Mobility and Solubility of Antioxidants and Oxygen in Glassy Polymers. I. Concentration and Temperature Dependence of Antioxidant Sorption

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ABSTRACT: Sorption experiments have been conducted at temperatures between 65 and 135°C using five phenolic antioxidants in polycarbonate at different antioxidant concentrations. A model based on the free volume was used to predict the mobility of the additives. In this model, the ratio of the specific volume of a jumping unit to the free volume available in the polymer determines the diffusion behavior of the additives. It was found that the mobility of the antioxidant was predicted accurately using literature and experimental data on the free volume in polycarbonate. Furthermore, the solubility of the antioxidants was predicted very well, based on thermodynamic considerations. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 2163–2178, 2003

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INTRODUCTION

The efficiency of the stabilization of a polymer product by antioxidants against oxidation depends on the consumption and loss (evaporation) of the antioxidants from the material. Experimental work showed a direct relationship between the physical parameters, the solubility and mobility of the antioxidant, and the service life of the polymer product. Reliable predictions of these parameters can simplify the choice of an antioxidant for a certain application significantly. A number of papers have been published concerning the mobility of antioxidants in rubbery polymers[1–5]. However, few data are available on the mobility and solubility of antioxidants in glassy polymers.

Thermo- and photooxidation can be suppressed by the use of the appropriate antioxidants. The efficiency of this reaction depends on certain physical properties of the antioxidant molecules. In order to obtain a good efficiency of the stabilizer against oxidation in the polymer, antioxidant molecules must be able to inactivate the radicals and decompose the hydroperoxide groups as soon as they are formed. The availability of the antioxidants at the oxidation site is thought to be determined by the solubility and mobility of the antioxidant in the polymer. Much work has been done concerning the diffusion and solubility of antioxidants in polyolefins.[1–5] Typical values for the diffusion coefficient of antioxidants in polyolefins are in the range of $10^{-13} - 10^{-15}$ m²/s at room temperature. The diffusion coefficient of macroradicals in these polymers is on the order of 10^{-22} m²/s. However, the diffusion of small radicals, such as hydroxyl radicals, is probably much faster than the antioxidant diffusion.

For polyolefins, an empirical relation was found to exist between the protection time (τ), the diffusion coefficient (D) and the solubility (S) of antioxidants according to the approximation: $\tau \sim (S^2/D)$. It was found that a very high mobility of the antioxidant does not guarantee a high stabilization efficiency.[4,5]

Billingham and Calvert[1,6–8] performed diffusion and solubility measurements on polyolefins and proposed a model to predict the loss of additives and a resulting service lifetime. This model is based on antioxidant loss by surface evaporation or blooming, in relation to the solubility and mobility of the stabilizer. An arbitrary end of life was defined as being an antioxidant level of 10% of the starting value. Malík[9] modified this model and introduced a critical antioxidant concentration below which the polymer is no longer stabilized. However, this model becomes very complex, and a straightforward relation among diffusion coefficient, solubility and protection time cannot be given. Földes[2,10–12] measured the transport of some antioxidants in ethylene polymers. She related the solubility to the Hildebrand solubility parameters and the diffusion to the fractional free volume in the polymer. She found that the solubilities of antioxidants such as Irganox 1010 and 1076 in polyolefins range

from 1–200 mg/mL. This indicates that the solubility is strongly determined by the molecular structure of the antioxidant. Diffusion coefficients for the range of antioxidants studied were found to be on the same order of magnitude: $1–10 \times 10^{-13}$ m^2/s (T = 40 –80°C).

The magnitude of the values for the mobility and solubility of the antioxidant in the polymer is governed by polymer-antioxidant interactions. Moreover, the physical state of the polymer can have a major influence on the mobility and solubility of the antioxidant. This physical state can be changed by ageing, rejuvenation, deformation, orientation and applied stress. Most of these phenomena change the free volume of the polymer, which is responsible for changes in diffusion and possibly solubility. These aspects will be addressed in a forthcoming paper.

In this article, the influence of the concentration and temperature on the mobility and solubility of five phenolic antioxidants in polycarbonate is investigated. The change of these parameters with temperature and concentration is compared with theoretical models.

Theory

The mobility of an additive in a polymer will be predicted using the free volume theory as presented by Vrentas et al. In this theory, diffusion is governed by the ratio of the volume needed for a diffusion jump and the free volume present in the polymer. A distinction must be made between self-diffusion at a low concentration and mutual diffusion at a high concentration of the additive. Diffusion coefficients are obtained through sorption experiments, which must be treated as mutual diffusion. Due to the high additive concentrations, the glass transition temperature of the polymer is changed, which has to be taken into account. Free volume parameters for the polymer are taken from the literature, whereas those for the additive are obtained using viscosity measurements. The solubility of the additive in the polymer is predicted starting with the classic Flory-Huggins theory using polymer-additive interaction parameters.

Diffusion and free volume

The diffusion transport of small molecules in amorphous polymers is related to the frozen-in "free volume."[13] According to this model, the transport is faster in more open matrices having a higher free volume. A diffusional step is possible by a rearrangement of a relatively large number of structural segments. This collective rearrangement is stimulated by the presence of free volume.

Molecular sorption and mobility in glassy polymers can be described by the dual-mode model.[14–16] This model assumes the presence of two types of morpho-

logical domains: the relaxed, which is in thermodynamic equilibrium, and the unrelaxed, where more loosely packed chains form microcavities in the bulk. It is a well-known phenomenon that the sorption of molecules in a polymer matrix often greatly depresses its glass transition temperature. This plasticization effect has a strong influence on the mobility of the polymer and thus on the diffusion and solubility of the molecules in the polymer.

Positron annihilation lifetime measurements, in which the free volume behavior in glassy polymers was studied, revealed that small molecules can effectively soften the polymer molecule packing and polymer segments, introduce excess free volume into the polymer matrix, and cause volume expansion. As a result, the mobility of polymer segments is greatly enhanced and the distribution of free volume becomes wider than in a pure polymer. Couchman and Karasz[17] derived an expression for the glass transition temperature, T_{gm}, for an additive-polymer mixture by calculating the entropy of a dilute-polymer mixture:

$$T_{gm} = \frac{w_1 \Delta C_{p1} T_{g1} + w_2 \Delta C_{p2} T_{g2}}{w_1 \Delta C_{p1} + w_2 \Delta C_{p2}} \quad (1)$$

The values of T_{g1} and T_{g2} represent the glass transition temperatures (K), w_1 and w_2 the weight fractions, and ΔC_{p1} and ΔC_{p2} the change in heat capacity (J g^{-1} K^{-1}) at T_{g1} and T_{g2} of the additive and the polymer, respectively.

Self-diffusion coefficient

The diffusion theory of low molecular weight additives in polymer systems developed by Vrentas et al.[18–26] is based on free volume. The specific volume of a polymer system is comprised of (1) the core volume of compact polymer chains, (2) the interstitial volume representing the volume occupied by segmental vibration of the polymer chains, and (3) the hole-free volume. The free volume theory assumes that molecule mobility is determined by the amount of empty space available for a diffusion jump. Vrentas et al. have published a number of papers concerning the relation between diffusion and free volume. Many other authors have used and extended this model to predict solvent diffusion.[27–32] The self-diffusion coefficient of an additive in a polymer, D_1, can be written as:

$$D_1 = D_0 \exp\left[-\frac{E}{RT}\right] \exp\left[-\frac{\gamma(w_1 V_1^* + w_2 \xi V_2^*)}{V_{FH}}\right] \quad (2)$$

D_0 is a pre-exponential factor, E the critical energy that a molecule must possess to overcome the attractive force holding it to its neighbors, R the universal gas constant and T the temperature. The value γ is an

overlap factor that is introduced because the same free volume is available to more than one molecule (this parameter should be between 1/2 and 1). $\hat{V}_1^*$ and $\hat{V}_2^*$ are the specific critical hole-free volumes of the additive and the polymer segment required for a diffusion jump. The value ξ is the ratio of the molar volume of the jumping unit of the additive to that of the polymer ($= \hat{V}_1^* M_{1j}/\hat{V}_2^* M_{2j}$). M_{1j} and M_{2j} are the molecular weight of the jumping unit of the additive and polymer respectively. The average free-hole volume, $\hat{V}_{FH}$ (cm^3/g), can be written as function of the weight fractions and free volumes of the additive ($\hat{V}_{FH1}$) and polymer ($\hat{V}_{FH2}$):

$$\hat{V}_{FH} = w_1 \hat{V}_{FH1} + w_2 \hat{V}_{FH2} \qquad (3)$$

Free volume of polymer

Below the glass transition temperature of the polymer, the specific hole free volume of the polymer, $\hat{V}_{FH2}$, is strongly dependent on the temperature history and additive weight fraction. The low molecular additive in the polymer reduces the glass transition temperature of the mixture, T_{gm} according to eq. (1). Above T_{gm}, the hole free volume of the polymer is given by[20]

$$\hat{V}_{FH2} = \hat{V}_2^0(T_{g2})[f_{H2}^g + (\alpha_2 - (1 - f_{H2}^g)\alpha_{c2})(T - T_{g2})]$$
$$= K_{12}(K_{22} + T - T_{g2}) \quad T > T_{gm} \quad (4)$$

The variables α_2 and α_{c2} are the thermal expansion coefficients of the equilibrium liquid polymer and of the sum of the specific occupied volume and the specific interstitial volume of the polymer respectively. $\hat{V}_2^0(T_{g2})$ is the specific volume of the equilibrium polymer at the glass transition temperature of the pure polymer. The value f_{H2}^g is the fractional hole free volume of the polymer at the glass transition temperature [$= \hat{V}_{FH2}(T_{g2})/\hat{V}_2^0(T_{g2})$].

