additions was taken as the "true" value. Conversion to a gravimetric basis was achieved by calibration of the counting unit using a standard solution of radioactive 2,4-dihydroxybenzophenone in water at a concentration comparable to those obtained in the experimental studies.

THEORETICAL TREATMENT

Diffusion Experiments

Evaluation of the diffusion coefficients was made using the nonsteady-state mathematical solutions applicable to diffusion in a plane sheet.³⁵ Utilization of the equations relevant to this study involve two important assumptions, namely, that the stabilizer is applied to the surface as a thin uniform layer and that diffusion is essentially one-dimensional in nature (i.e., perpendicular to the plane of the sheet). The design of the experimental apparatus and the previous observations regarding the uniformity of the stabilizer distribution would suggest that these conditions are satisfied to a considerable degree in the present study. In addition, it is implicitly assumed that the value of the diffusion coefficient remains essentially constant over the period of measurement.

For the case in which the diffusing species is initially present as a thin layer on one surface of the disc, two experimental approaches are possible.

The stabilizer may be applied in sufficient quantity to maintain the concentration at that surface constant throughout the course of the experiment, hereafter referred to as saturation conditions. Alternatively, a very low concentration of stabilizer may be employed, in which case diffusion takes place under conditions approaching zero concentration relative to the above situation (nonsaturation conditions). The mathematical analysis applicable to each of these situations is presented below.

Saturation Conditions

This corresponds to the case in which the concentration of stabilizer at one surface of the sample ($x = l$) is maintained constant and the initially stabilizer-free surface ($x = 0$) is impermeable in nature. The latter condition implies no "blooming" of the stabilizer at this surface. The mathematical solution for these conditions is identical to that for a sheet occupying the region $-l < x < l$, initially free of diffusant, with both surfaces held at a constant concentration c_1 , viz.,

$$\frac{c}{c_1} = 1 - \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n}{2n+1} e^{-D(2n+1)^2 \pi^2 t / 4l^2} \cos \frac{(2n+1) \pi x}{2l} \quad (1)$$

where D = diffusion coefficient (cm^2/sec), l = thickness of the disc (cm), and t = time (sec). However, as indicated by Jackson et al. in a similar study,¹⁴ the actual counting rate measured will depend upon the attenuation of the β -rays by the polymer which may have a noticeable effect on the calculated values of the diffusion coefficients, particularly in the case of very thin samples. Incorporation of this factor into the theoretical treatment is achieved using the following equation:¹⁴

$$R_0 = H \int_0^l cf(x)dx. \quad (2)$$

In this equation, R_0 is the counting rate at the surface $x = 0$; $f(x)$ is the fraction of β -rays reaching the surface from stabilizer molecules at a distance x ; and H is a constant encompassing terms for the specific activity of the stabilizer, the cross-sectional area of the sample surface exposed to the counter, and the counting efficiency.

Values for $f(x)$ may be determined from the exponential function

$$f(x) = e^{-\mu x} \quad (3)$$

where μ is the absorption coefficient of the polymer. Values of μ were calculated using the formula³⁶

$$\mu = \frac{22}{E_{\text{max}}^{4/3}} \cdot \rho \quad (4)$$

where μ = absorption coefficient (cm^{-1}), E_{max} = maximum energy of ^{14}C beta particles (MeV), and ρ = density of the polymeric species (g/cm^3).

Substitution of the expression for $f(x)$ and c into eq. (2), integrating, and evaluating the resulting integral at $t = \infty$ to determine the equilibrium counting rate gives rise to the final expression

$$\frac{R_0}{R_E} = 1 - \frac{4\mu}{\pi(1 - e^{-\mu l})} \times \left\{ \sum_{n=0}^{\infty} \frac{1}{(2n+1)} \cdot \frac{(-1)^n \mu + \frac{(2n+1)\pi}{2l} e^{-\mu l}}{(\mu^2 + (2n+1)^2 \pi^2 / 4l^2)} \cdot e^{-D(2n+1)^2 \pi^2 t / 4l^2} \right\} \quad (5)$$

where R_E is the equilibrium counting rate.

