

Diffusion of Stabilizers in Polymers. III. 2,4-Dihydroxybenzophenone and 2-Hydroxy-4-Octoxybenzophenone in Polyurethanes

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Synopsis

The diffusion of the radioactively labeled ultraviolet stabilizers 2,4-dihydroxybenzophenone and 2-hydroxy-4-octoxybenzophenone in two linear poly(ester-urethanes) was studied over the temperature range 36–75°C. Within this temperature range, both stabilizers diffused faster in the polyurethane which had a polyester of molecular weight 2000 in its chain rather than in the polyurethane with a polyester of molecular weight 1000 in its chain. 2,4-Dihydroxybenzophenone diffused slightly faster than 2-hydroxy-4-octoxybenzophenone in both polyurethanes. In each case, the results can be represented by an Arrhenius expression $D = D_0 \exp(-E/RT)$. The values of D_0 and E are discussed in terms of the size of the stabilizer molecule and the structure of the polymer.

INTRODUCTION

The stabilization of polyurethanes against the effect of UV light can be an important aspect in the commercial exploitation of many polyurethanes. Polyurethanes are used extensively for coatings of various types of materials, e.g., coatings for fabrics, glass, wood, etc. Where the polyurethane is exposed to UV light which may be in conjunction with oxygen, heat, and water vapor, various photo-initiated degradation processes can occur¹⁻⁴ which would be detrimental to the properties of a polyurethane coating. In these circumstances, it is therefore advantageous to use additives in order to stabilize the polyurethane.

Several factors which may influence the efficiency with which an additive acts as a UV stabilizer have been investigated. These include studies on compatibility of stabilizers with polymers,^{5,6} migration of stabilizers through polymers,⁷⁻⁹ and loss of stabilizers by volatilization from the surface of polymers.^{10,11}

The present paper reports results obtained in connection with the diffusion of two UV stabilizers, 2,4-dihydroxybenzophenone and 2-hydroxy-4-octoxybenzophenone, in two linear polyurethanes.

EXPERIMENTAL

Materials

Ultraviolet Stabilizers. The preparations and purifications of the ¹⁴C-labeled samples of 2,4-dihydroxybenzophenone⁸ and 2-hydroxy-4-octoxybenzophenone⁹ have been reported previously.

TABLE I
 Compression Molding Conditions

Polymer	Thickness of sheet, cm	Mold temperature, °C	Mold pressure, tons on 4-in. diameter ram	Pre-heat time, min	Compression time, min
E.1	0.03–0.06	165	7	5	2
E.1	0.06–0.09	167.5	10	5	3
E.1	0.09–0.11	170	12	6	2
E.1	0.11–0.15	170	13	6	2.5
E.2	0.03–0.06	157.5	8	7	2
E.2	0.06–0.09	160	10	6	2
E.2	0.09–0.11	165	12	5	2
E.2	0.11–0.15	165	12	6	2

Polymers. Commercial samples of two linear polyurethanes in the form of irregular chips were used in the present work. One polymer (referred to as E.1) was based on poly(1,4-butanediol adipate) units of molecular weight 1000, diphenylmethane diisocyanate (MDI), and 1,4-butanediol as a chain extender. The other polymer (referred to as E.2) was based on poly(1,4-butanediol adipate) units of molecular weight 2000 with the diisocyanate and chain extender both the same as in E.1.

Procedure

Formation of Polymer Sheets. Compression and injection molding techniques were used to prepare sheets of the polyurethanes.

Compression-Molded Sheets. The machine used was a 20-ton hydraulic press (George E. Moore and Son, Birmingham, Ltd.). A quantity of the polymer, varying in weight from 1 g up to 15 g, depending on the thickness of the sheet required, was placed between two squares (20 cm × 20 cm) of mold release paper (Multithane 701, Wiggins Teape, London, Ltd.) which were separated by metal shims. This was then placed in contact with the platens which were at the required temperature and the polymer allowed to warm up over a period of several minutes. Pressure was then applied to spread the polymer into a sheet of uniform thickness. After 2–3 min, the pressure was released and the polymer sheet, together with the mold release paper, removed to cool at room temperature. The exact conditions of time, temperature, and pressure varied somewhat with the polymer used and the thickness of the sheet required; these conditions are shown in Table I.