The free volume parameters of the polymer liquid, K_{12} and K_{22}, are defined as[20]

$$K_{12} = \hat{V}_2^0(T_{g2})[\alpha_2 - (1 - f_{H2}^g)\alpha_{c2}]$$

$$K_{22} = \frac{f_{H2}^g}{\alpha_2 - (1 - f_{H2}^g)\alpha_{c2}} \quad (5)$$

At temperatures below T_{gm}, the hole free volume of the polymer is equal to the free volume at T_{gm} [$\hat{V}_{FH2}(T_{gm})$] minus the decrease in free volume below glass transition, which can be written as[23,25]

$$\hat{V}_{FH2} = \hat{V}_{FH2}(T_{gm}) + \hat{V}_2^0(T_{gm})[(\alpha_{2g} - (1 - f_{H2}^{gm})\alpha_{c2})(T - T_{gm})] = K_{12}(K_{22} + T_{gm} - T_{g2})$$
$$+ K_{12}^g(T - T_{gm}) \quad T < T_{gm} \quad (6)$$

$K_{12}{}^g$ is the change in free volume with temperature for temperatures below the glass transition of the mixture and is defined as

$$K_{12}^g = \hat{V}_2^0(T_{gm})[\alpha_{2g} - (1 - f_{H2}^{gm})\alpha_{c2}] \qquad (7)$$

$\hat{V}_2^0(T_{gm})$ is the specific volume and f_{H2}^{gm} the fractional hole free volume of the equilibrium liquid polymer at T_{gm}. The variable α_{2g} is the thermal expansion coefficient of the glassy polymer.

The values of the free volume parameters of the polymer can be found in the literature from positron annihilation measurements or can be predicted by the Williams-Landel-Ferry (WLF) theory. Positron annihilation is the only direct measurement of free volume.

Free volume of additive

Analogous to eq. (4), the specific hole free volume of the pure additive (V_{FH1}) at temperature T is given by

$$V_{FH1} = K_{11}(K_{21} + T - T_{g1}) \qquad (8)$$

K_{11} and K_{21} are the free-volume parameters for the additive. The free volume parameters for the additive can be derived from viscosity-temperature data:[29]

$$\ln \eta_1 = \ln A_1 + \frac{\gamma \hat{V}_1^*/K_{11}}{K_{21} - T_{g1} + T} \qquad (9)$$

K_{11}/γ and $K_{21} - T_{g1}$ can be determined from a plot of the viscosity of the additive, η_1 (mPa · s), versus the temperature. A_1 is the viscosity at infinite temperature.

The prefactor, $D_0 \exp(-E/RT)$, in eq. (2) can be estimated using a method given by Hong,[29] who combined the relation between the self-diffusion coefficient and the viscosity of pure liquids with the diffusion theory of Vrentas. Assuming that this parameter does not depend on the volume fraction of additive in the polymer, the value can be obtained from measurements on pure additive:

$$D_{01} = D_0 \exp\left(-\frac{E}{RT}\right)$$
$$= \frac{0.124 \times 10^{-11} \tilde{V}_c^{2/3} RT}{\eta_1 M_1 \hat{V}_1} \exp\left[\frac{\gamma \hat{V}_1^*/K_{11}}{K_{21} - T_{g1} + T}\right] \quad (10)$$

$\tilde{V}_c$ (cm^3/mol) and M_1 (g/mol) are the additive's critical molar volume and molecular weight, respectively, and 0.124×10^{-11} is a constant with units of mol$^{2/3}$. $\hat{V}_1$ (cm^3/g) is the specific volume of the pure additive. The diffusion prefactor, D_{01}, is thus determined from viscosity data.
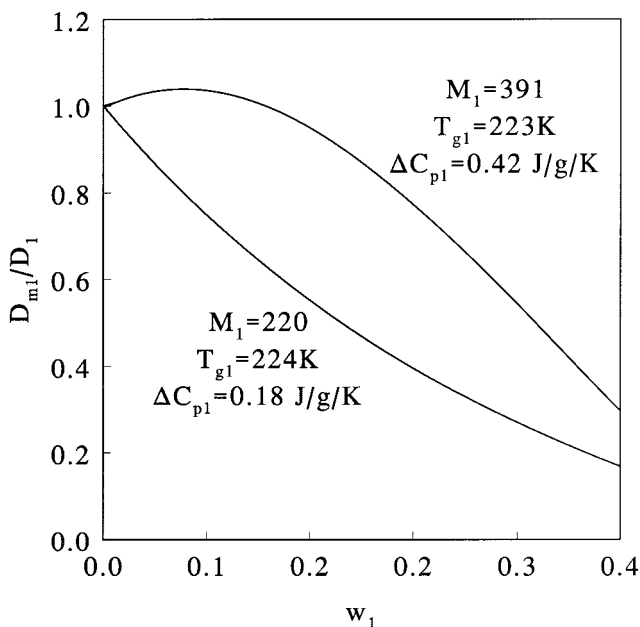
Figure 1 Ratio of mutual and self diffusion coefficients (D_{m1}/D_1) versus weight fraction additives calculated from eq. (11) for two antioxidants, with $\Delta C_{p2} = 0.41$, $T = 353$ K, $T_{g2} = 418$ K, and $\chi = 1$.

Mutual diffusion coefficient

For higher concentrations of additives in glassy polymers, the mutual diffusion coefficient has to be applied. The mutual diffusion coefficient, D_{m1}, can be calculated using the following equation:[24]

$$D_{m1} = D_1 \frac{M_1 w_2^2 \Delta C_{p2}[T_{g2} - T_{gm}]}{RT}\left[2\left(1 - \frac{T}{T_{gm}}\right)\right.$$
$$\left. + \frac{w_2[T_{g2} - T_{gm}]T}{w_1 T_{gm}^2}\right] + D_1(1 - \phi_1)^2(1 - 2\chi\phi_1) \quad (11)$$

The symbol ϕ_1 is the volume fraction additive and χ the polymer solvent interaction parameter (see next section). The second term on the right side of the equation is the Flory-Huggins theory for rubbery systems, and the first term on the right side is a modification of the theory applied for diffusion behavior in glassy polymers. In Figure 1 the dependence of the ratio of mutual to self diffusion coefficients on the fraction additive is shown. Examples are given for two antioxidants in polycarbonate. From Figure 1, it is clear that the mutual diffusion coefficient depends on the physical properties of the additives used. In one case ($M_1 = 391$, $\Delta C_{p1} = 0.42$ J g^{-1} K^{-1} and $T_{g1} = 223$ K), the mutual diffusion coefficient becomes larger than the self diffusion coefficient for small weight fractions and at larger weight fractions. In the other case, the ratio D_{m1}/D_1 decreases continuously.

The application of the model for mutual diffusion of small molecules in a polymer is complicated by the

number of parameters needed. Some parameters can be found in the literature, while others should be measured or estimated.

The model simplifies significantly at low concentrations of small molecules in polymers. This holds for the diffusion of low concentrations of antioxidants in commercial polymers. The concentration of these stabilizers is normally less than 1%. When w_1 approaches zero ($\phi_1 \to 0$), eq. (11) simplifies to

$$D_{m1} = D_1 = D_0\exp\left[-\frac{E}{RT}\right]\exp\left[-\frac{\gamma\xi\hat{V}_2^*}{\hat{V}_{FH}}\right] \quad (12)$$

In this limit ($w_1 \to 0$), it is expected that the free volume effects are much more important than the energy effects in determining the temperature dependence of D_{m1} and hence, the energy term $\exp(-E/RT)$ can be incorporated into the pre-exponential factor D_{01}.

