

# Identification of Fluorescent Products Produced by the Thermal Treatment of Bisphenol-A-Based Polycarbonate

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## SYNOPSIS

Polycarbonate is routinely subjected to heat treatment, and the thermal degradation products formed during this thermal treatment give rise to a distinct structured fluorescence spectrum. The structured fluorescence emission is observed when polycarbonate is subjected to thermal treatment in air as well as in nitrogen. A mixture of thermal rearrangement products of polycarbonate including dibenzofuran and phenyl-2-phenoxybenzoate are mainly responsible for the structured fluorescence emission. Most of the thermal degradation products of polycarbonate undergo photolysis, leading to the formation of photoproducts, which subsequently undergo a photoinduced bleaching process, with the noted exception of phenyl-2-phenoxybenzoate. The exposure of polycarbonate to high temperature for only short time periods, simulating mild industrial processing conditions, results in the formation of a relatively small amount of thermal degradation products, which, accordingly, has only a minor effect on the photodegradation of polycarbonate. © 1994 John Wiley & Sons, Inc.

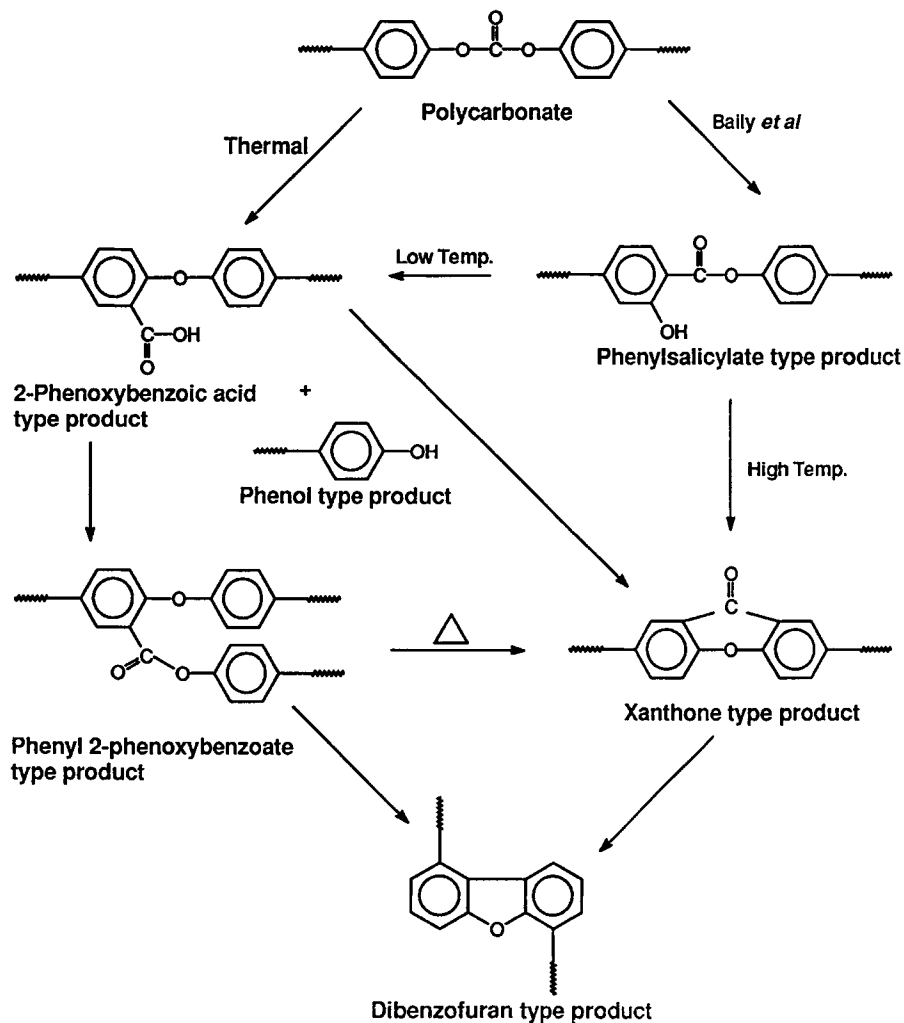
## INTRODUCTION

Bisphenol-A-based polycarbonate is an engineering plastic with excellent mechanical and physical properties. Even though polycarbonate is quite stable at low temperatures, it is usually subjected to higher temperatures during processing, leading to at least some thermal degradation. Hence, in the past, a number of research groups have investigated the thermal degradation of polycarbonate and diphenylcarbonate.<sup>1-5</sup> It has been reported that the thermal degradation of polycarbonate leads to the loss of mechanical properties and lowering of molecular weight.<sup>1,2,5</sup> Chipalkatti and Laski<sup>6</sup> also reported that thermal degradation of polycarbonate lowers its molecular weight, affects the creep compliance, and leads to the formation of phenyl-2-phenoxybenzoate. Further, thermal degradation of polycarbonate or diphenylcarbonate has been reported to lead to yellowing and the formation of CO<sub>2</sub>,