Nonsaturation Conditions

For this case, both surfaces are considered impermeable, the mathematical solution being of the form

$$c = c_0 \left\{ \frac{h}{l} + \frac{2}{\pi} \sum_{n=1}^{\infty} \frac{1}{n} \sin \frac{n\pi h}{l} e^{-Dn^2 \pi^2 t / l^2} \cos \frac{n\pi x}{l} \right\} \quad (6)$$

with initial stabilizer distribution

$$\left. \begin{aligned} g(x) &= c_0 & 0 < x < h \\ g(x) &= 0 & h < x < l \end{aligned} \right\} \quad (7)$$

This expression may be simplified by using the relationships $c_0 h = c_E l$ (c_E being the equilibrium concentration) and $\sin \alpha \sim \alpha$ (for small values of α):

$$\frac{c}{c_E} = 1 + 2 \sum_{n=1}^{\infty} \cos \frac{n\pi x}{l} e^{-Dn^2 \pi^2 t / l^2} \quad (8)$$

In the above equations, the terminology is the same as that for saturation conditions. Application of the expression to account for β -ray attenuation by the polymer yields the final equation

$$\frac{R_t}{R_E} = 1 + 2 \sum_{n=1}^{\infty} \frac{\mu^2}{\mu^2 + n^2 \pi^2 / l^2} \cdot \frac{\cos(n\pi) - e^{-\mu l}}{1 - e^{-\mu l}} \cdot e^{-Dn^2 \pi^2 t / l^2} \quad (9)$$

In this equation, R_t and R_E are the counting rates at the surface at time t and at equilibrium, respectively. This development has assumed the application of the stabilizer to the surface $x = 0$ as opposed to $x = l$ in the saturation case.

For the case of both the saturation and nonsaturation conditions, the theoretical treatment yields an expression with only one unknown quantity, namely, the value of the diffusion coefficient. Hence, a comparison of theoretically generated values of R_0/E_E (or R_t/R_E) versus time with the corresponding values determined experimentally allows evaluation of D . In the present study, this was accomplished using the university computing facilities. It will be appreciated, however, that the values obtained by this

analysis, although useful in a practical sense, must be considered as average values. The actual mechanism of diffusion in polymers, in particular those of a semicrystalline nature, will be governed to a considerable extent by the morphology of the particular polymer in question. The calculated values of the diffusion coefficients will reflect this morphologic influence in a qualitative manner only.

Extraction Experiments

Determination of values for the diffusion coefficients may be made from the results obtained in the extraction experiments using the mathematical equation applicable to desorption from a membrane initially at uniform concentration with both surfaces held at zero concentration. The appropriate equation is³⁵

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2\pi^2} e^{-D(2n+1)^2\pi^2 t/4l^2} \quad (10)$$

In the above expression, M_t is the total amount of stabilizer having diffused out of the disc at time t , and M_∞ is the corresponding quantity after infinite time. The remaining variables are defined as previously, with the exception of l , which is now the half-thickness of the disc. In order that the diffusion coefficients determined by this approach are defined on the same basis as those determined in the diffusion studies, certain experimental conditions must be fulfilled. The stabilizer must have a greater affinity for water than for the polymer, thus ensuring that the concentration of stabilizer at the surfaces of the disc is zero. In addition, the solubility of the stabilizer in water must be high relative to the concentrations encountered during the experiment and the solubility of water in the polymer itself negligible in order to avoid changes in the morphology of the sample. However, even if these conditions are not met, it may still be possible to calculate an "effective" diffusion coefficient for loss of stabilizer from the polymer in an aqueous environment using the above equation. The method of computing the values of the diffusion coefficients is analogous to that used in the diffusion studies.

RESULTS AND DISCUSSION

In order to calculate values for the diffusion coefficients by comparison of experimentally determined and theoretically generated curves, it is necessary that experimental conditions with respect to the concentration of stabilizer applied to the surface of the disc closely approximate that corresponding to either the saturation or the nonsaturation condition. The equilibrium counting rates attained under conditions of saturation were therefore determined at 60°C by trial and error using stabilizer solutions of various concentrations while maintaining the volume of the solution applied to the disc and the thickness of the disc itself constant.