Solubility

The solubility of small molecules in polymers can be derived from the classic Flory-Huggins theory of mixing of liquids with polymers.[12] The partial molar free energy of mixing is

$$\Delta G_m = RT\left[\ln \varphi_1 + \left(1 - \frac{V_1}{V_2}\right)\varphi_2 + \chi\varphi_2^2\right] \quad (13)$$

Here ϕ_1 and ϕ_2 are the volume fractions and V_1 and V_2 the molar volume of the additive and polymer respectively. In the case of antioxidants, at temperatures below their melting points, the free energy of fusion also has to be taken into account:[12]

$$\Delta G_f = \Delta H_f\left(1 - \frac{T}{T_m}\right) \quad (14)$$

The value ΔH_f is the heat of fusion. For antioxidants in the liquid state, the free energy of fusion is zero. At equilibrium, the sum of free energies is equal to zero:

$$\Delta G_f + \Delta G_m = 0 \quad (15)$$

And, when it is assumed that the molar volume of the polymer is much larger than that of the additive ($V_2 \gg V_1$), eq. (15) can be rewritten as:

$$-\ln \varphi_{antioxidant} = \frac{\Delta H_f}{RT}\left(1 - \frac{T}{T_m}\right) + \varphi_{polymer} + \chi\varphi_{polymer}^2 \quad (16)$$

The interaction parameter, χ, can be calculated from the molar volume of the additive and the partial solubility parameters according to Hansen[33]:
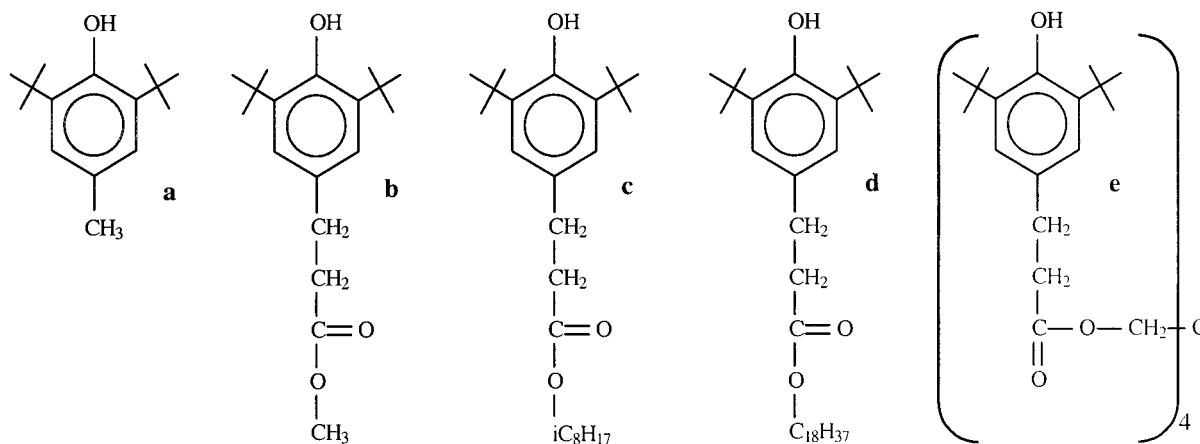
Scheme 1 Antioxidants used in the diffusion experiments: a) 3,5-di-*t*-butyl-4-hydroxytoluene (BHT); b) Methyl-3-(3,5-di-*t*-butyl-4-hydroxyphenyl)-propionate (MBHP); c) Octyl-3-(3,5-di-*t*-butyl-4-hydroxyphenyl)-propionate (OBHP); d) Octadecyl-3-(3,5-di-*t*-butyl-4-hydroxyphenyl)-propionate (ODBHP); e) Pentaerythritol Tetrakis(3-(3,5-di-*t*-butyl-4-hydroxyphenyl)-propionate) (PTBHP)

$$\chi = \frac{V_1}{RT}\left[(\delta_{d1} - \delta_{d2})^2 + 0.25(\delta_{p1} - \delta_{p2})^2 \right.$$

$$\left. + 0.25(\delta_{h1} - \delta_{h2})^2\right] \quad (17)$$

The values δ_{d1} and δ_{d2} are the dispersion, δ_{p1} and δ_{p2} the polarity and δ_{h1} and δ_{h2} the hydrogen bond solubility parameters for the additive and polymer, respectively. Eq. (16) can be simplified for temperatures above the melting points of the antioxidants:

$$-\ln \varphi_{antioxidant} = \varphi_{polymer} + \chi\varphi_{polymer}^2 \quad (18)$$

EXPERIMENTAL

Preparation of films

Additive free polycarbonate (Lexan 105) was received from General Electric Plastics. Solutions of 20 wt % were prepared by dissolving the appropriate amount in methylene chloride (Fluka p.a.). A homogeneous solution was obtained after 2 h stirring at room temperature. This solution was cast on a glass plate, and polycarbonate films were obtained with thicknesses between 70 and 90 μm. The films were dried at room temperature for at least two days before further experiments were conducted.

Antioxidants

A number of commercially available antioxidants were selected. The functional group of these antioxidants was a sterically hindered phenolic group. The side chain at the para-position was varied. The five antioxidants studied are depicted in Scheme 1 and are listed in Table I, together with the molecular weights (MW) and melting points (MP).

Diffusion experiments

The antioxidant was dissolved in a solvent that will not react with the polymer used. For the phenol-polycarbonate system decane (Fluka p.a.) was chosen. Solutions were made of approximately 5, 10, 20, 40 and 100 vol % antioxidant in decane. The temperatures chosen for the diffusion experiments ranged from 65 to 135°C, depending on the antioxidant.

Small polycarbonate films were immersed in the antioxidant solution. After certain time intervals, a sample was removed from the solution and rinsed twice with isooctane and once with ethanol. After drying, the total amount of antioxidant that diffused into the sample was measured using UV spectroscopy.

The sorption of the antioxidants into the polymer film can be modeled by simple Fickian diffusion. The

TABLE I
Antioxidants Used in Sorption Experiments

Name	MW (g/mol)	MP (°C)	Name
BHT	220	72	Butylated Hydroxy Toluene (BHT)
MBHP	292	68	Methyl-3-(3,5,-di-*t*-*B*utyl-4-hydroxyphenyl)-propionate (Ralox 35)
OBHP	391	<RT	Octyl-3-(3,5,-di-*t*-*B*utyl-4-*H*ydroxyphenyl)-*P*ropionate (Irganox 1135)
ODBHP	531	53	Octa*D*ecyl-3-(3,5,-di-*t*-*B*utyl-4-*H*ydroxyphenyl)-*P*ropionate (Irganox 1076)
PTBHP	1178	118	Pentaerythritol *T*etrakis-3-3-(3,5,-di-*t*-*B*utyl-4-*H*ydroxyphenyl)-*P*ropionate (Irganox 1010)

total amount of antioxidant in the polymer films at time t (M_t) was measured. The mass increase can be described by the following equation:[34]

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left[\frac{-D_{m1}(2n+1)^2\pi^2 t}{d^2}\right]$$

(19)

M_∞ is the total amount of antioxidant in the film at equilibrium, and d is the thickness of the film. For the initial part of the diffusion process ($M_t/M_\infty < 0.6$), this equation can be approximated by:

$$\frac{M_t}{M_\infty} = 4\sqrt{\frac{D_{m1}t}{\pi d^2}}$$

(20)

A straight line should be obtained for small time intervals, plotting the mass increase of the film versus the square root of the time. The slope can be recalculated to obtain the diffusion coefficient once the thickness and equilibrium solubility are known.

UV spectroscopy on antioxidants

The antioxidant concentration was determined by UV spectroscopy, using a Hitachi U-2001 spectrophotometer. Caution was necessary to avoid possible interference by peaks of oxidized antioxidants. The reaction mechanisms of the phenolic antioxidants depend on the nature of the group at the para-position of the phenol ring.[35] Quinonemethides formed during the oxidation of phenolic antioxidants can react with alkyl, alkoxy and peroxy radicals. Klemchuk et al.[36] described the UV-absorption maxima and extinction coefficients of a number of possible reaction products. They found that the oxidation product has an absorption maximum at 314 nm, with a very high extinction coefficient ($\epsilon = 44870$ L mol^{-1} cm^{-1}). Absorption maxima between 312 and 316 nm are typical for the oxidation products of phenolic alkyl propionates. The absorption maximum and extinction coefficient of the non-oxidized antioxidants are (282 nm and 2010 L mol^{-1} cm^{-1}). The oxidation product will therefore be clearly visible, even at very low levels.

Figure 2 shows the absorption spectra of the five antioxidants at a concentration of phenolic groups of 0.7 mmol/L. It is clear that the spectra of the five antioxidants almost overlap when the molar concentrations of the phenolic groups are equal. This is an indication that the phenolic group is the absorbing moiety.

Figure 2 also shows the absorption spectrum of polycarbonate. Unfortunately, polycarbonate absorbs UV light below 280 nm, obscuring the lower wavelength part of the antioxidant absorptions. However,
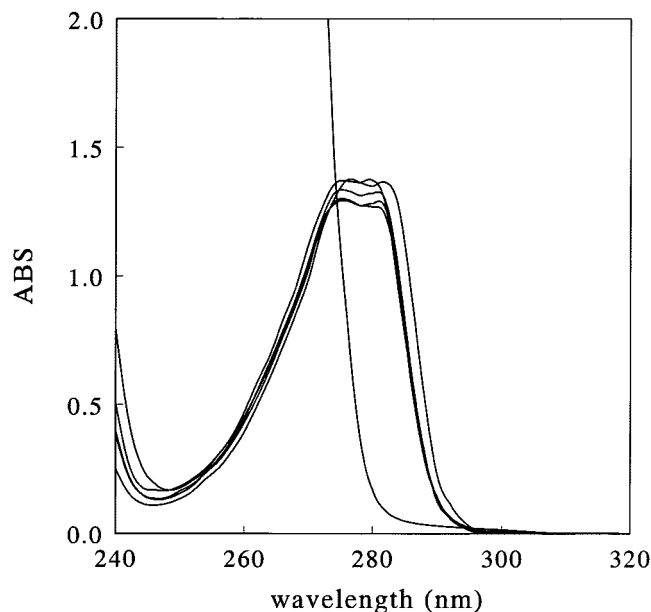

Figure 2 UV absorption spectra of the antioxidants (0.7 mmol/L phenolic groups): BHT, MBHP, OBHP, ODBHP and PTBHP.

the higher wavelength part (>282 nm) gives enough information about the antioxidant peak for concentration calculations.