Injection-Molded Sheets. Since it was found to be extremely difficult to compression mold sheets of thickness greater than 0.15 cm because of heat transfer problems and the formation of bubbles, thicker sheets were therefore formed by using an injection molding machine (Unimolder, Fox and Offord, Birmingham, Ltd.). The conditions used are shown in Table II. A mold was chosen which produced a circular sheet 6.0 cm in diameter and 0.19 cm thick.

Diffusion Experiments. Diffusion studies were carried out using discs 3.5 cm in diameter which were cut from the compression- and injection-molded sheets.

TABLE II
Injection Molding Conditions

Polymer	Cylinder temp., °C		Mold temp., °C	Mold pressure, lb/in. ²	Cylinder pressure, lb/in. ²	Injection time, sec
	Front	Rear				
E.1	190	180	55	1000	2300	3
E.2	170	165	50	1500	2000	3

The apparatus and procedure used to follow the diffusion has already been described in detail.^{8,9} An amount of stabilizer solution (at a concentration of 0.05 g/5 ml in acetone) was used to give a final equilibrium counting rate of between 100 and 250 counts/min, this amount was within the range 0.02–0.20 ml depending on the thickness of the disc and was applied to the polymer using a microliter pipet.

The experiments were carried out in the temperature range of 36–75°C, and the thicknesses of the discs used were such that the times required to reach the equilibrium counting rates varied between 100 and 700 hr.

Determination of Diffusion Coefficient. Two diffusion equations have been formulated^{8,9} which are applicable to two different situations. One equation is applicable to when the stabilizer is present in sufficient quantity to maintain the concentration constant at one of the polymer surfaces (saturation conditions); and the other equation is applicable to when the concentration of the stabilizer is so low that diffusion occurs under conditions approaching zero concentration (nonsaturation conditions). Both equations can be used to generate theoretical diffusion curves which on comparison with the experimental curves lead to evaluation of the diffusion coefficient D .^{8,9}

RESULTS AND DISCUSSION

The theoretical diffusion equations mentioned above require a knowledge of the absorption coefficient of the polymer for the ¹⁴C-beta particles; this can be obtained from a value of the density of the polymer.⁸ The densities of the polymers E.1 and E.2 were measured by weighing several discs (3.5 cm in diameter) of each of the polymers in air and water and were found to be 1.221 and 1.201 g/cm³, respectively.

In order to determine which of the two diffusion equations (saturation or nonsaturation) was satisfied by the experimental conditions, a relatively concentrated solution of 2,4-dihydroxybenzophenone was made up in acetone (0.5 g/5 ml). Three discs of E.1 (each ~0.01 cm thick) were stacked together and the concentrated solution (0.03 ml, which corresponded to approximately ten times the usual weight of stabilizer) was applied to one surface. The three discs were tightly stacked together in a diffusion cell, and the increase in counting rate at 36°C was followed as usual. The equilibrium counting rate reached was 3103 counts/min. The stack was then separated and the center disc was counted in the diffusion cell. The equilibrium counting rates of this disc were 3236 counts/min at the top of the disc and 3271 counts/min