bisphenol-A, diphenylcarbonate, phenol,<sup>1</sup> phenylsalicylate,<sup>4</sup> xanthone, and phenyl-2-phenoxybenzoate with CO, diphenylether, dibenzofuran, and 2-phenoxyphenylcarbonate as minor products.<sup>2</sup> A general mechanism for the thermal degradation of polycarbonate is shown in Scheme 1, which depicts formation of the thermal rearrangement products such as phenylsalicylate, 2-phenoxybenzoic acid, phenyl-2-phenoxybenzoate, xanthone, and dibenzofuran. Scheme 1 also shows that dibenzofuran can be formed from xanthone as well as from phenyl-2-phenoxybenzoate. As most of the commercial polycarbonates undergo some sort of heat treatment during processing, they are certain to contain some or all of the aforementioned thermal degradation products. It is important to detect these degradation products as well as to determine their effect on the ultimate photostability of polycarbonate. In this article, we report on the use of fluorescence spectroscopy, which has recently<sup>6</sup> been shown to be a versatile technique for detecting small amounts of polycarbonate thermal degradation products, to monitor the thermal decomposition of polycarbonate. We also analyze the effect of mild thermal treatment, as might be expected in thermally processed samples, on its photostability.

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## THERMAL DEGRADATION OF POLYCARBONATE



Scheme 1

## EXPERIMENTAL

Phenyl-2-phenoxybenzoate was synthesized by converting 2-phenoxybenzoic acid into its acid chloride and then reacting the acid chloride with phenol using triethylamine as the catalyst at 0°C in a nitrogen atmosphere. The final product was recrystallized from methanol.

Dibenzofuran, 2-phenoxybenzoic acid, bisphenol-A, diphenylether, and xanthone were used as received from Aldrich Chemical Co. Lexan polycarbonate powder from GE with little or no high-temperature thermal history designated as sample A was used as received. A second sample of polycarbonate from Aldrich Chemical Co., with at least some ther-

mal/processing history, designated as sample B, was also used without further purification. A bisphenol-A polycarbonate sample, designated as sample C, was synthesized in our laboratory following the procedure reported by Riffle *et al.* Triphosgene was used instead of phosgene.

The peak maximum molecular weight (compared to polystyrene) of polymer samples A, B, and C determined by GPC were 28,800, 28,900, and 26,700. All the three samples were characterized by infrared and UV absorption spectroscopy. The IR and the UV spectra of samples A, B, and C are essentially those reported<sup>8</sup> for bisphenol-A polycarbonate. The polycarbonate made in the laboratory did have some residual hydroxyl end groups as identified by FTIR.

Polycarbonate films were cast from a solution in dichloromethane. Films cast in nitrogen were prepared by casting the film in a nitrogen glove box from a nitrogen-purged solution of polycarbonate in dichloromethane. Clean quartz plates were used as substrates. The residual solvent present in the films was removed by pulling a vacuum for 1 h. Polycarbonate films used in Figures 9 and 11 are thinner than those used in the other samples in this article. Relatively thin films had to be used to ensure that the absorbencies ( $< 2.0$ ) at 265 nm were identical for the photolysis experiments.

UV spectra were obtained on a Perkin-Elmer Lambda-6 spectrophotometer and fluorescence studies were carried out using a SPEX Fluorolog-2 spectrofluorometer. Thermogravimetric analysis and thermal treatment of polycarbonate films were carried out on a DuPont 9900 thermal analyzer. IR spectra were obtained on a Perkin-Elmer 1600 FTIR spectrometer. Burdick and Jackson spectrophotometric-grade solvents were used for UV and fluorescence spectral studies.

TGAs of samples B and C are similar to that of sample A within the experimental conditions employed: All three samples have an onset of weight loss at 300°C in air. The TGA of sample A given in this article is representative of the TGA obtained for all three samples.

Fluorescence quantum yields of phenyl-2-phenoxybenzoate, 2-phenoxybenzoic acid, and dibenzofuran were determined in dichloromethane using 9,10-diphenylanthracene as the standard. The method of determination of the fluorescence quantum yield is reported elsewhere<sup>9</sup>:

Fluorescence quantum yield,  $\Phi_{FL}$

$$= \frac{\text{number of quanta emitted}}{\text{number of quanta absorbed}}$$

Photolysis of polycarbonate films was conducted in a Rayonet reactor from Southern New England Radiation Corp. fitted with 300 nm broad-band lamps. The model compounds were photolyzed using 302 nm broad-band table-top lamps (Model XX-15B) from Spectronics Corp., Westbury, New York.

## RESULTS AND DISCUSSION

The TGA of unprocessed polycarbonate (sample A) (Fig. 1) shows that in air polycarbonate begins decomposing at 300°C with about 65% weight loss at