Four wavelengths were used for concentration measurements: 282, 286, 290 and 294 nm. Polycarbonate samples with varying antioxidant concentrations and varying thicknesses were made by dissolving additive-free polycarbonate and the antioxidant in methylene chloride and casting a film. The absorption of the five antioxidants was measured in these samples. These measurements were used to calibrate the UV absorption measurements. Typical errors in the antioxidant concentrations obtained in this way were in the order of 5–10%.

The molar extinction coefficients for low concentrations in polycarbonate and methylene chloride are listed in Table II. The calibration curves for antioxidants dissolved in methylene chloride are slightly different than those in polycarbonate (Table II) when comparing the extinction coefficients, ϵ_{pc} and ϵ_{mc}.

A PTBHP molecule has four functional groups. Thus the molar extinction coefficient is four times higher than that of the other antioxidants. The extinction coefficients obtained for the five antioxidants are in good agreement with each other.

Two different methods were executed to obtain the antioxidant concentration in the samples. The first involved measuring the absorption of the total polymer film and subtracting the absorption of an additive free sample, and the second involved dissolving the polymer film in methylene chloride and measuring the absorption of the solution. The latter method is preferred when the concentration of antioxidant is

TABLE II
Extinction Coefficients (Lmol^{-1} cm^{-1}) for the Calibration Curves of UV Absorption of Antioxidants in Polycarbonate (ε_{pc}) and Methylene Chloride (ε).

Wavelength (nm)	BHT		MBHP		OBHP		ODBHP		PTBHP	
	ε_{pc}	ε_{mc}	ε_{pc}	ε_{mc}	ε_{pc}	ε_{mc}	ε_{pc}	ε_{mc}	ε_{pc}	ε_{mc}
282	2290	2426	1775	1782	1820	1842	1718	1736	7208	7480
286	1708	1642	1038	895	1191	950	1131	855	4228	4005
290	540	501	245	196	305	210	345	215	1212	912
294	92	91	38	28	55	46	61	35	204	119

very high, and it was used to confirm some of the measurements carried out on films. In addition, it was found that polycarbonate sometimes crystallizes when the antioxidant concentration becomes high. The UV absorption of this crystallization process interferes with the antioxidant absorption.

DSC

DSC measurements were performed on the pure antioxidants, using a TA Instruments, DSC 2920. The samples were heated to 150°C, quenched to −75°C and heated at 3°C/min to 200°C in nitrogen. The heat flow and heat capacity were measured with temperature. The glass transition temperature and heat capacities thus obtained can be used to calculate the glass transition temperature of the mixtures as function of the mole fraction according to eq. (1).

Viscometry

In eq. (9), it was explained that the free volume parameters for the antioxidants can be obtained from viscosity measurements versus temperature. A Brookfield DV-II+ viscometer with SC4-18 spindle was used to obtain the viscosity of the antioxidants from 30–120°C. For the four smallest antioxidants, a speed of 100 rpm (=132 s^{-1}) was used, whereas the antioxidant PTBHP was measured at 0.5 rpm (0.66 s^{-1}), due to its high viscosity.

Solubility parameters

For modelling mobility and solubility, polymer-solvent interaction parameters, χ, are needed. These interaction parameters can be calculated according to eq. (17). This calculation requires the partial solubility parameters for the various components. The solubility parameters for polycarbonate can be found in the literature. Those for the antioxidants were obtained by dissolving them in nine different solvents at room temperature. A simple relation between the experimental interaction parameter and the mole fraction of dissolved antioxidant for an ideal situation is given by[37]

$$\chi_{exp} = -\ln(x_{AO}) \quad (21)$$

The value of x_{AO} is the mole fraction of antioxidant in the solution. This fraction is obtained by making a saturated solution of antioxidant in the solvents. Then the solvent is evaporated and the mass of the remaining antioxidant is measured. The theoretical antioxidant-solvent interaction parameter can be obtained from:

$$\chi_{theo} = \frac{V_{AO}}{RT} \left[(\delta_{d_{AO}} - \delta_{d_{SOL}})^2 + 0.25(\delta_{p_{AO}} - \delta_{p_{SOL}})^2 \right.$$
$$\left. + 0.25(\delta_{h_{AO}} - \delta_{h_{SOL}})^2 \right] \quad (22)$$

From the solubility of the antioxidant in the nine solvents, the solubility parameters are calculated by combining eqs. (21) and (22). The solvents and their solubility parameters are given in Table III.[33,37] The partial solubility parameters of the antioxidants, δ_{dAO}, δ_{pAO} and δ_{hAO} are obtained by finding the minimum value of the sum:

$$\sum_{i=1}^{9} (\chi_{exp,i} - \chi_{theo,i})^2 \quad (23)$$

Here, i represents the solvent used. This method was not possible for OBHP, which is a liquid at room temperature. The partial solubility parameters of this

TABLE III
Solvents for Antioxidants and Their Partial Solubility Parameters and Molar Volumes

Solvent	δ_d (MPa$^{1/2}$)	δ_p (MPa$^{1/2}$)	δ_h (MPa$^{1/2}$)
2-Butanon	16.0	9.0	5.1
Dichloromethane	18.2	6.3	6.1
Cyclohxanon	17.8	6.3	5.1
Aceton	15.5	10.4	7.0
Decane	15.7	0.0	0.0
THF	16.8	5.7	8.0
Dioxaan	19.0	1.8	7.4
Toluene	18.0	1.4	2.0
1-Butanol	15.8	5.7	14.5

TABLE IV
Heat Capacity Changes and Glass Transition
Temperatures of Antioxidants and Polycarbonate

	ΔC_p (J/g°C)	T_g (°C)	T_m (°C)
BHT	0.18 ± 0.03	−49 ± 1	72 ± 1
MBHP	0.38 ± 0.03	−39 ± 1	68 ± 1
OBHP	0.42 ± 0.05	−50 ± 1	<RT
ODBHP	0.41 ± 0.1	−90 ± 5	—
PTBHP	0.30 ± 0.01	45 ± 1	125 ± 1
Polycarbonate	0.41	145	335

antioxidant were estimated by comparison to the other four.

RESULTS AND DISCUSSION

DSC on antioxidants

The results from the DSC measurements on the antioxidants are listed in Table IV. The glass transition temperature and change in heat capacity of the polycarbonate were obtained from the literature.[38] The parameters for the antioxidant ODBHP could not be determined accurately.

The glass transition temperature of polycarbonate is a function of the antioxidant fraction and can now be calculated according to eq. (1). The influence of the largest antioxidant (PTBHP) on the glass transition temperature of polycarbonate is the smallest. The antioxidant with the longest aliphatic tail and lowest solubility, ODBHP, decreases the glass transition temperature the most.
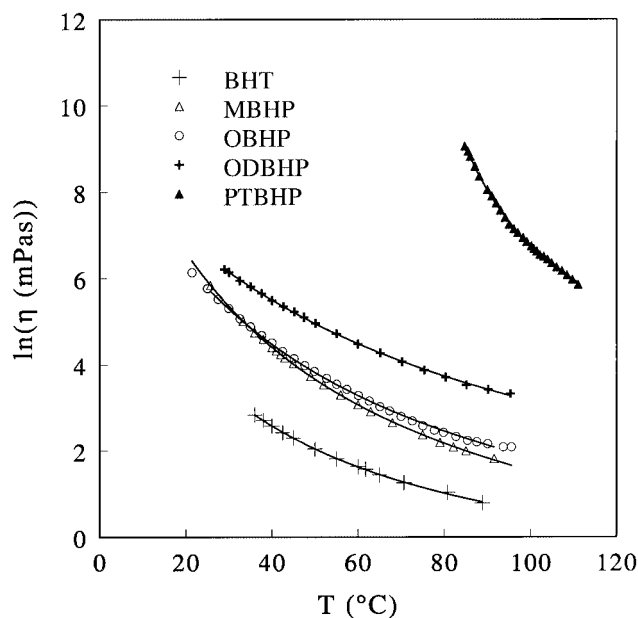

Figure 3 Viscosity of the antioxidants as function of temperature.

TABLE V
Fit Parameters for Viscosity Temperature
Behavior of Antioxidants

	A_1 (mPas)	$\gamma \hat{V}_1^*/K_{11}$ (K)	$K_{21} - T_{g1}$ (K)
BHT	0.17 ± 0.03	307 ± 15	−242 ± 3
MBHP	0.37 ± 0.05	327 ± 11	−252 ± 1
OBHP	0.61 ± 0.07	274 ± 19	−260 ± 3
ODBHP	1.6 ± 0.1	381 ± 25	−236 ± 5
PTBHP	15 ± 2	172 ± 10	−331 ± 1

Rheology of antioxidants

The viscosity of the five antioxidants versus temperature is shown in Figure 3.

These data were obtained by cooling the liquid antioxidants to temperatures below their melting points. The antioxidants can be supercooled significantly before crystallization sets in. The viscosity-temperature curves were fitted using relation (9). The fit parameters for the five antioxidants are listed in Table V.

The largest antioxidant differs significantly from the others. The viscosity of PTBHP is much higher at comparable temperatures above the glass transition temperature.

