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Thermal Loss of Ultraviolet Absorbers from BPA–Polycarbonate

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ABSTRACT: The thermal loss from BPA–polycarbonate films of 15 UV absorbers from 4 generic classes of chemical compounds was determined at 125 and 190 °C, temperatures well above and below the glass transition temperature of the resin. The loss rates at 190 °C for all of the UV absorbers were rapid, with diffusion coefficients ranging from 0.3×10^{-8} to about 60×10^{-8} cm^2/s. While several UV absorbers were lost only very slowly at 125 °C, others were not lost at all. These results were correlated with the UV absorbers' molar volumes as determined by density measurements. UV absorbers with molar volumes of 230 cm^3/mol or less were lost and those with molar volumes of at least 260 cm^3/mol were not.

Introduction

Most organic polymers degrade when they are exposed to ultraviolet light. Since degradation can reduce both the aesthetic and physical properties of polymers, various methods have been used to improve their UV stability. A common approach has been to use UV absorbers as bulk additives for polymers. In most cases, UV absorbers function by preferentially absorbing damaging UV radiation and dissipating the energy harmlessly. Their effectiveness depends on numerous factors including absorptivity, compatibility, stability, and distribution within the polymer. Above all, their effectiveness is dependent upon their concentration in the polymer, especially near the surface. It is critical, therefore, for polymers to have effective concentrations of UV absorbers after processing and long-term use.

Concentration changes of UV absorbers in polymers may be due to either chemical or physical losses. Chemical losses result from thermal, photooxidative, and oxidative reactions. Billingham and Calvert have outlined a model for the physical losses of additives from polymers.[1] According to their model, three parameters are required to allow prediction of loss under all conditions: the

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solubility of the additive, its volatility, and its diffusion coefficient. A UV absorber that is present in a polymer at a concentration above its solubility limit will precipitate either in the polymer or on its surface and be physically lost. Extraction by water or solvents is another process by which UV absorbers can be lost. Thermal loss, the topic of this study, results from migration of a UV absorber to a polymer surface and subsequent evaporation.

Thermal losses of stabilizers from low T_g polymers, especially polyolefins, have been studied quite extensively while losses from other polymers have received relatively little attention. In early work, evaporation rates of UV absorbers and other stabilizers dispersed on free surfaces were determined by thermogravimetric methods,[2–7] and, in some instances, correlations between these rates and stabilizer loss rates from rubber slabs[6] and polyolefins[4,5,7] were made. However, evaporation rate studies only determine the volatility of a stabilizer, which in turn is a function of its vapor pressure. When the migration rate of a stabilizer to a polymer surface is rate limiting, its evaporation rate from the surface may correlate poorly with its overall rate of loss from the polymer.

More recently, studies have focused on thermal losses of stabilizers from polymers and their migration rates within polymers. Temchin et al. determined the relative loss rates of UV absorbers from polyethylene.[8] Rate constants, diffusion constants, and activation energies for thermal losses of UV absorbers and antioxidants from polyethylene and polypropylene have also been determined.[9–14] Activation energies and diffusion coefficients were determined for the diffusion of 2,4-dihydroxybenzophenone and 2-hydroxy-4-(octyloxy)-benzophenone in two linear poly(ester–urethanes).[15] Diffusion coefficients of the UV absorbers were about 5 times as high in the polyurethane prepared from a poly(ester diol) of a molecular weight 2000 as they were in the polyurethane prepared from a poly(ester diol) with a molecular weight of 1000. Johnson and Hauserman determined diffusion coefficients for 2,4-dihydrohydroxybenzophenone in plasticized poly(vinyl chloride). Their most important finding was that no detectable diffusion occurred in 0–10% plasticized poly(vinyl chloride) when the diffusion temperature was below the glass transition temperatures of the polymers.[16] An excellent review on the physical loss of stabilizers from polymers has been recently published.[17]

Experimental Section

Materials. The UV absorbers used in this study, listed in Table I, are commercial materials and were used without further purification. The polycarbonate used to prepare films, Lexan (a registered trademark of the General Electric Co.) BPA–polycarbonate 135-111, was free of stabilizers and had $\bar{M}_n = 23\,800$ and $\bar{M}_w = 68\,500$ as determined by GPC using polystyrene as a standard.