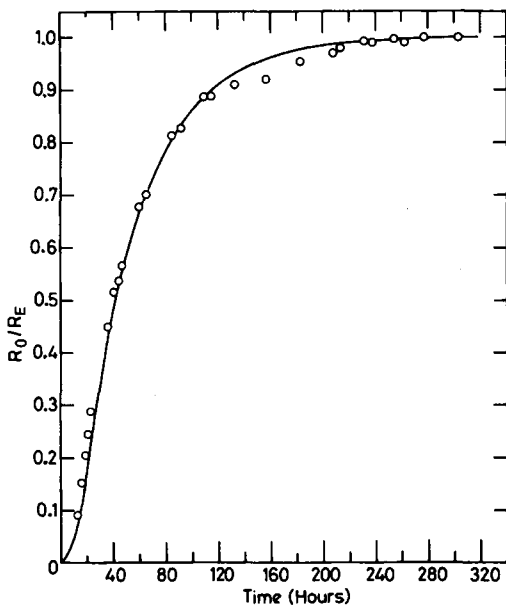


Fig. 2. Diffusion data. Plot of R_0/R_E vs. time: polymer, low-density polyethylene; temperature, 75°C; disc thickness, 0.156 cm; (OOOOOOOOOO) experimental points; (————) theoretical curve for $D = 6.03 \times 10^{-8}$ cm²/sec.

Application of stabilizer solutions of 10.0, 3.3, and 0.7 wt-% resulted in a maximum variation of 25% in the equilibrium counting rate for any given polymer, indicating that saturation conditions were being achieved. The values of the counting rates were found to be approximately 250 c/min for both the low-density polyethylene and polypropylene samples and 50 c/min in the case of the high-density polyethylenes. In view of the relatively low values of these counting rates in comparison with the background (~ 20 c/min) and the possibility of a decrease in the equilibrium concentration of stabilizer with decreasing temperature, it was decided to conduct all studies under conditions corresponding to those for saturation. Consequently, values of the diffusion coefficients were calculated using eq. (5). In addition, since it was frequently necessary to reduce the thickness of the polymer discs to a substantial degree in order to obtain the required experimental data within a reasonable period of time, studies were conducted with low-density and high-density polyethylene to assess the effect (if any) of this procedure on the values determined for D . Studies encompassing a two- to threefold variation in the thickness yielded values of the diffusion coefficients which agreed within 15% of each other, indicating no apparent effect on the calculated values of the diffusion coefficients as the result of using thin test specimens.

Experiments were conducted over the temperature range of 44°–75°C, with a minimum of two experimental determinations being made at each temperature investigated. Results typical of those obtained are illustrated

TABLE III
Comparison of Diffusion Coefficients

Polymer	Diffusion coefficient (75°C), cm ² /sec		Overall activation energy, kcal/mole	
	Present study	Previous study ^a	Present study	Previous study ^a
Low-density polyethylene	4.1×10^{-8}	5.5×10^{-8}	18.3	12.0
High-density polyethylene A	1.5×10^{-8}	3.5×10^{-9}	22.3	17.4
High-density polyethylene B	1.2×10^{-8}		24.4	
Isotactic polypropylene	1.9×10^{-9}	2.5×10^{-9}	34.0	18.2

^a References 15 and 16.

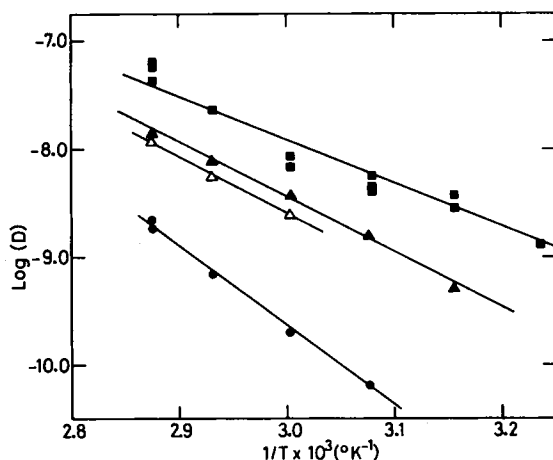


Fig. 3. Arrhenius plot of $\log D$ vs. $1/T$: (■) low-density polyethylene; (▲) high-density polyethylene A; (△) high-density polyethylene B; (●) isotactic polypropylene.