Solubility parameters

The solubility of the antioxidants in the various solvents was determined by a concentration measurement in saturated solutions. The corresponding molar fractions were then calculated. Table VI lists the molar fractions of four antioxidants in the nine solvents.

The partial solubility parameters of the antioxidants were obtained by a trial and error method that minimized eq. (23). These solubility parameters are listed in Table VII. This table also gives the average partial solubility parameters of polycarbonate found in the literature.[38–40]

Modelling parameters

For modelling the diffusion coefficients, the parameters needed are listed in Table VIII. The values of the

TABLE VI
Solubility (mol/mol) of Antioxidants
in Different Solvents

Solvent	BHT	MBHP	ODBHP	PTBHP
2-Butanon	0.51	0.36	0.13	0.083
Dichloromethane	0.45	0.33	0.17	0.12
Cyclohexanon	0.60	0.38	0.15	0.10
Aceton	0.54	0.35	0.049	0.073
Decane	0.32	0.064	0.073	0.0004
THF	0.77	0.43	0.25	0.053
Dioxaan	0.14	0.35	0.039	0.0071
Toluene	0.48	0.33	0.21	0.067
1-Butanol	0.13	0.083	0.011	0.0015

TABLE VII
Partial solubility Parameters of Antioxidants and Polycarbonate

	δ_d (MPa$^{1/2}$)	δ_p (MPa$^{1/2}$)	δ_h (MPa$^{1/2}$)	V_{sol} (ml/mol)
BHT	15.2	5.2	4.6	210
MBHP	15.8	3.7	6.9	292
OBHP	15.6	3.3	6.2	383
ODBHP	15.5	3	5.6	528
PTBHP	16.4	4.8	6.5	1103
PC	18.3	7.0	7.6	208

specific critical hole-free volumes required for a diffusion jump, $\hat{V}_1^*$ and $\hat{V}_2^*$, were obtained using a method given by Van Krevelen.[38] The parameter ξ was obtained from the relation: $\xi = M_{1j}\hat{V}_1^*/M_{2j}\hat{V}_2^*$. The jumping unit of the polycarbonate was assumed to be the bis-phenol group and not the monomer unit. This is supported by conformational studies by Hutnik et al,[41] who found that the energy required for rotation around the C^{ar}–O bond is lower than that required for rotations around the O–$C^{C=O}$ bond and the C^{ar}–C^{al} bonds. The fact that the complete monomer unit is not involved in the jump can be derived from the empirical relation between the size of the jumping unit and the glass transition temperature given by Zielinski.[28] Furthermore, diffusion experiments on low molecular weight alkanes suggest the same.[42] Therefore it was assumed that M_{2j} = 195 g/mol.

The jumping unit of the antioxidants does not consist of the complete molecule but only a segment. This segmental mobility was demonstrated by Arnould et al.[27] and Vrentas et al.[22] They found that the size of the jumping unit of penetrant molecules levels of with increasing size of alkyl side chains. For example, the jumping unit for methyl acetate is almost equal to that of pentyl acetate,[27] and the jumping units of butane and hexadecane are equal as well.[22] It is therefore assumed that the jumping unit is the same for all of the phenolic antioxidants used in the present study, and this unit consists of the phenolic BHT group.

Experimentally it was found that even for the largest antioxidant the jumping unit was one phenolic group. Therefore, M_{1j} = 220 g/mol.

The free volume parameters of the pure antioxidants were derived from the viscosity data. The data of the free volume parameters of the polycarbonate were taken from various sources. Hong[29] gave a value of 5.6×10^{-4} cm^3 g^{-1} K^{-1} for K_{12}/γ. Furthermore, many positron annihilation lifetime spectroscopy (PALS) data are available, which are used to calculate the free volume behavior directly from the measurements.[43–49] The values for K_{12}/γ and $K_{22} - T_{g2}$ are averaged from these PALS experiments. This yields a free volume of 0.075 cm^3/g at the glass transition temperature. Free volume values derived from viscosity or relaxation experiments fitted to the WLF equation are much smaller than the PALS results. Since PALS experiments are the most direct way of measuring the free volume, these results are used. The positron annihilation experiments on glassy polycarbonate were used to estimate the values for K_{12}^g/γ. Taking the average value of data found in ten publications,[43–52] a value of 2.5×10^{-4} cm^3 g^{-1} K^{-1} was obtained for K_{12}^g/γ.

From the behavior of eq. (10) versus temperature, it appeared that the activation energy was very low (200–300 J/mol). Therefore the prefactor D_{01} was taken to be constant over the temperature range investigated. The error introduced is also given in Table VIII.

The value of the critical molar volume of the antioxidants is not readily available. For a number of solvents, the critical molar volume is given in the literature.[53] When a plot is made of the critical molar volume versus the zero point molar volume ($= \hat{V}_1^*M_1$), a straight line can be obtained having a slope of four (Fig. 4). It is now possible to calculate the critical volume of the antioxidants from this empirical relationship.

TABLE VIII
Parameters for Modelling Diffusion and Solubility of Antioxidants in Polycarbonate

|	BHT	MBHP	OBHP	ODBHP	PTBHP	PC	Ref
$\hat{V}_1^*$ (cm^3/g)	0.879	0.821	0.851	0.877	0.757		38
$\hat{V}_2^*$ (cm^3/g)						0.732	29
ξ	1.35	1.35	1.35	1.35	1.35		This work
V_2^0 (T_{g2}) (cm^3/g)						0.857	15
α_2 (K^{-1})						5.8×10^{-4}	38
α_{2g} (K^{-1})						2.9×10^{-4}	38
K_{11}/γ (cm^3/gK)	2.9×10^{-3}		3.1×10^{-3}	2.3×10^{-3}	4.4×10^{-3}		This work
K_{21}-T_{g1} (K)	−242	−252	−260	−236	−331		This work
K_{12}/γ (cm^3/gK)						5.6×10^{-4}	29, 43–49
K_{22}-T_{g2} (K)						−284	43–49
K_{12}^g/γ (cm^3/gK)						2.5×10^{-4}	43–52
$D_{01} \times 10^9$ (m^2/s)	7.5 ± 0.2	3.4 ± 0.1	1.8 ± 0.1	0.61 ± 0.03	0.056 ± 0.002		This work
$\bar{V}_c$ (cm^3/mol)	774	959	1331	1863	3567		This work
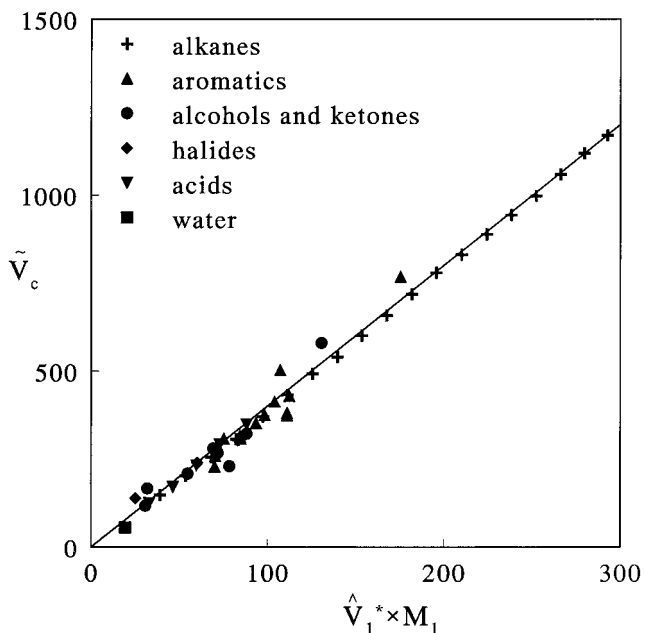
Figure 4 Critical volume of several solvents versus the zero point molar volume ($V_1 M_1$). The slope of the line is 4.

Besides these parameters, the polymer-antioxidant interaction parameter, χ, is needed for the theoretical description of the sorption behavior. This interaction parameter depends on the temperature according to eq. (17).