Procedures. Film Preparation. Solutions were prepared by dissolving 15 g of polycarbonate and 0.15 g of UV absorber in 85 g of methylene chloride. An aliquot of solution was placed on a level glass plate, drawn down by a 250-μm "doctor blade", and immediately covered with a shallow dish. After 15 h, the film edges were rimmed and the films were floated from the glass by using water and stapled in 2 in. × 2 in. cardboard projection slide holders to facilitate handling. While little or no methylene chloride could be detected by infrared analyses, films were either heated 2 h at 125 °C or allowed to stand at least 2 weeks at ambient conditions before beginning thermal loss studies.

Film thicknesses, measured with a micrometer, were 0.0033 ± 0.0005 cm. In the thermal loss study conducted at 190 °C (vide infra), film thicknesses were measured before and after the study. The largest measured change in film thickness was 0.0003 cm, and the average of the measured thicknesses was used in determining diffusion coefficients.

Analysis. The absorbance at λ_{max} for each film was determined by placing the film in the sample beam and a polycarbonate film with no additives, prepared in the same way, in the reference beam of a Perkin-Elmer Coleman Model 575 UV/visible spectrophotometer and recording the UV spectrum from 250 to 400 nm. The absorbance values at λ_{max} for the UV absorbers ranged from 1 to 2 before any thermal aging.

Thermal Loss Studies. Thermal losses of UV absorbers from the films at 125 and 190 °C were determined by heating the films with UV absorbers and a reference film with no UV absorber in a constant-temperature oven for varying lengths of time and measuring the concentration of the remaining UV absorber by using the thermally aged film with no UV absorber as the reference. In the study conducted at 190 °C, the oven was preheated to 197 °C before the oven door was opened, the forced air in the oven was turned off, and the films, held vertically on a rack so that the film surfaces were at least 5 cm from each other, were rapidly placed in the oven. The temperature dropped and remained at 190 ± 2 °C during the 2.0-min residence times of the films.

T_g Measurements. T_g determinations were made by sealing polycarbonate films containing UV absorbers in aluminum pans and scanning in a Perkin-Elmer DSC-2 differential scanning calorimeter at 20 °C/min. The onsets of the transitions were taken as the T_g values following the method of Tan and Challa.[18]

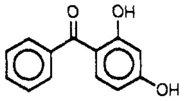
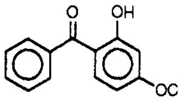
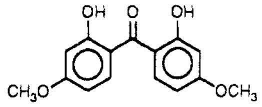
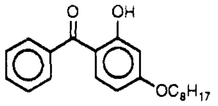
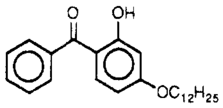
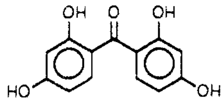
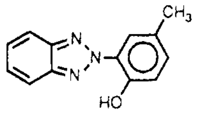
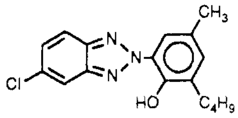
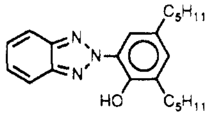
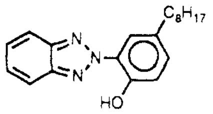
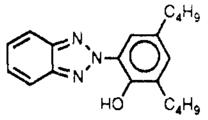
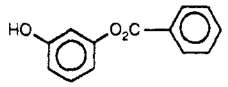
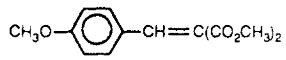
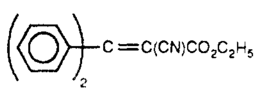
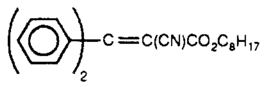
Calculations of Diffusion Coefficients. To determine diffusion coefficients for the loss of UV absorbers from polycarbonate films at 190 °C, the method of Masuko et al. was used;[19] that is, the amount of UV absorber desorbed during time t, M_t, was estimated from $M_\infty - M_t'$ where M_t' is the amount of UV absorber remaining in the film after desorption time t, and M_∞ is the value of M_t for $t = \infty$. M_∞ was experimentally equal to the initial amount of UV absorber held in the film for 5 of the 15 UV absorbers studied and was assumed to be equal to the initial amount of UV absorber held in the film for the 10 other UV absorbers. This is probably a good assumption except for the studies with 2,2′,4,4′-tetrahydroxybenzophenone and 2,4-dihydroxybenzophenone since they can conceivably react with the polycarbonate at 190 °C and become bound to the polymer so that M_∞ would be less than the amount of UV absorber initially held in the film. The diffusion coefficients of the UV absorbers in the polymer films were determined from the equation $D = \pi/16I^2$ where I is the initial slope of the reduced desorption curve of M_t/M_∞ vs $t^{1/2}/l$ where l is the film thickness.