in Figure 2 for the diffusion of 2,4-dihydroxybenzophenone in low-density polyethylene at 75°C. The open circles represent the experimental points, the solid curve being the theoretical curve corresponding to a value of 6.03×10^{-8} cm²/sec for the diffusion coefficient. In general, it was found that good agreement between theoretically generated and experimentally determined data could be achieved by proper choice of the value of D . A plot of $\log D$ versus $1/T$ is presented in Figure 3. The values of the diffusion coefficients decrease in the order low-density polyethylene > high-density polyethylene A > high-density polyethylene B > isotactic polypropylene over the temperature range investigated, the overall activation energies being 18.3, 22.3, 24.4, and 34.0 kcal/mole. Comparison of the results obtained for 2,4-dihydroxybenzophenone in the present study with those previously obtained for the structurally similar UV stabilizer 2-hydroxy-4-methoxybenzophenone are presented in Table III. At conditions of temperature essentially common to both studies (i.e., 75°C), the values of the diffusion coefficients are in qualitative agreement. However,

values of the overall activation energies determined in the present study (lower temperature range) are significantly higher. Values of the diffusion coefficients were also calculated for samples chosen at random using the intercept method proposed by Jackson et al.¹⁴ The equation applicable to saturation conditions is

$$D = \frac{4a(l)l^2}{\pi^2 t_m} \quad (11)$$

In the above equation, $a(l)$ is the intercept value defined by the tangent of maximum slope to the theoretical curve of R_0/R_E versus $D\pi^2 t/4l^2$; t_m is the corresponding intercept value obtained from the experimental plot of R_0/R_E versus time; and l is the thickness of the disc. Having generated values of $a(l)$ as a function of l , values of D may be calculated once t_m is known. Since t_m is evaluated using data corresponding to the initial portion of the experimental curve (i.e., $R_0/R_E \sim 0.1$ to 0.5), this approach entails a substantial reduction in the experimental time involved, as evidenced by reference to Figure 2.

Evaluation of the diffusion coefficients by both methods in the case of low-density and high-density polyethylene yielded results which agreed within 40%, the difference between the values being random in nature with respect to the experimental variables. For the polypropylene samples, the values determined by the intercept techniques were consistently higher by a factor of approximately 3 than those calculated using the entire curve. Analysis of the experimental data for all samples, however, indicated that the values of t_m were quite sensitive to the accuracy of the data constituting the initial portion of the curve. In view of this, it was concluded that the results obtained by this approach would be somewhat less reliable in nature.

Consideration of the equilibrium counting rates attained under saturation conditions provides information, on a qualitative basis, with respect to the distribution and solubility of the stabilizers in the polymers. Although the rate of diffusion in high-density polyethylene is less than that observed in low-density samples, one would expect that the equilibrium counting rates would be similar if diffusion occurs to approximately the same extent in both the crystalline and amorphous phases. Experimental results indicated, however, that the final counting rates for low-density polyethylene were four to six times greater than those observed for high-density samples, there being no systematic variation with temperature. Since the ratio of the amorphous regions of these polymers, as determined by density measurements, is approximately 2:1, these results are indicative of diffusion occurring essentially in the more accessible amorphous regions of the polymer, the stabilizer being incompatible with the crystalline phase. From a practical viewpoint of stabilization, the observed distribution of the stabilizer in the amorphous regions of the polymer is efficient since the initial formation of photochemical products and subsequent degradation is generally confined to the disordered regions of the polymer.^{37,38}

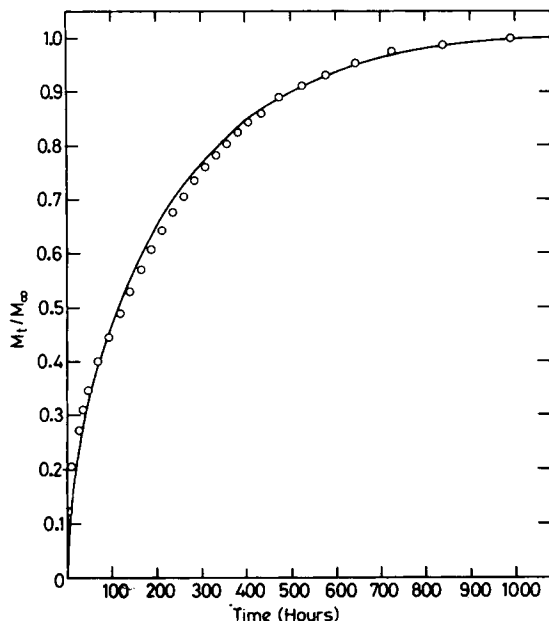


Fig. 4. Extraction data. Plot of M_t/M_∞ vs. time: polymer, isotactic polypropylene; temperature, 44°C; disc thickness, 0.022 cm; (O) experimental points; (—) theoretical curve for $D = 5.5 \times 10^{-11}$ cm²/sec.