Crystallization in polycarbonate

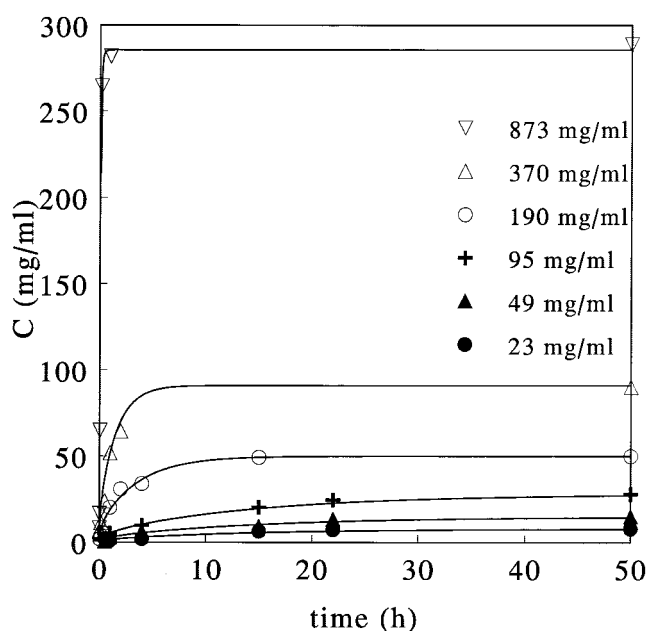It is known from the literature that polycarbonate can crystallize due to the influence of certain solvents. For

Figure 6 Concentration BHT in polycarbonate as a function of immersion time in pure BHT for four temperatures.

example, when immersed in acetone, the polymer immediately starts to turn white. Crystallization was also observed in contact with the smallest antioxidants, BHT and MBHP at all temperatures used. PC exposed to pure OBHP also shows this phenomenon, only much slower and at higher temperatures. The crystallization behavior is associated with the plasticizing effect of the additive. The additive penetrates into the
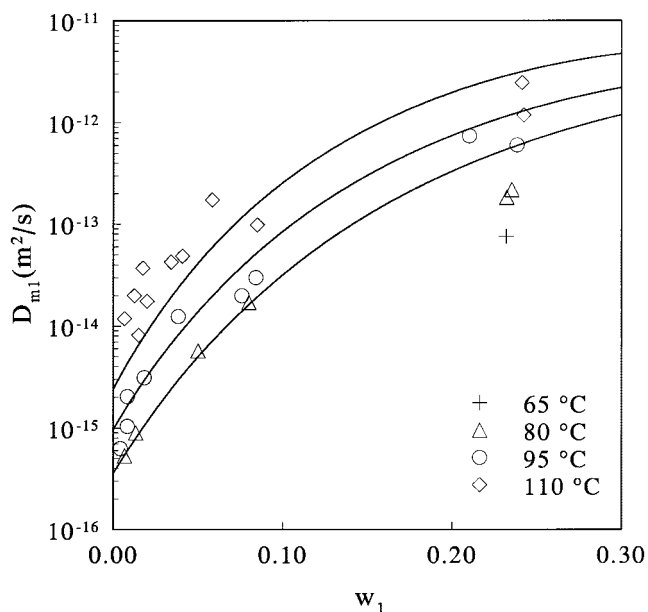

Figure 5 Concentration BHT in polycarbonate as a function of immersion time at 110°C for six antioxidant concentrations in the surrounding decane solution.

Figure 7 Plot of the mutual diffusion coefficients of BHT in polycarbonate versus the concentrations at different temperatures. The solid lines are predictions using the model and parameters previously given.

TABLE IX
Theoretical and Experimental Solubility of BHT
in Polycarbonate Versus Temperature

T (°C)	ϕ (ml/ml)$_{theoretical}$	S (mg/g)$_{theoretical}$	S (mg/g)$_{experimental}$
65	0.278	231	232 ± 9
80	0.289	235	234 ± 11
95	0.299	240	238 ± 12
110	0.316	252	242 ± 10

polymer, giving the polymer chains more freedom of motion and a possibility to crystallize. This additive induced crystallization can influence the measured mobility significantly. When samples had lost their transparency because of crystallization, the sample was dissolved in methylene chloride. The antioxidant concentration of the solution was measured and converted to the corresponding concentration in the film.

Diffusion and solubility of antioxidants in polycarbonate

Butylated hydroxy toluene (BHT)

The diffusion of BHT into polycarbonate is fast compared to the other antioxidants. The sorption temperatures were chosen in order to perform the experiments in a suitable time. It was found that the diffusion of BHT at low concentrations and low temperatures (<80°C) is very slow. So, at the lowest temperature only the diffusion of 100% BHT was monitored. The diffusion of BHT is so fast above 110°C that accurate measurements are no longer possible.
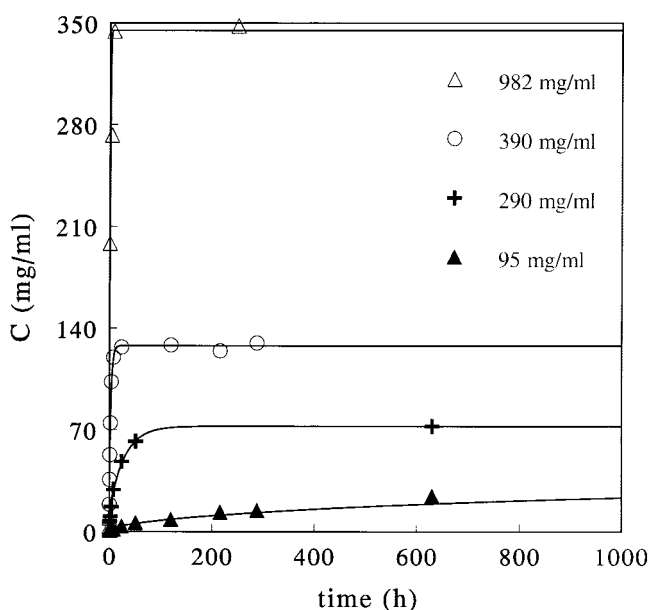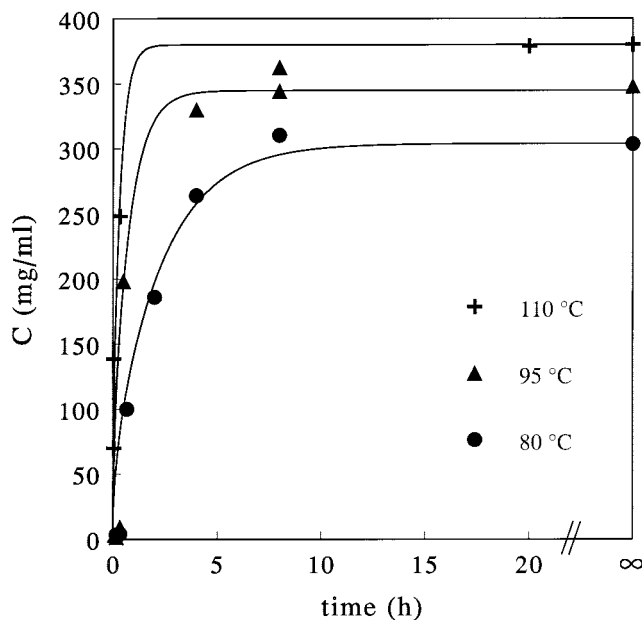

Figure 9 Sorption of MBHP in polycarbonate immersed in pure antioxidant versus time for three temperatures.

When polycarbonate films are immersed in pure BHT at all temperatures, the polymer starts to crystallize immediately. This means that UV spectroscopy can only be applied on dissolved samples.

In order to determine whether the diffusion and solubility of the antioxidant in polycarbonate is concentration dependent, sorption experiments were performed with six different antioxidant concentrations in decane. A plot of these experiments at 110°C is
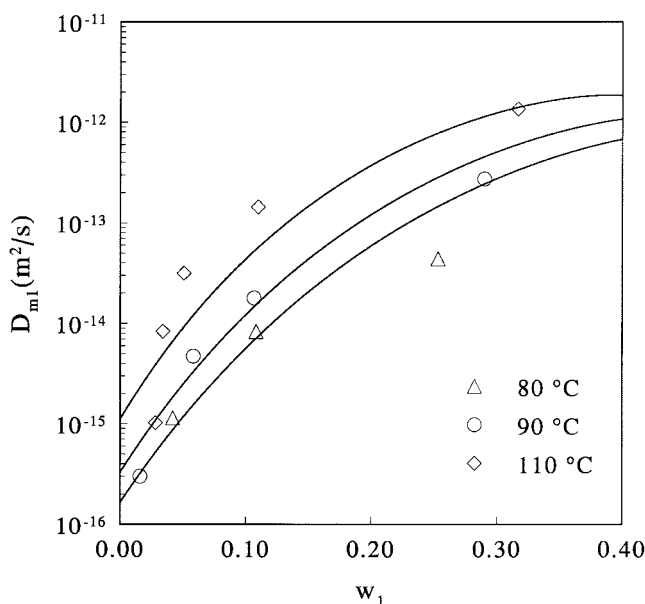

Figure 8 Sorption of MBHP in polycarbonate versus time for four antioxidant concentrations in the surrounding liquid.

Figure 10 Mutual diffusion coefficient of MBHP in polycarbonate versus concentration for three temperatures.

TABLE X
Theoretical and Experimental Solubility of MBHP
in Polycarbonate Versus Temperature

T (°C)	ϕ (ml/ml)$_{theoretical}$	S (mg/g)$_{theoretical}$	S (mg/g)$_{experimental}$
80	0.376	334	254 ± 16
95	0.391	344	290 ± 18
110	0.407	354	317 ± 21

given in Figure 5. The curve of 873 mg/ml is that of pure BHT.

An example of the temperature dependence of the sorption of pure BHT in polycarbonate is shown in Figure 6. From this graph, it becomes clear that the solubility of BHT in polycarbonate is not very sensitive to temperature variations between 65 and 110°C. However, the diffusion coefficient clearly decreases with decreasing temperature.

The mutual diffusion coefficients obtained from the experiments are plotted versus the equilibrium concentration in the polymer [C(mg/ml) at $t = \infty$] for four different temperatures in Figure 7. The figure also shows the predictions using the free volume model and the parameters from Table VIII.