Density Measurements. The densities of the UV absorbers at 125 ± 1 °C were determined by placing a 5.00-mL volumetric flask, calibrated with water at 25 °C, in a constant-temperature bath set at 125 °C and adding UV absorber. After heating the UV absorbers to ca. 125 °C, they were degassed by using a 40-mmHg vacuum line. A thermometer was then placed in the molten UV absorber until the temperature equilibrated at 125 ± 1 °C at which time the thermometer was removed and the melt was brought to volume by adding or taking away a small amount of UV absorber. Several UV absorbers are ordinarily solids at 125 °C. To determine their densities, they were heated to melting and then placed in the 125 ± 1 °C bath and supercooled to 125 ± 1 °C. The volume and mass of the supercooled liquid were used to determined the density.

Results and Discussion

UV absorbers can be thermally lost from polymers during processing as well as during service. To understand these phenomena in a polymer with a high glass transition temperature, T_g, a study of the thermal loss of UV absorbers from BPA–polycarbonate at temperatures above and below its T_g was undertaken. In earlier unpublished work, we determined that the rates of evaporation of the UV absorbers used in this study were much greater than their migration rates in BPA–polycarbonate. Thus, the thermal losses described below concern diffusion, not evaporation.

Table I
Commercial UV Absorbers Used in This Study

structure	chemical name	trade name
	2,4-dihydroxybenzophenone	Uvinul 400[a]
	2-hydroxy-4-methoxybenzophenone	Cyasorb UV 9[b]
	2,2′-dihydroxy-4,4′-dimethoxybenzophenone	Uvinul D-49
	2-hydroxy-4-(*n*-octyloxy)benzophenone	Cyasorb UV 531
	2-hydroxy-4-(dodecyloxy)benzophenone	Eastman Inhibitor DOBP[c]
	2,2′,4,4′-tetrahydroxybenzophenone	Uvinul D-50
	2-(2′-hydroxy-5′-methylphenyl)benzotriazole	Tinuvin P[d]
	2-(3′-*tert*-butyl-2′-hydroxy-5′-methylphenyl)-5-chlorobenzotriazole	Tinuvin 326
	2-(2′-hydroxy-3′,5′-di-*tert*-amylphenyl)benzotriazole	Tinuvin 328
	2-(2′-hydroxy-5′-*tert*-octylphenyl)benzotriazole	Cyasorb UV 5411
	2-(2′-hydroxy-3′,5′-di-*tert*-butylphenyl)benzotriazole	Tinuvin 320
	resorcinol monobenzoate	Eastman RMB***
	dimethyl *p*-methoxybenzylidenemalonate	Cyasorb UV 1988
	ethyl 2-cyano-3,3-diphenylacrylate	Uvinul N-35
	2-ethylhexyl 2-cyano-3,3-diphenylacrylate	Uvinul N-539

[a] Uvinul is a registered trademark of BASF Wyandotte. [b] Cyasorb is a registered trademark of American Cyanamid. [c] DOBP and RMB are registered trademarks of Eastman Chemical Products. [d] Tinuvin is a registered trademark of Ciba-Geigy.

Thermal Losses of UV Absorbers from Polycarbonate Films at 190 °C. The amount of desorption of the 15 UV absorbers, shown in Table I, from polycarbonate films was determined as a function of time at 190 °C, a temperature well above the polycarbonate's T_g of 149 °C. The UV absorbers fall into three categories with respect to their losses at this temperature (Table II). 2,2′,4,4′-Tetrahydroxybenzophenone and 2-hydroxy-4-(dodecyloxy)benzophenone are lost relatively slowly; 2-hydroxy-4-methoxybenzophenone, 2-(2′-hydroxy-5′-methylphenyl)benzotriazole, dimethyl *p*-methoxybenzylidenemalonate, resorcinol monobenzoate, and 2,4-dihy-