400°C. In nitrogen, polycarbonate starts to decompose at 325°C with only about 35% weight loss at 400°C (Fig. 1). This indicates that thermal oxidation can be avoided when polycarbonate is subjected to heat treatment in nitrogen, and in an inert gas flow polycarbonate can be processed at a higher temperature without much weight loss. Polycarbonate (sample A) film does not exhibit structured emission prior to heat treatment. However, when polycarbonate is heated to only 250°C in air, structured emission appears and its intensity increases with an increase in the temperature at which the films are treated (Fig. 2). In nitrogen-cast polycarbonate film, there is no trapped oxygen present, and hence, thermal oxidation is completely avoided when heated in nitrogen. Interestingly, the structured emission is observed when nitrogen-cast polycarbonate film is heated to 250°C in a nitrogen atmosphere (Fig. 3), even though thermal oxidation cannot occur and weight loss is not observed at this temperature (Fig. 1,  $N_2$ ). This clearly shows that when polycarbonate is heated above its glass transition temperature (149°C) it gives nonoxidative thermal rearrangement products that are primarily responsible for the structured fluorescence emission. Reprecipitation of the thermally treated polycarbonate does not affect the structured emission, indicating that the thermal degradation products are formed in the backbone of polycarbonate and remain chemically bound to the polymer. A wide variety of commercial polycarbonate samples exhibit, to a greater or lesser extent, a structured fluorescence emission similar to that observed for the thermally degraded samples shown in Figures 2 and 3. A typical polycarbonate (sample B) exhibiting the structured emission is shown in Figure 4. Thus, even though the exact thermal/processing history of the polycarbonate sample B is not known, it is assumed that it has undergone at least some thermal treatment. The polycarbonate sample from Aldrich is in the form of pellets. To obtain pellets, polycarbonate is usually heated between 290 and 320°C for about 10–20 min in an extruder.) In contrast to sample B, polycarbonate sample C, which was synthesized in our laboratory and not subjected to any heat treatment, shows no structured emission (Fig. 4), as in the case of non-heat-treated sample A. These results confirm that the structured fluorescence emission observed in heat-treated polycarbonate is due to the presence of thermal degradation products.

To identify the species that give rise to structured emission in thermally degraded polycarbonate (Figs. 2 and 3), the fluorescence emission spectra

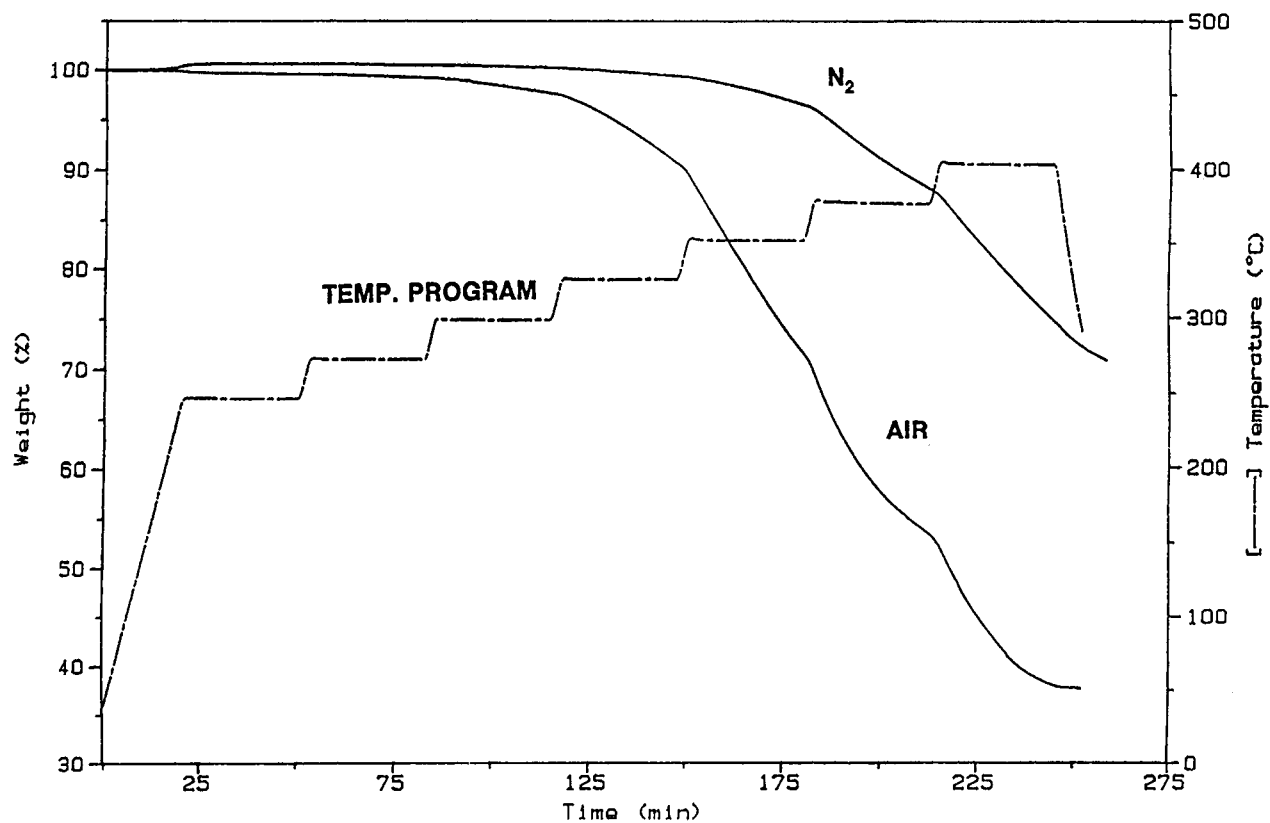


Figure 1 Thermogravimetric analysis of polycarbonate (sample A).