From Figure 7 it is clear that the mutual diffusion coefficient depends very strongly on the concentration of antioxidant in the polymer. Furthermore, the predictions made using the diffusion model are in good agreement with the measurements. Only the measurements at the highest temperature deviate to some extent from the predictions. The diffusion coefficients obtained during immersion in pure BHT are not in
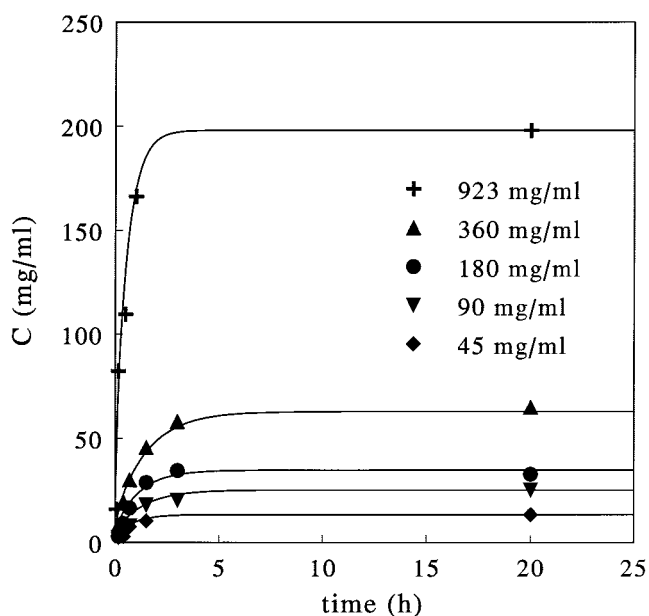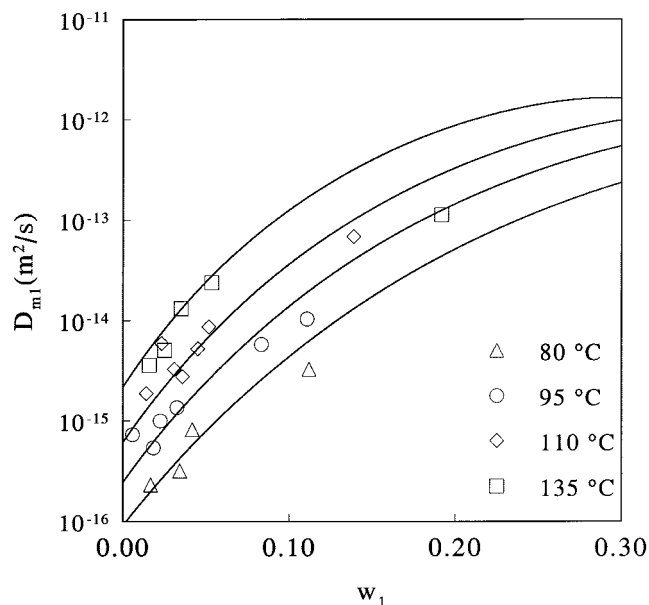

Figure 12 Mutual diffusion coefficient of OBHP in polycarbonate versus concentration for four temperatures

good agreement, because of the solvent induced crystallization of the polycarbonate.

The solubility of BHT in polycarbonate can be calculated using eqs. (17) and (18). These theoretical values are compared to the experimental values derived from the sorption measurements in Table IX. The agreement between the theoretical and experimental values for the solubility is excellent, within the experimental accuracy.

Methyl-3-(3,5-di-*t*-butyl-4-hydroxyphenyl)-propionate

The results of the sorption experiments of MBHP in polycarbonate are presented in Figure 8 for various concentrations at 95°C and Figure 9 for pure antioxidants at three temperatures. From Figures 8 and 9 it is clear that diffusion coefficient and solubility are both temperature and concentration dependent. The mutual diffusion coefficients of MBHP in polycarbonate for five concentrations and three temperatures are given in Figure 10.

The experimental values of the diffusion coefficient agree less with the predictions made using diffusion theory than the values of BHT sorption. Values at the highest temperature deviate more from the predictions than values at lower temperatures. However, it is clear that the order of magnitude of the diffusion coefficients can be predicted rather well.

The theoretical and experimental values of the solubility of MBHP in polycarbonate, calculated using eqs. (17) and (18), are listed in Table X. The agreement is less than that for BHT, especially at lower temperatures, but it is still strong.

Figure 11 Development of antioxidant concentration in time in polycarbonate immersed in five different solutions of OBHP at 135°C.

TABLE XI
Theoretical and Experimental Solubility of OBHP
in Polycarbonate Versus Temperature

T (°C)	ϕ (ml/ml)$_{\text{theoretical}}$	S (mg/g)$_{\text{theoretical}}$	S (mg/g)$_{\text{experimental}}$
80	0.120	96	112 ± 7
95	0.129	103	120 ± 6
110	0.141	112	139 ± 8
135	0.162	129	175 ± 10

Octyl-3-(3,5-di-*t*-butyl-4-hydroxyphenyl)-propionate

Similar experiments like the ones described above for BHT and MBHP have been performed for the diffusion of OBHP in polycarbonate. The diffusion rate is slower than that of the other antioxidants because of the larger side groups. Therefore, the experiments were also conducted at 135°C. It was found that at temperatures above 110°C, the polycarbonate started to crystallize, in the pure antioxidant as well as in the solutions in decane.

At higher concentrations, a peak at 312 nm appears. As was mentioned earlier, this peak is caused by the oxidation products of this antioxidant. From the molar extinction coefficient (ϵ = 44870 L mol^{-1} cm^{-1}) it is possible to calculate the concentration. This extinction coefficient is very high in comparison with the extinction coefficient of the non-oxidized antioxidant. Therefore, the concentration of the oxidation product will be very small, even if this peak at 312 nm is high. For example, the peak at 312 nm after 2 h in pure OBHP has a maximum of 0.18. This means that the concentration is approx. 0.2 mg/ml [= 0.18 × 391 (g/mol) / 44870 (l mol^{-1} cm^{-1}) / 0.008 (cm)]. This is very low compared to the concentration of almost 200 mg/ml antioxidant in the sample.

The concentration of OBHP in polycarbonate versus time at 135°C is plotted in Figure 11. After 20 h, the equilibrium concentration was established. The first part of the curve was used to calculate the diffusion coefficient according to eq. (20). The solubility was taken from $t > 10$ h. The results of these calculations for 80, 95, 110 and 135°C are shown in Figure 12 and Table XI.

Like for BHT and MBHP, the mutual diffusion coefficients at the lowest temperature and concentration are in better agreement with the predictions than those at higher temperatures and concentrations. The theoretical solubilities are comparable to the experimental ones. The experimental values are more dependent on the temperature than the theoretical ones.

Octadecyl-3-(3,5-di-*t*-butyl-4-hydroxyphenyl)-propionate and pentaerythritol tetrakis[3-(3,5-di-*t*-butyl-4-hydroxyphenyl)-propionate]

The antioxidants ODBHP and PTBHP are much larger molecules than BHT, MBHP and OBHP. ODBHP has a long aliphatic side chain, and PTBHP contains four functional phenol groups. This means that the diffusion coefficients are much smaller than those found for BHT, MBHP and OBHP. Consequently, the diffusion times are much longer. For this reason, the diffusion experiments are preferably performed at higher temperatures. However, since the glass transition temperature of polycarbonate is around 150°C, higher temperatures than 135°C were not used.

Furthermore, since the solubilities were expected to be low, only pure antioxidants were evaluated. The higher molecular weight antioxidants induce slight crystallization in polycarbonate. For the determination of the antioxidant concentrations, the measured UV absorption spectra were corrected for this crystallization and the previously mentioned oxidation peak. The results of the sorption experiments are listed in Tables XII and XIII.

The theoretical solubility of PTBHP at 110 and 120°C was calculated using eq. (16), using a value for ΔH_f of 54 J/g as was obtained from DSC measurements. (Földes et al.[10] found a value of 55 J/g.) For both ODBHP and PTBHP, the values of the solubility agree better with experimental values obtained at lower temperatures. The order of magnitude can be predicted very well from the solubility parameters. The predictions of the mutual diffusion coefficients are also within one order of magnitude of the experimental values.

General discussion

Földes et al.[2,3] also correlated the diffusion of antioxidants in polybutadiene to the free volume in the polymer system. They suggested that a plot of the logarithm of the diffusion coefficient versus the ratio of the specific volume and the free volume (ln(D) versus $\hat{V}_1^0/\hat{V}_{FH}$) yields a straight line. If we make the same

TABLE XII
Theoretical and Experimental Solubilities and Mutual Diffusion Coefficients of ODBHP in Polycarbonate

T (°C)	S (mg/g)$_{\text{theory}}$	S (mg/g)$_{\text{exp}}$	D_{ml} (10^{-14} m^2/s)$_{\text{theory}}$	D_{ml} (10^{-14} m^2/s)$_{\text{exp}}$
95	28	17 ± 2	0.015	0.004 ± 0.001
110	31	29 ± 2	0.059	0.020 ± 0.003
120	33	34 ± 3	0.12	0.11 ± 0.02
135	37	84 ± 6	0.92	1.1 ± 0.2

TABLE XIII
Theoretical and Experimental Solubilities and Mutual Diffusion Coefficients of PTBHP in Polycarbonate

T (°C)	S (mg/g)$_{theory}$	S (mg/g)$_{exp}$	D_{ml} (10^{-14} m^2/s)$_{theory}$	D_{ml} (10^{-14} m^2/s)$_{exp}$
110	28	25 ± 2	0.0039	0.004 ± 0.001
120	56	39 ± 3	0.012	0.022 ± 0.02
135	87	175 ± 5	0.73	0.35 ± 0.05

plot using the data derived for polycarbonate, the fit is not as linear as that described by Földes. A wide scatter of points is obtained. The free volume theory described above does not predict a linear relationship between ln(D) and the ratio $\hat{V}_1^0/\hat{V}_{FH}$. Furthermore, the difference in prefactor, D_{01}, of the various additives is not accounted for. A plot of ln(D) versus ($w_1\hat{V}_1^*$ + $w_2\xi\hat{V}_2^*$)/$\hat{V}_{FH}$ yields a better linear relation for each antioxidant, as can be seen in Figure 13.