Table II
Desorption of UV Absorbers from Polycarbonate Films at 190 °C

		amount desorbed, M_t/M_∞, at various values of t, min							
UV absorber	l, cm	2	4	6	8	10	12	14	16
	Slow								
2,2′,4,4′-tetrahydroxybenzophenone	0.0033	0.15	0.17	0.19	0.20	0.21	0.23	0.25	0.27
2-hydroxy-4-(dodecyloxy)benzophenone	0.0031	0.17	0.20	0.25	0.28	0.32	0.36	0.39	0.42
	Intermediate								
2-hydroxy-4-(octyloxy)benzophenone	0.0035	0.22	0.38	0.50	0.57	0.64	0.69	0.74	0.78
2,2′-dihydroxy-4,4′-dimethoxybenzophenone	0.0033	0.33	0.48	0.56	0.62	0.69	0.75	0.78	0.80
2-(3′-*tert*-butyl-2′-hydroxy-5′-methylphenyl)-5-chlorobenzotriazole	0.0031	0.28	0.40	0.50	0.59	0.68	0.74	0.80	0.83
2-(2′-hydroxy-3′,5′-di-*tert*-amylphenyl)benzotriazole	0.0027	0.37	0.50	0.58	0.66	0.72	0.77	0.80	0.82
2-(2′-hydroxy-5′-*tert*-octylphenyl)benzotriazole	0.0030	0.34	0.44	0.52	0.59	0.65	0.70	0.75	0.79
2-(2′-hydroxy-3′,5′-di-*tert*-butylphenyl)benzotriazole	0.0033	0.24	0.36	0.46	0.51	0.56	0.60	0.64	0.67
ethyl 2-cyano-3,3-diphenylacrylate	0.0036	0.44	0.57	0.69	0.76	0.81	0.84	0.87	0.89
2-ethylhexyl 2-cyano-3,3-diphenylacrylate	0.0034	0.26	0.35	0.44	0.53	0.61	0.67	0.71	0.75
	Fast								
2,4-dihydroxybenzophenone	0.0029	0.50	0.74	0.83	0.88				
resorcinol monobenzoate	0.0029	0.70	0.89						
dimethyl *p*-methoxybenzylidenemalonate	0.0029	0.55	0.86	0.95					
2-(2′-hydroxy-5′-methylphenyl)benzotriazole	0.0033	0.77	0.91	0.96					
2-hydroxy-4-methoxybenzophenone	0.0030	0.85	0.96						

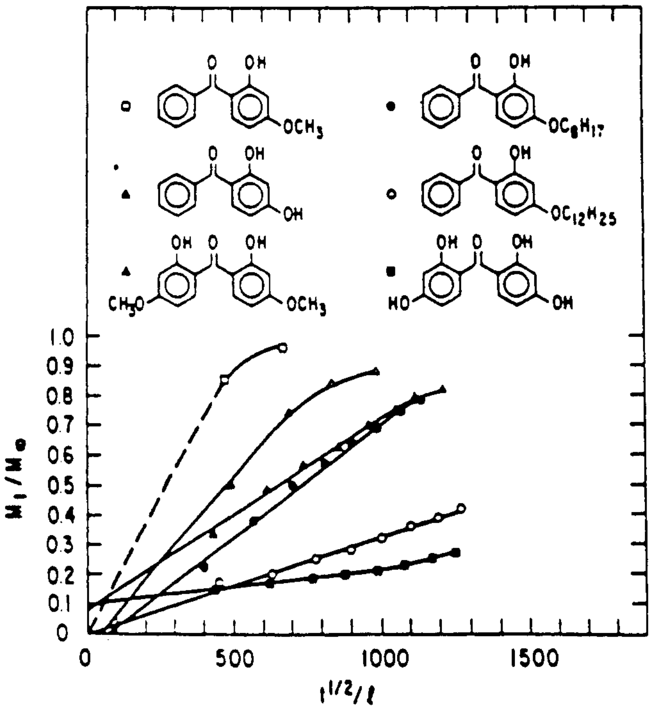
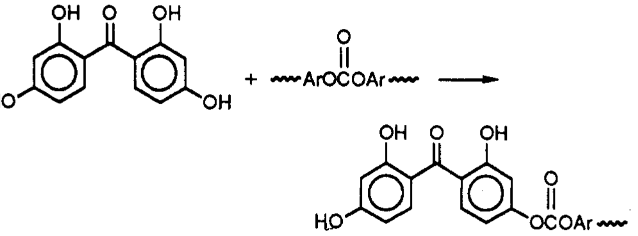


Figure 1. Reduced desorption curves for hydroxybenzophenone UV absorbers.

droxybenzophenone are lost rapidly, and the rest of the UV absorbers, at intermediate rates.