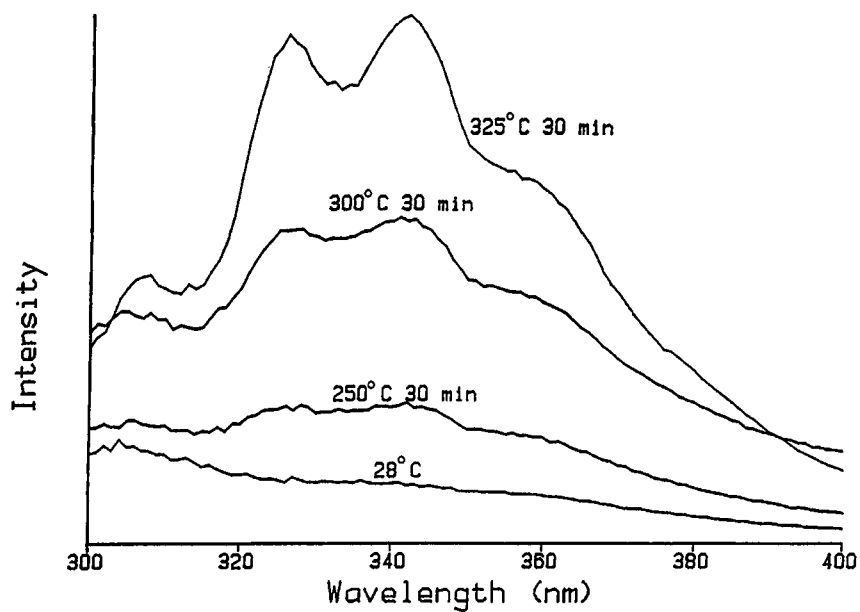
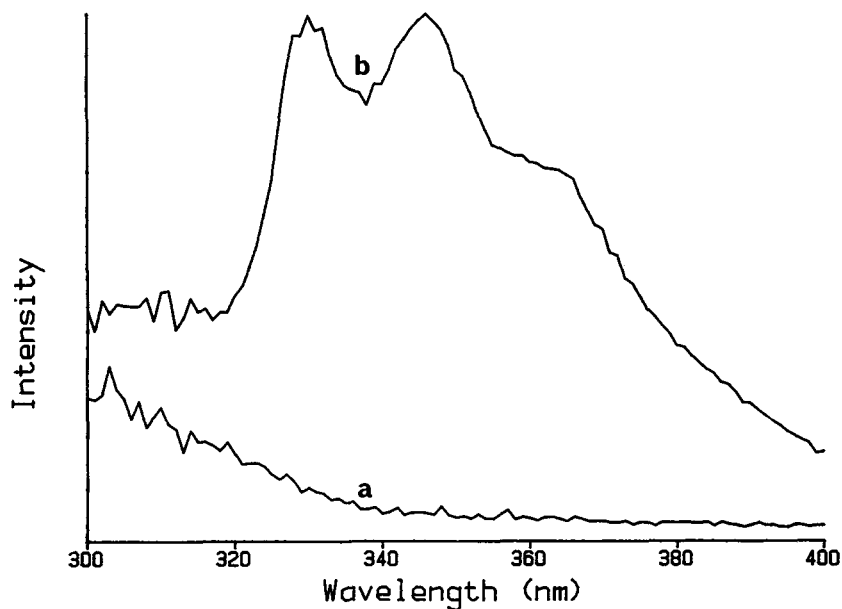


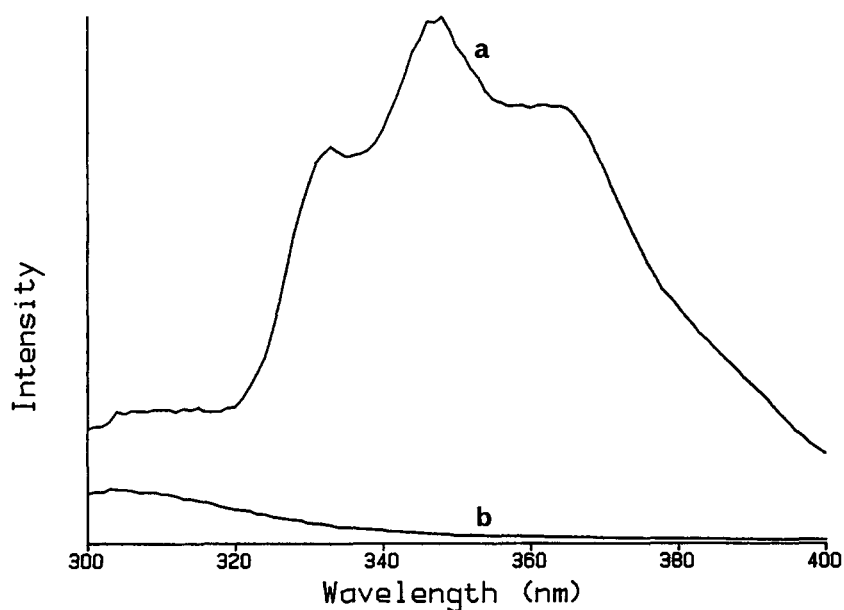
Figure 2 Fluorescence emission spectra of polycarbonate film (sample A) as a function of exposure temperature in air.  $\lambda_{ex} = 290 \text{ nm}$ .