In addition, observed variations in the equilibrium counting rates with temperature for the polymers investigated yield qualitative information regarding the change in solubility of the stabilizer over the temperature range considered. For the high-density and low-density polyethylene samples, the solubilities were found to increase by a factor of 3 with increasing temperature between 44°C and 75°C. However, in the case of polypropylene, no change in solubility with temperature was apparent.

Studies were also conducted at 44°C to determine the rate of loss of stabilizer from the polyolefins while immersed in water. Typical results are presented in Figure 4 for the extraction of 2,4-dihydroxybenzophenone from polypropylene, the solid curve corresponding to the theoretical values, eq. (10), for $D = 5.5 \times 10^{-11}$ cm²/sec. The values of the diffusion coefficients determined from these experiments, together with the corresponding values obtained in the diffusion experiments, may be found in Table IV. These results indicate that the rate of migration is enhanced somewhat in the extraction studies for both the low-density polyethylene and the polypropylene samples, whereas an apparent reduction is observed in the case of high-density polyethylene. Although these preliminary extraction studies with water are of interest from a practical viewpoint, generalization of the results and their interpretation will require further study. In addition to permitting evaluation of the diffusion coefficients, the extraction experiments provide a method of determining the solubilities of the

TABLE IV
Comparison of Diffusion Coefficients Obtained by Diffusion and Extraction Procedures

Polymer	D , cm ² /sec	
	diffusion expt.	extraction expt.
Low-density polyethylene	2.7×10^{-9}	4.2×10^{-9}
High-density polyethylene	5.8×10^{-10}	9.9×10^{-11}
Polypropylene	1.7×10^{-11}	5.5×10^{-11}

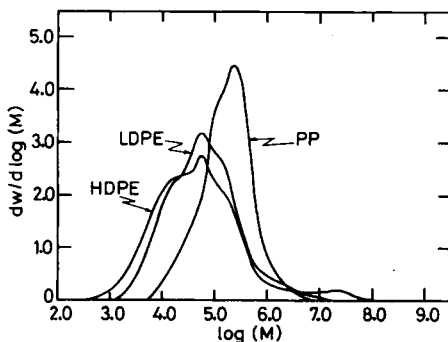


Fig. 5. Molecular weight distribution data for polypropylene, low-density polyethylene and high-density polyethylene A.

stabilizer in the polymers on a quantitative basis. These were found to be 0.003, 0.03, and 0.07 wt-% at 44°C for high-density polyethylene, low-density polyethylene, and polypropylene, respectively.

It should be noted at this point, however, that the value obtained in the case of high-density polyethylene may be somewhat less reliable than those determined for the other polymers in view of the very low solubility of 2,4-dihydroxybenzophenone in this polymer. In addition, from the results previously obtained for the distribution of the stabilizer in the polymers, the corresponding effective concentrations in the amorphous regions would be approximately 0.01, 0.05, and 0.18 wt-%. These results, in combination with those for the relative solubilities at different temperatures, permit the evaluation of the stabilizer solubilities in the polymers over the temperature range considered.

In summary, then, the preceding results indicate that a number of parameters relevant to the overall effectiveness of ultraviolet stabilizers in polyolefins may be quantitatively evaluated at stabilizer concentrations normally encountered in practice. A comparison of the results obtained in the present study with those determined for the ultraviolet stabilizer 2-hydroxy-4-octoxybenzophenone will be presented in a subsequent publication.

Appendix

The molecular weight distributions of the polypropylene, low-density polyethylene, and high-density polyethylene A samples used in the present study were determined by

the Polymer Supply and Characterization Centre of RAPRA using gel permeation chromatography. The differential molecular weight distributions, uncorrected for spreading, are presented in Figure 5. The experimental conditions employed are as follows:

Column set: 700–2000 Å, 1.5×10^4 – 5×10^4 Å, 1.5×10^6 – 7.5×10^6 Å, 5×10^8 – 10^7 Å

Solvent: *o*-dichlorobenzene + 0.1% Ionox 330 as antioxidant

Temperature: 137–138°C

Flow rate: 1 ml/min.

The characterization of the polyolefin samples by the Rubber and Plastics Research Association of Great Britain is gratefully acknowledged. J. F. Westlake wishes to thank the National Research Council of Canada for the award of a Postdoctorate Fellowship in 1971–72 and 1972–73.

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Received January 30, 1974

Revised June 27, 1974