Diffusion coefficients were determined from the data in Table II by using the method of Masuko et al.;[19] that is, the values of D are the initial gradients of the reduced desorption curve, M_t/M_∞ vs $t^{1/2}/l$, as described in the Experimental Section. Figures 1–3 show the reduced desorption curves. For the UV absorbers that were lost at moderate to relatively slow rates, reasonable values for D can be determined. Diffusion coefficients for UV absorbers that were lost rapidly, the bottom five UV absorbers listed in Table II, were obtained by extrapolating limited data through the origin as shown. Such diffusion coefficients are obviously very unreliable, but they are probably within 1 order of magnitude of being correct. Table III contains the diffusion coefficient values that were obtained by these methods. Diffusion coefficients greater than 15×10^{-8} cm^2/s were obtained from limited data, as described above, and are listed only as approximate values. The purpose of this study was to compare diffusion coefficients for various UV absorbers, and no attempt was made to determine the effect of concentration on diffusion coefficients for any of the UV absorbers.

The rates of diffusion of the UV absorbers decreased with either increasing molecular weight or polarity. Of the UV absorbers that were studied, 2,2′,4,4′-tetrahydroxybenzophenone has the least propensity for thermal loss from polycarbonate films at 190 °C. This may be due to its high polarity, a property that contributes to considerable decrease in diffusion rates in polyolefins.[20] Alternatively, it may be due to a chemical transesterification reaction between the hydroxyls in the 4 or 4′ positions with the carbonate linkages, as follows.



By becoming chemically bound to the polymer backbone, its thermal loss would, of course, be considerably retarded.

2-Hydroxy-4-(dodecyloxy)benzophenone was also lost very slowly in this experiment. This is most likely due to its high molecular weight and its dodecyl hydrocarbon tail.

The UV absorbers that were lost rapidly in these experiments all had low molecular weights, ranging from 214 to 250. While the diffusion coefficients for these UV absorbers are not accurate, it is clear that they are significantly larger than those for the rest of the UV absorbers that were studied. Both resorcinol monobenzoate and 2,4-dihydroxybenzophenone were lost more slowly than 2-hydroxy-4-methoxybenzophenone, 2-(2′-hydroxy-5′-methylphenyl)benzotriazole, or dimethyl *p*-methoxybenzylidenemalonate. This is expected because the former molecules have a noninternally hydrogen-bonded OH group, as opposed to strong intramolecularly hydrogen-bonded OH groups on the latter molecules, that is free to interact with either an OH group on another UV absorber molecule or with the carbonate linkage in the polymer backbone. The interactions could, for example, be dipole–dipole or hydrogen-bonding interactions that would retard diffusion through the polymer.

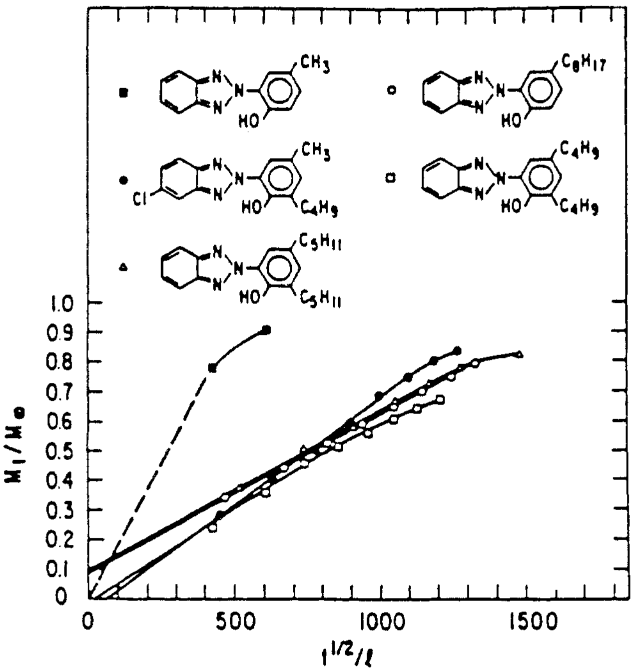


Figure 2. Reduced desorption curves for benzotriazole UV absorbers.

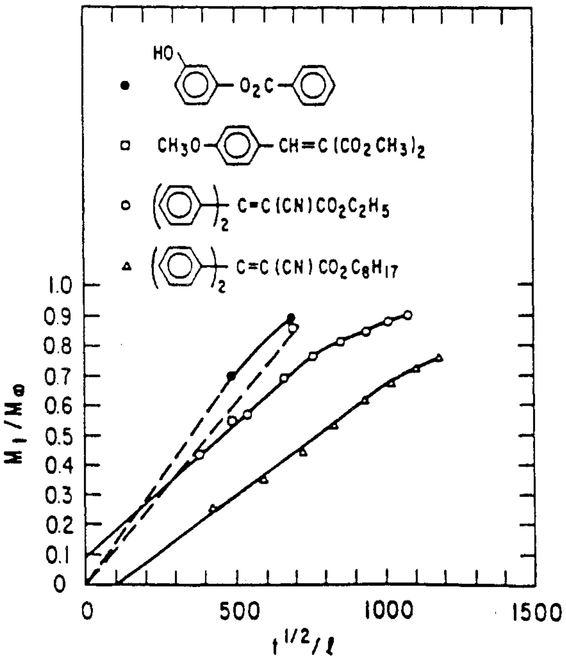


Figure 3. Reduced desorption curves for various UV absorbers.