When the mobility of additives in polymers is explained by the presence of free volume, the use of activation energies must be treated with care. The temperature dependence of the diffusion coefficient is caused by the increasing amount of free volume, and an Arrhenius plot should not yield a straight line. It is therefore only possible to derive an apparent activation energy and not an actual one. This apparent activation energy is temperature dependent. Furthermore, one has to take into account that the diffusion coefficient is concentration dependent, and consequently, the apparent activation energy also becomes concentration dependent.

The antioxidant concentration in a commercial polymer is very low (<1%). This means that the diffusion

coefficient given in eq. (12) can be used to predict the mobility of the antioxidants. In Figure 14, the predicted diffusion coefficients of the five antioxidants in PC versus temperature are plotted. These values can be used in the calculations of the polymer stability.

Diffusion and solubility measurements of the antioxidants performed on engineering polymers instead of polyolefins indicate differences in behavior between the two types of polymers. The most important differences are (1) the polarity of the polymers, which influences the solubility of the phenolic antioxidant, and (2) the glassy instead of rubbery state of the polymer, which influences the mobility of the antioxidants. Furthermore, the processing conditions are more extreme for most engineering polymers, resulting in different oxidation and stabilizing processes.

In the introduction, a relation was presented between the protection time of an antioxidant and the sorption parameters D and S. This indicates that the lifetime of a polymer product under thermal stress is largely influenced by the mobility and solubility of the antioxidants used. Reliable predictions of these parameters together with a well-supported theoretical relation for the protection time will simplify the screening for the most suitable antioxidant. The em-
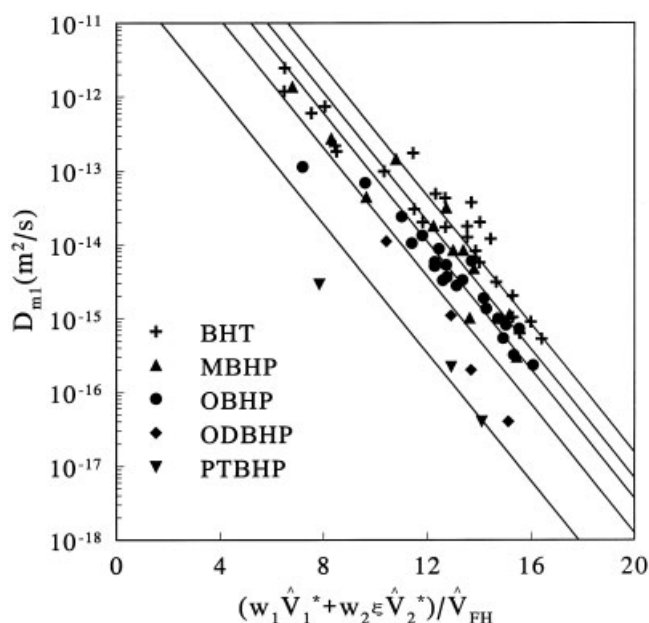

Figure 13 Relationship between the diffusion coefficient and the ratio of the additive specific volume to the total free volume of the polymer system.
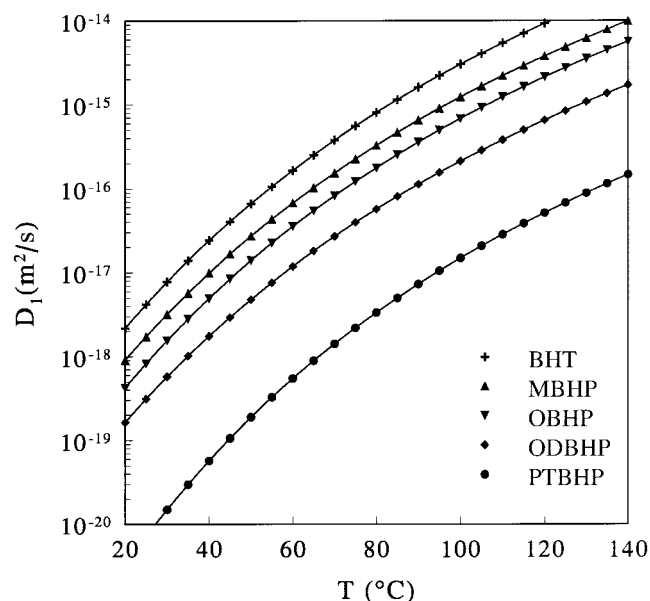

Figure 14 Predicted self diffusion coefficients of the five antioxidants in polycarbonate versus temperature.
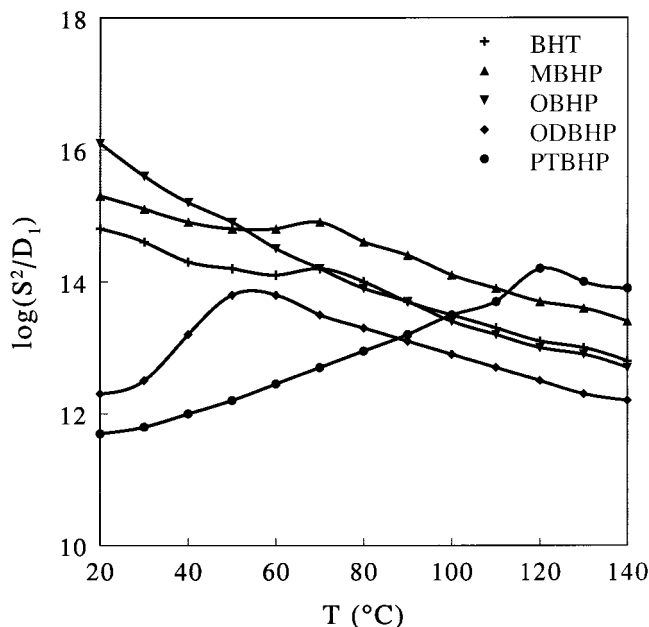
Figure 15 $\log(S^2/D_1)$ versus temperature for the five antioxidants studied.

pirical relation $\tau \sim (S^2/D)$ will probably not be accurate enough to be used in the screening procedure. Furthermore, other parameters have to be taken into account, such as evaporation rate and product design. However, a first estimate can be obtained combining the empirical relation and the sorption parameters. This is shown in Figure 15 for polycarbonate. $\log(S^2/D_1)$ is plotted versus the temperature. S was calculated using eqs. (16) and (18), D_1 was obtained from eq. (12) and Figure 14. The most suitable antioxidant clearly depends on the temperature. At low temperatures, OBHP is the best choice, since it is a liquid at room temperature. From 50 to 110°C MBHP is the most suitable due to its high solubility in polycarbonate. At even higher temperatures, the largest antioxidant PTBHP protects the polymer best against oxidation, because the mobility of this antioxidant becomes very low. Oxidation experiments at 110°C in an air circulation oven with polycarbonate films containing peroxide and 1 wt % antioxidant, measuring the time to brittle fracture, gave the same sequence as was found in Figure 15: $\tau_{\text{blanco}} < \tau_{\text{ODBHP}} < \tau_{\text{OBHP}} < \tau_{\text{BHT}} < \tau_{1010}$.

It can now be concluded that knowledge of the physical parameters, mobility and solubility, can be of great importance in the screening procedure of antioxidants.

CONCLUSIONS

The Vrentas model has been used to predict the self and mutual diffusion coefficients of a series of five antioxidants in polycarbonate. This model is based on the ratio between the volume needed for the mobile

units to jump and the free volume in the polymer. The following factors were taken into account: (1) the jumping unit of all the phenolic antioxidants is the di-*t*-butyl-hydroxyphenyl group, (2) the jumping unit of the polycarbonate is the bisphenol group, (3) free volume parameters are derived from PALS measurements, and (4) the critical molar volume of the antioxidants is derived from extrapolation of literature values for other solvents.

The predictions of the mutual diffusion coefficients using this model appeared to be in excellent agreement with the values obtained from diffusion experiments.

The solubility of the antioxidants was predicted using the classical Flory-Huggins theory. These predictions also agreed well with the measured values of the solubility of the antioxidants in polycarbonate.

Since the mobility and solubility of antioxidants are important parameters in the degradation behavior of a polymer under thermal stress, the prediction of these parameters will be very useful in screening the most suitable antioxidant for a given polymer product. Reliable predictions of these physical parameters will open up the possibility of designing the most appropriate antioxidant for a certain polymer.

A clear correlation was found between the free volume of the polymer and the diffusion coefficient in this study. Several external factors, such as aging, rejuvenation, stress, and others, have an effect on the free volume and thus on the mobility. This will be discussed in two forthcoming papers.[54,55]

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