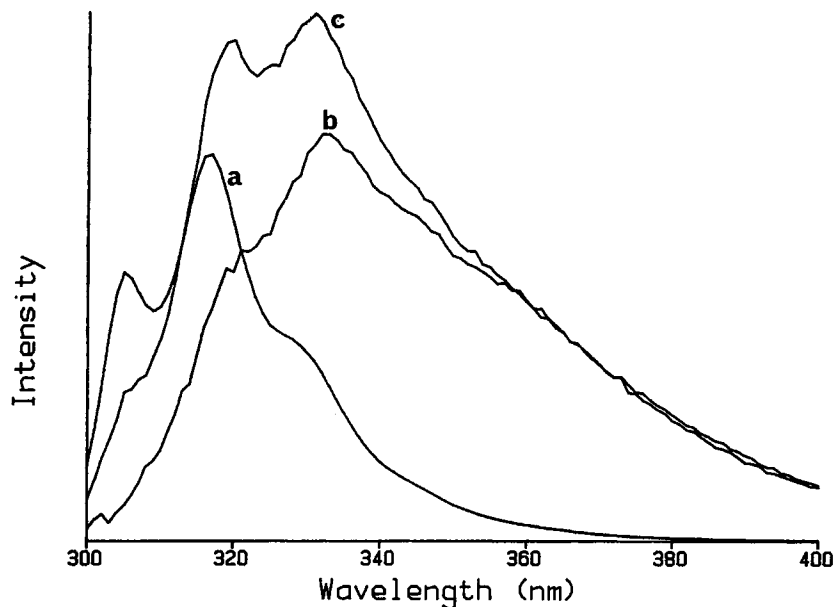
**Figure 3** Fluorescence emission spectra of nitrogen-cast polycarbonate film (sample A) (a) before heat treatment and (b) after 30 min heat treatment at 250°C in nitrogen atmosphere.  $\lambda_{\text{Ex}} = 290$  nm.

of a number of reported thermal degradation products of polycarbonate, like phenol, bisphenol-A, diphenylether, diphenylcarbonate, xanthone, 2-phenoxybenzoic acid, dibenzofuran, and phenyl-2-phenoxybenzoate, were checked. Of the above-mentioned compounds, only dibenzofuran shows

structured emission (Fig. 5), although its vibrational fine structure is not identical to the structured emission observed for the thermally degraded polycarbonate films (Figs. 2 and 3). A mixture of phenyl-2-phenoxybenzoate and dibenzofuran, however, shows a structured fluorescence emission (Fig. 5)



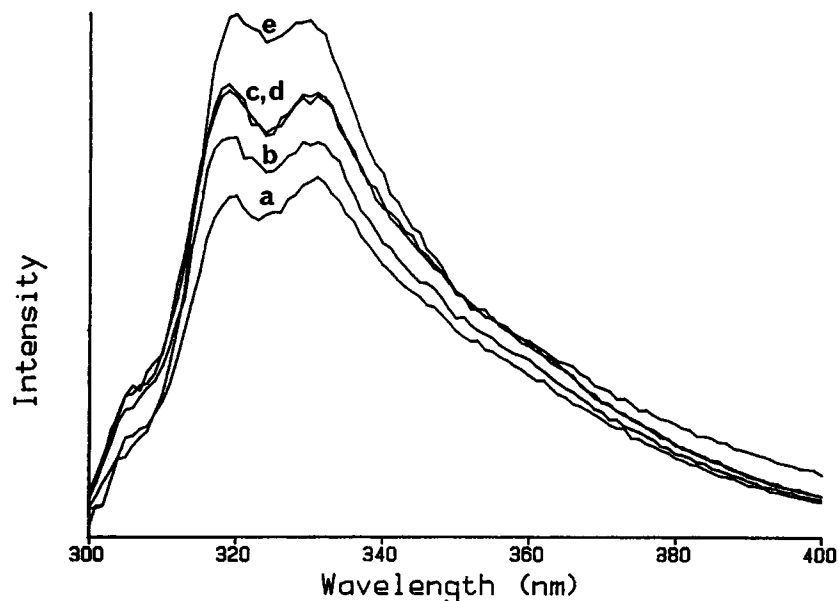
**Figure 4** Fluorescence emission spectra of polycarbonate films: (a) sample B; (b) sample C.  $\lambda_{\text{Ex}} = 290$  nm.



**Figure 5** Fluorescence emission spectra of (a) dibenzofuran, (b) phenyl-2-phenoxybenzoate, and (c) mixture of (a) and (b).  $\lambda_{\text{Ex}} = 290 \text{ nm}$ .

very similar to that observed for the thermally degraded polycarbonate films (Figs. 2 and 3). Addition of other thermal degradation products like xanthone, 2-phenoxybenzoic acid, and diphenylether to the above-mentioned mixture of products does not

change the vibrational fine structure of the structured emission (Fig. 6), indicating that a mixture of thermal rearrangement products of polycarbonate containing at least phenyl-2-phenoxybenzoate and dibenzofuran is consistent with the structured



**Figure 6** Fluorescence emission spectra of (a) phenyl-2-phenoxybenzoate + dibenzofuran, (b) polycarbonate + dibenzofuran + phenyl-2-phenoxybenzoate + diphenylether + xanthone, (c) polycarbonate + dibenzofuran + phenyl-2-phenoxybenzoate + diphenylether, (d) polycarbonate + phenyl-2-phenoxybenzoate + dibenzofuran, and (e) dibenzofuran + phenyl-2-phenoxybenzoate + 2-phenoxybenzoic acid.  $\lambda_{\text{Ex}} = 290 \text{ nm}$ .

emission observed in the case of thermally treated polycarbonate. Incidentally, the dual component combination of dibenzofuran and xanthone, phenol, 2-phenoxybenzoic acid, or diphenylether did not give the same spectrum as did dibenzofuran and phenyl-2-phenoxybenzoate.