There is nothing really distinguishing or unusual among the UV absorbers lost at moderate rates relative to the previously mentioned UV absorbers. Their molecular weights range from 274 to 351 g/mol. It might be mildly surprising that 2-(2′-hydroxy-3′,5′-di-*tert*-amylphenyl)benzotriazole, with a molecular weight of 351 g/mol, has a diffusion coefficient about 2–3 times larger than that for 2-hydroxy-4-(dodecyloxy)benzophenone, which has a molecular weight of 382 g/mol. This may be due to the presence of two fused rings with a third attached ring in the benzotriazole UV absorber, whereas the hydroxybenzophenone only has two rings. For example, it has been noted that molecules containing aromatic rings diffuse "much more rapidly" than aliphatic migrants of comparable molecular weight in polyolefins.[20]

Thermal Losses of UV Absorbers from Polycarbonate Films at 125 °C. Most studies on the thermal losses of stabilizers from polymers have been done at temperatures above the polymer's T_g. Since nothing was known about thermal losses of UV absorbers from polycarbonate below its T_g and in general very little was known about thermal losses of stabilizers from high T_g polymers at temperatures below their T_g's, it was of interest to

Table III
Diffusion Coefficients for Desorption of UV Absorbers from Polycarbonate Films at 190 °C

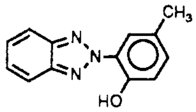
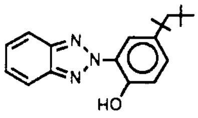
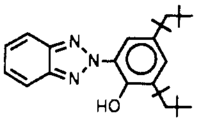
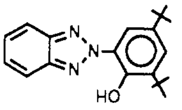
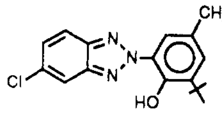
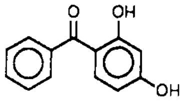
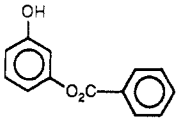
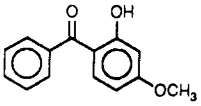
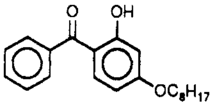
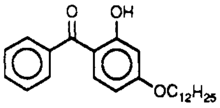
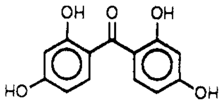
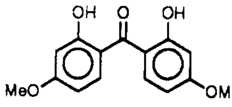
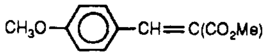
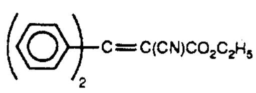
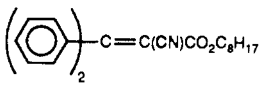
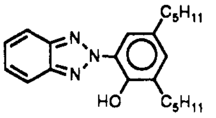
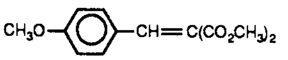
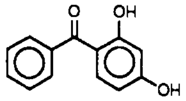
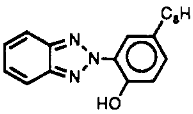
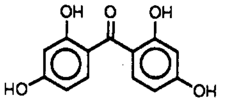
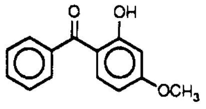
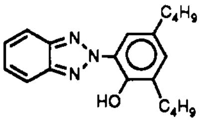
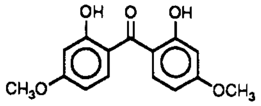
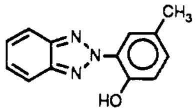
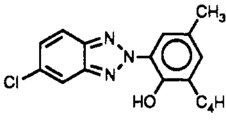
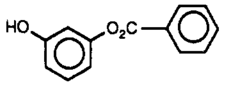
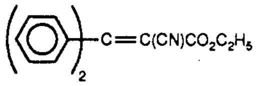
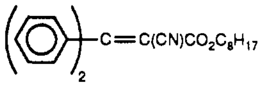
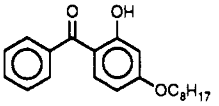
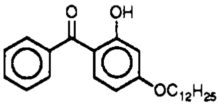
UV absorber	mol wt	D, cm^2/min
	225.3	$\sim 60 \times 10^{-8}$
	323.4	6.1×10^{-8}
	351.7	5.5×10^{-8}
	323.4	6.3×10^{-8}
	315.8	11×10^{-8}
	214.2	$\sim 30 \times 10^{-8}$
	214.2	$\sim 40 \times 10^{-8}$
	228.2	$\sim 60 \times 10^{-8}$
	326.4	12×10^{-8}
	382.5	2.2×10^{-8}
	246.2	0.3×10^{-8}
	274.2	9.1×10^{-8}
	250.2	$\sim 60 \times 10^{-8}$
	277	15×10^{-8}
	361	11×10^{-8}