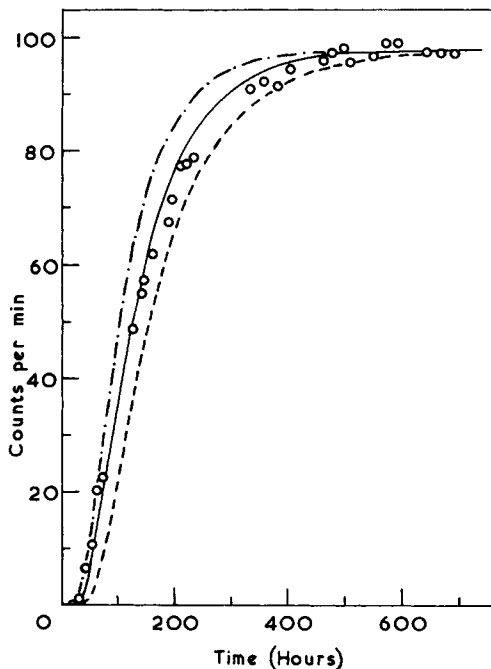


Fig. 1. Variation in surface counting rate for the diffusion of 2-hydroxy-4-octoxybenzophenone in polymer E.1: temperature, 60°C; disc thickness, 0.101 cm; (O) experimental points; (—) theoretical curve for $D = 3.20 \times 10^{-9} \text{ cm}^2/\text{sec}$; (- · - · -) theoretical curve for $D = 3.84 \times 10^{-9} \text{ cm}^2/\text{sec}$; (- - -) theoretical curve for $D = 2.56 \times 10^{-9} \text{ cm}^2/\text{sec}$.

at the bottom of the disc. This experiment showed that the polymer could hold a concentration of stabilizer at the least equivalent to 3000 counts/min, without any significant blooming to the top surface. It also showed that the equilibrium counting rates of between 100 and 250 counts/min obtained in

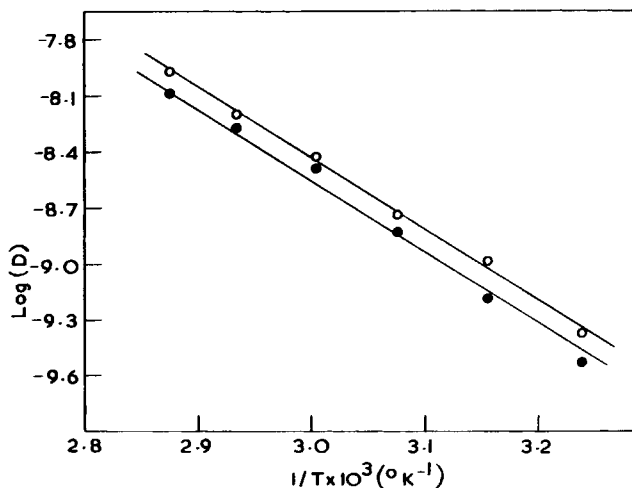


Fig. 2. Arrhenius plot of $\log D$ vs. $1/T$ for diffusion of 2,4-dihydroxybenzophenone (O) and 2-hydroxy-4-octoxybenzophenone (●) in polymer E.1.

TABLE III
 Arrhenius Parameters for Diffusion

Polymer	Stabilizer	D_0 , (cm^2/sec)	Activation energy, kcal/mole
E.1	2,4-dihydroxybenzophenone	940	17.4
E.1	2-hydroxy-4-octoxybenzophenone	710	17.4
E.2	2,4-dihydroxybenzophenone	2.0	12.1
E.2	2-hydroxy-4-octoxybenzophenone	1.7	12.1

the studies with the more dilute solutions of the stabilizers (0.05 g/5 ml) corresponded to stabilizer concentrations that were well below those required to saturate the polymers. The nonsaturation equation was therefore used throughout to evaluate the diffusion coefficients.

Diffusion studies were carried out in the temperature range of 36–75°C. Typical experimental results are shown in Figure 1 for the diffusion of 2-hydroxy-4-octoxybenzophenone in polymer E.1 at 60°C. The open circles representing the experimental data are a good fit with the solid curve, which is the theoretical curve corresponding to a value of $3.2 \times 10^{-9} \text{ cm}^2/\text{sec}$. It can also be seen from Figure 1 that the curve-fitting procedure yields an accurate value of the diffusion coefficient since a 20% change in the value of the diffusion coefficient markedly alters the position of the theoretical curve. Duplicate experiments, which were carried out at most temperatures, indicated good reproducibility (within 15%) in the calculated values of the diffusion coefficients. In addition, experiments at 60°C, where it was possible to use both compression- and injection-molded discs of the two polymers, showed that there were no measurable differences in the diffusion coefficients for the stabilizers in either type of disc. The diffusion coefficients were thus independent of the mode of preparation of the discs.