Finally, we note that the addition of polycarbonate itself to the mixture of thermal degradation products does not affect the structured fluorescence emission (Fig. 6). However, we observe that the peak maxima of the fluorescence spectra of thermally treated polycarbonate films (Figs. 2 and 3) are slightly red-shifted from those exhibited by the mixture of dibenzofuran and phenyl-2-phenoxybenzoate (Fig. 5), which are models for the thermal degradation products formed in the backbone of polycarbonate. The difference in substitution between the actual degradation products in polycarbonate and the models could easily account for the differences in the peak maxima. Finally, from the literature<sup>1,3</sup> we note that the dibenzofuran-type product is only formed in relatively small quantities in thermally degraded polycarbonate and diphenylcarbonate. Since its fluorescence quantum yield is about 200 times higher than that of phenyl-2-phenoxybenzoate (Table I), it is easily detected by fluorescence spectroscopy in our analysis.

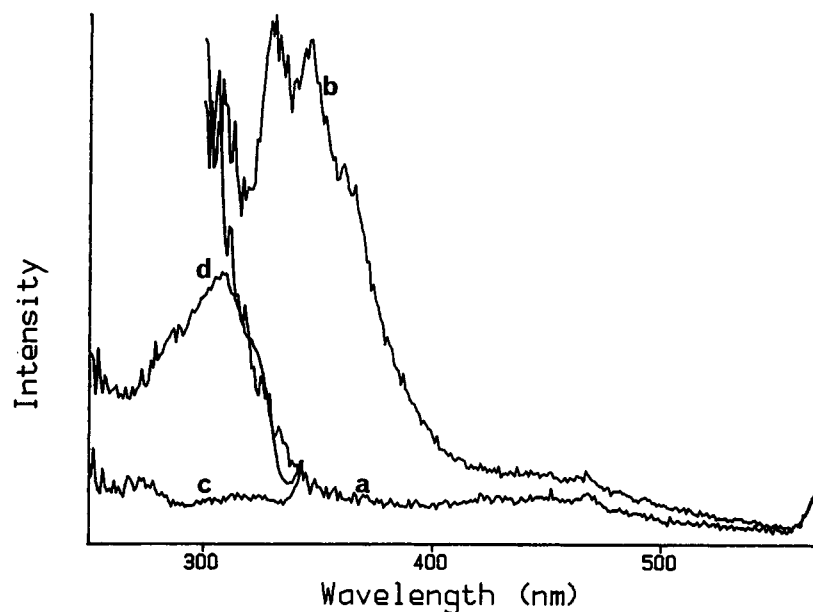
We have shown that when polycarbonate is subjected to heat treatment, even as low as 250°C, thermal degradation products (mainly thermal rearrangement products) readily form that can easily be detected by fluorescence spectroscopy. Normally during processing (extrusion, molding, pelletization, etc.), polycarbonate is heated to at least 290°C and above for a short period of time. To study the effect of prethermal treatment of polycarbonate on its photodegradation, two polycarbonate films were prepared. One was subjected to 10 min heat treatment in air at 300°C (a typical 10 min heat treatment at 300°C is selected since polycarbonate begins to degrade at about 300°C in air; in addition, poly-

carbonate is usually processed between 290 and 320°C for about 10–20 min in air and the conditions chosen are thus representative of mild thermal processing conditions), while the other received no thermal treatment: Optical densities of these films were matched at 265 nm. The two films were then subjected to photolysis in a Rayonet reactor with 300 nm lamps. The photolysis was followed by both fluorescence and UV-visible absorption spectroscopy. Fluorescence spectra [Fig. 7(a) and (b)] show that a 10 min thermal treatment of polycarbonate in air at 300°C gives rise to structured emission. Although the untreated polycarbonate film [Fig. 7(c)] exhibits no excitation spectrum when the emission monochromator is set at 360 nm, the excitation scan [Fig. 7(d)] of the structured emission ( $\lambda_{Em} = 360$  nm) shows that the thermal degradation product(s) of polycarbonate formed during the thermal treatment of polycarbonate absorb around 300 nm. From the UV-visible absorption spectrum in Figure 8, we confirm that the thermal degradation product(s) formed during the heat treatment of polycarbonate does (do) indeed absorb light around 300 nm. Fluorescence emission spectra (Fig. 9) show that photolysis of thermally treated (300°C, 10 min, air) polycarbonate film leads to the disappearance of the species responsible for the thermally generated structured emission, i.e., degradation of the thermal degradation products occurs upon photolysis. [Note that the appearance of the emission with maximum centered around 460–470 nm (Fig. 9) on photolysis is due to the formation of phenylsalicylate and/or salicylic acid-type products generated by photolysis of the parent polycarbonate<sup>10</sup>].