Table IV
Thermal Loss of UV Absorbers from Polycarbonate Films after 800 h at 125 °C

little or no thermal loss				partial thermal loss				nearly complete thermal loss			
UV absorber	A/A_0[a]	mol wt	V_l[b]	UV absorber	A/A_0[a]	mol wt	V_l[b]	UV absorber	A/A_0[a]	mol wt	V_l[b]
	1.02	315.8	c		0.61	250	230		0.18	214.2	180
	1.04	351.7	350		0.63	246.2	c		0.17	228.2	200
	1.01	323.4	320		0.53	274.2	225		0.15	225.3	200
	1.04	323.4	c						0.17	214.2	190
	0.99	277	260								
	1.01	361	370								
	0.96	326.4									
	1.00	382.5	400								

[a] A is absorbance at λ_{max} for the UV absorber in the film after 800 h at 125 °C and A_0 is initial absorbance. The A/A_0 values shown are averages from two experiments; the greatest deviation from the values shown was ±0.04. [b] V_l is the molar volume, in cm^3/mol, determined from density measurements of the liquid UV absorber at 125 °C. [c] Not determined. UV absorber is a solid at 125 °C.

determine what kind of losses, if any, would occur from the glassy state of polycarbonate. The results of the study, described below, appear to be quite novel.

Thermal losses from polycarbonate films of the 15 UV absorbers shown in Table I were determined as a function of time at 125 °C, a temperature well below the polycarbonate's normal T_g of 149 °C. The films were analyzed spectrophotometrically several times during the study, but the most interesting data were obtained after 800 h, the point at which the experiment was concluded. Thermal losses were determined as A/A_0 where A is the absorbance at λ_{max} for the UV absorbers in the films after aging and A_0 is the initial absorbance.

The UV absorbers fall into three categories with respect to their thermal losses at 125 °C, as shown in Table IV. 2,4-Dihydroxybenzophenone, 2-(2′-hydroxy-5′-methylphenyl)benzotriazole, 2-hydroxy-4-methoxybenzophenone, and resorcinol monobenzoate were nearly completely lost from the films when the study was completed. But in contrast to the study at 190 °C where >90% of them was lost in <10 min, 15–20% of each of them was still retained after 800 h at 125 °C. The results obtained from the eight UV absorbers shown in the left-hand column of Table IV were the most intriguing. *Little or no thermal loss was found, even after 800 h at 125 °C.* Except for Johnson and Hauserman's report that no detectable diffusion of 2,4-dihydroxybenzophenone was observed in poly(vinyl chloride) at temperatures below its T_g,[16] this result appears to be novel. For example, 2-hydroxy-4-(dodecyloxy)benzophenone, 2-ethylhexyl 2-cyano-3,3-diphenylacrylate and 2-(2′-hydroxy-5′-*tert*-octylphenyl)benzotriazole, UV absorbers that were not lost in this study, were thermally lost from 0.05-cm poly(ethyl methacrylate) films with first-order rate constants of 5 × 10^{-3}, 3 × 10^{-2}, and 1 × 10^{-1} h^{-1}, respectively, at 130 °C.[21] In the third category of the present study, dimethyl *p*-methoxybenzylidenemalonate, 2,2′,4,4′-tetrahydroxybenzophenone, and 2,2′-dihydroxy-4,4′-dimethoxybenzophenone were partially lost.

Losses of the UV absorbers at 125 °C follow the same order as those in the 190 °C study, with the highest molecular weight UV absorbers generally showing the least thermal loss. It is interesting to note, however, that 2,2′,4,4′-tetrahydroxybenzophenone, the UV absorber that was lost least rapidly in the 190 °C study, falls into the "partial thermal loss category" in the 125 °C study. It is also intriguing that nearly 50% of 2,2′-dihydroxy-4,4′-dimethoxybenzophenone, with a molecular weight of 274 g/mol, was lost after 800 h at 125 °C, whereas virtually no ethyl 2-cyano-3,3-diphenylacrylate, with a molecular weight of 277 g/mol, was lost. Thus, while molecular weight may be a good indicator of whether or not these molecules will be lost from polycarbonate at 125 °C, it is not the only factor that dictates thermal loss.