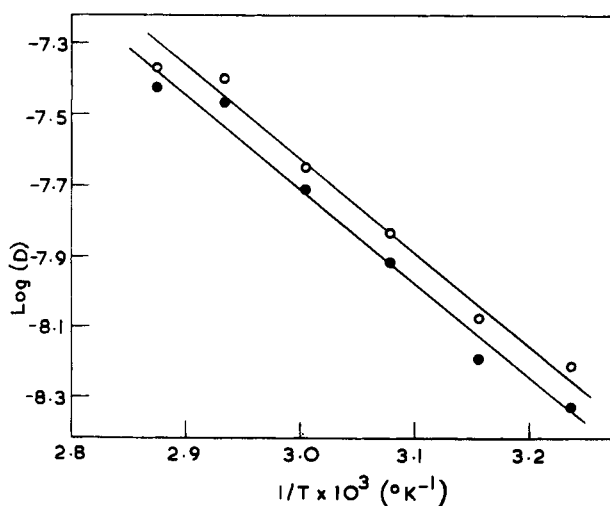


Fig. 3. Arrhenius plot of $\log D$ vs. $1/T$ for diffusion of 2,4-dihydroxybenzophenone (O) and 2-hydroxy-4-octoxybenzophenone (●) in polymer E.2.

The results can be satisfactorily represented by an Arrhenius expression $D=D_0 \exp(-E/RT)$, where E is the activation energy and D_0 is a constant related to the entropy of activation. The plots of $\log D$ versus $1/T$ for the two stabilizers in the polymer E.1 are presented in Figure 2, and the corresponding plots for the polymer E.2 are shown in Figure 3. Values of D_0 and E obtained from these graphs are given in Table III.

2,4-Dihydroxybenzophenone diffuses slightly faster than 2-hydroxy-4-octoxybenzophenone in both polyurethanes. The activation energies of the two stabilizers in a given polyurethane are the same so that the slower rate of diffusion of the octoxy compound is due to its lower value of D_0 which can be explained as arising from a steric effect caused by the presence of the bulky octyl side group.

Polymer E.1 has a shorter soft segment (polyester of molecular weight 1000) than polymer E.2 (polyester of molecular weight 2000), which leads to E.1 being a more rigid polymer than E.2. This was confirmed by measuring the glass transition temperatures of the two polymers by differential scanning calorimetry, the values obtained being $-18 \pm 5^\circ\text{C}$ for E.1 and $-40 \pm 5^\circ\text{C}$ for E.2. Therefore, a substance diffusing in the polymer E.1 will require a higher activation energy than when the same substance is diffusing in the more flexible polymer E.2. This was borne out by the fact that 2,4-dihydroxybenzophenone and 2-hydroxy-4-octoxybenzophenone both had higher activation energies for diffusion in E.1 rather than in E.2.

An increase in activation energy is often accompanied by an increase in the corresponding value of $\log D_0$, e.g., for diffusion of gases in rubbers,^{12,13} for organic compounds in polyolefins,^{5,6} for viscous flow processes,¹⁴ and for a wide range of chemical reactions.¹⁵ The results in the present work show the same trend. The higher activation energy for diffusion of a particular stabilizer in E.1 as compared with that for diffusion in E.2 is compensated somewhat by an increase in the corresponding value of D_0 (Table III). The increase in D_0 is equivalent to an increase in the entropy of activation, which is to be expected since there will be a relatively greater disruption of the polymer chains on diffusion of a substance in E.1 rather than for diffusion in the more flexible E.2.

Some caution should be exercised in extrapolating the results of the present study to more practical cases where polyurethanes are employed as very thin coatings which have been cast from the melt or from solvents, since the method of sample preparation and morphologic structure of the polymer can have a pronounced effect on the rate of diffusion. The degree of confidence in this extrapolation is somewhat increased since consistent results were obtained here over a fairly wide range of thickness, and also two different (although in some respects similar) methods of preparation of the polymer discs gave similar results.

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