It is essential to know the effect of photolysis of the thermal degradation products of polycarbonate in order to assess the effect of thermal treatment of polycarbonate on its subsequent photostability. Thus, representative models of the thermal degradation products of polycarbonate, like dibenzofuran, bisphenol-A, phenyl-2-phenoxybenzoate, and xanthone, were photolyzed at 302 nm (table-top lamps—broad spectrum) and the photolyses were followed by UV-visible absorption spectroscopy. Long-term photolysis of dibenzofuran, bisphenol-A, and xanthone ultimately leads to the formation of photoproducts that absorb at lower energies than do the thermal degradation products themselves. Of all the thermal degradation products of polycarbonate that we evaluated, only phenyl-2-phenoxybenzoate (Fig. 10) shows a continued buildup in photoproducts upon long-term photolysis. Since the thermal degradation product resembling phenyl-2-phenoxybenzoate formed during the thermal treat-

**Table I** Fluorescence Quantum Yields of Some of the Thermal Degradation Products of Diphenylcarbonate (Solvent: Dichloromethane; Standard: 9,10-Diphenylanthracene)

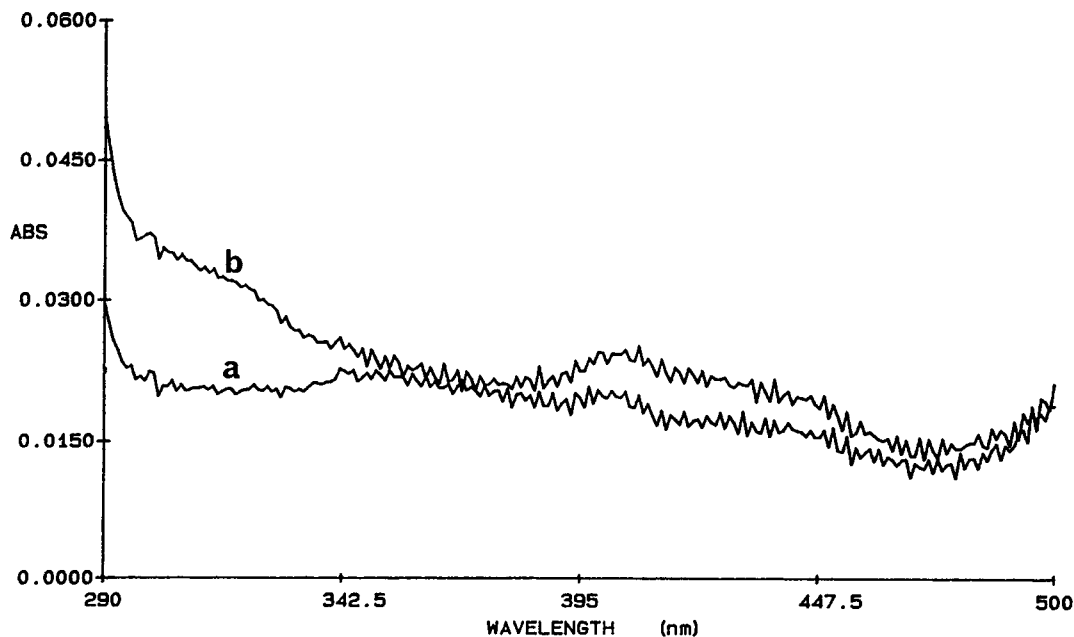
Compounds	Fluorescence Quantum Yield ( $\Phi_{Fl}$ )
Phenyl-2-phenoxybenzoate	$3.44 \times 10^{-3}$
2-Phenoxybenzoic acid	0.041
Dibenzofuran	0.76



**Figure 7** Fluorescence emission spectra of (a) polycarbonate film (sample A) before heat treatment and (b) after 10 min heat treatment at 300°C in air; (c) excitation scan of the untreated polycarbonate film taken at 360 nm; (d) excitation scan of the structured emission of the thermally treated (300°C, air, 10 min) polycarbonate film (sample A).  $\lambda_{Ex}$  = 290 nm and  $\lambda_{Em}$  = 360 nm.

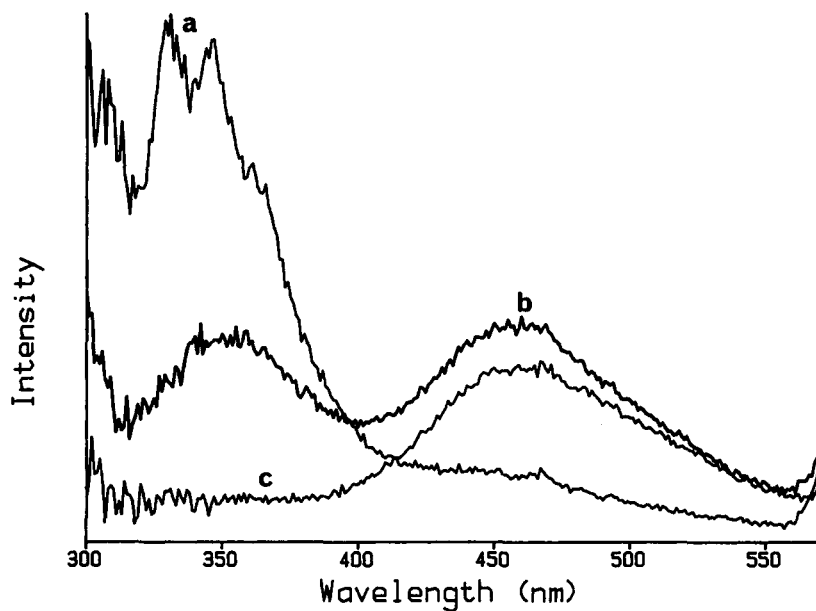
ment of polycarbonate is expected to display similar behavior when photolyzed, we might expect differences to occur between the photolysis of thermally degraded polycarbonate and nontreated polycar-

bonate. Indeed, there are some minor differences in the photolysis of the heat-treated and untreated polycarbonate films discernible by UV analysis upon long-term photolysis (Fig. 11): Discoloration upon



**Figure 8** UV-visible absorption spectra of polycarbonate film (sample A) (a) before heat treatment and (b) after 10 min heat treatment at 300°C in air.