As described, it is difficult to completely rationalize the results shown in Table IV on molecular weight considerations alone. It is also difficult to ascribe the differences in thermal loss behavior to compatibility, polarity, or functional groups on the molecules. The degree of plasticization of the films by the UV absorbers was considered as a possible reason for the differences observed. However, the T_g's of the films containing 1 wt % UV absorber were all 147 ± 3 °C and had little correlation with loss.

The size of the UV absorber molecules apparently determines whether they will be thermally lost from polycarbonate films at 125 °C. The molar volume, as determined from density measurements of the UV absorbers as liquids at 125 °C, was found to be a good indicator of whether or not the UV absorbers will be thermally lost from polycarbonate films at 125 °C. The UV absorbers that were nearly completely lost had molar volumes ranging from 180 to 200 cm^3/mol. It is probably fortuitous, but the A/A_0 values for those four UV absorbers were the same, within experimental error, every time they were determined during the course of the experiment. The molar volumes that could be determined for the UV absorbers that were partially lost were 225 and 230 cm^3/mol. These molecules are larger than those that were nearly completely lost, but they are apparently still small enough to migrate to the surface of the polymer and evaporate. Finally, the UV absorbers that suffered little or no thermal loss at 125 °C had molar volumes ranging upward from 260 cm^3/mol. The results suggest that molecules of these sizes and geometric shapes are too big to migrate through polycarbonate at 125 °C.

As pointed out by Billingham and Calvert,[1] the evaporative loss rate of additives from polymers is determined by their diffusion rate to the surface and their rate of volatilization from the polymer surface. At temperatures well above the polycarbonate's T_g, like 190 °C, there is greatly increased segmental mobility that can facilitate the migration of UV absorbers through the polymer.[22] By use of eq 1, where the terms are as defined

$$\frac{M_t}{M_\infty} = 1 - 8/\pi^2 \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left(-\frac{(2n+1)^2\pi^2 Dt}{l^2}\right) \qquad (1)$$

earlier, and the diffusion coefficients in Table III, it is possible to calculate desorption values that are in good agreement with the experimental M_t/M_∞ desorption values in Table II, indicating that the migration process is Fickian diffusion.[19,23] On the other hand, migration at temperatures below T_g is exceedingly complex. The results in Table IV suggest that the size of the migrating molecule is important. The importance of size for gases, small organic molecules, dye molecules, and ions has been described[24] so that this concept is not new. Migration may involve repeated movement from one existing cavity in the polymer to another so that the molecule ultimately finds its way to the surface. Since the UV absorbers used in this study are reasonably large molecules, it may take a rather large number of monomer segments within the polymer to rearrange so that the UV absorber molecule can pass from one cavity to another.

Conclusion

Thermal losses of 15 UV absorbers from polycarbonate films were determined at 190 and 125 °C, temperatures well above and below the T_g of 149 °C. At 190 °C, diffusion coefficients ranged from 0.3×10^{-8} to about 60×10^{-8} cm^2/s. The diffusion rates decreased with either increasing molecular weight or polarity. At 125 °C, a correlation was found between the UV absorbers' molar volumes, determined from density measurements of the UV absorbers as liquids at 125 °C, and their propensity for thermal loss; little or not thermal loss occurred when the UV absorbers had molar volumes of at least 260 cm^3/mol.

Acknowledgment. We thank Drs. A. R. Schultz, J. W. Verbicky, and D. G. LeGrand for helpful discussions and suggestions.

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Registry No. DOBP, 2985-59-3; (BPA)(polycarbonate) (SRU), 24936-68-3; (BPA)(polycarbonate) (copolymer), 25037-45-0; Uvinul 400, 131-56-6; Cyasorb UV, 131-57-7; Uvinul D-49, 131-54-4; Cyasorb UV 531, 1843-05-6; Uvinul D-50, 131-55-5; Tinuvin, 2440-22-4; Tinuvin 326, 54711-41-0; Tinuvin 328, 21615-49-6; Cyasorb UV 5411, 20017-83-8; Tinuvin 320, 93928-93-9; Eastman RMB, 136-36-7; Cyasorb UV 1988, 7443-25-6; Uvinul N-35, 5232-99-5; Uvinul N-539, 6197-30-4.