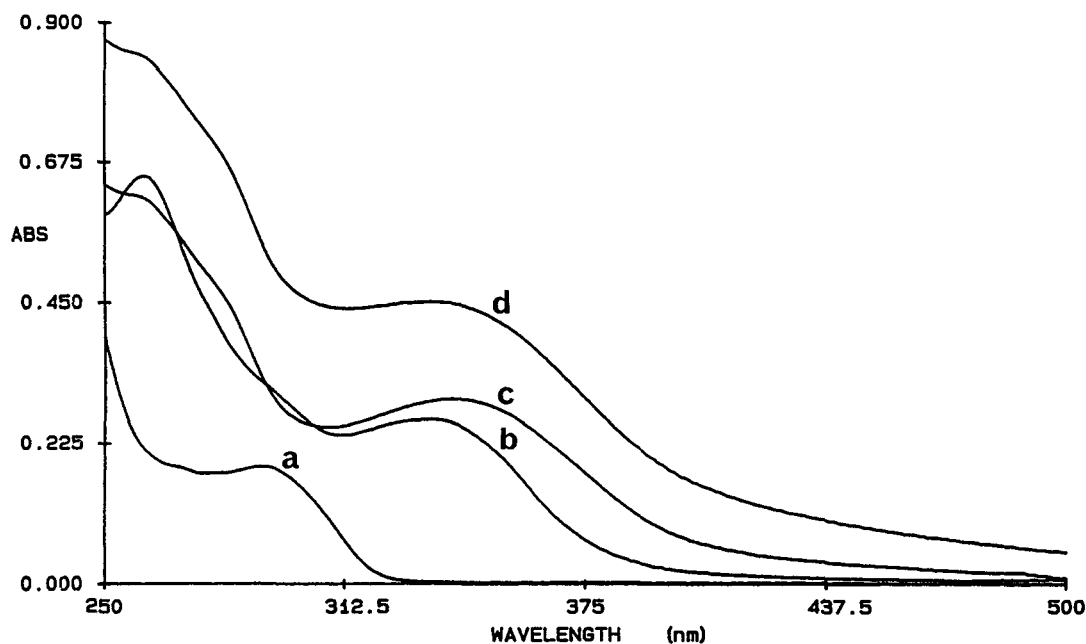




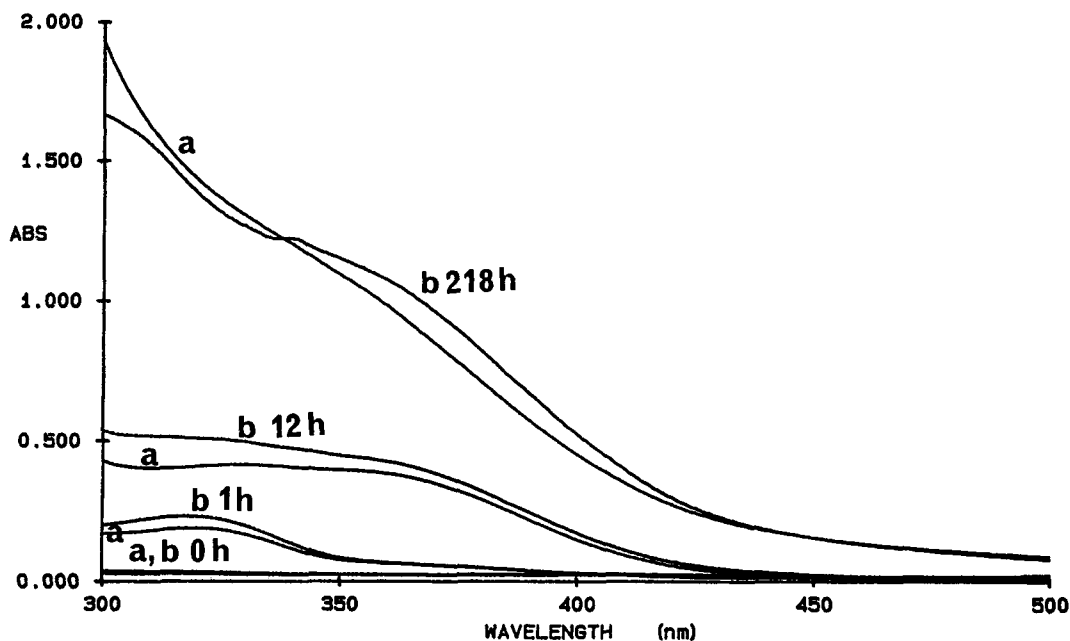
**Figure 9** Fluorescence emission spectra of polycarbonate film (sample A) (a) after 10 min heat treatment at 300°C in air, (b) after 1 h photolysis of the heat-treated polycarbonate film in a Rayonet photoreactor with 300 nm broad-band lamps, and (c) after 6 h of photolysis.  $\lambda_{\text{Ex}} = 290$  nm.

photolysis is marginally higher in the case of heat-treated polycarbonate than that in the case of untreated polycarbonate. The difference observed between the thermally treated and nonthermally treated samples is probably due to the contribution

from photoproducts generated from the direct photolysis of the phenyl-2-phenoxybenzoate-type structure present in the thermally treated polycarbonate. We stress that the amount of the phenyl-2-phenoxybenzoate-type product present in the ther-



**Figure 10** UV-visible absorption spectra of phenyl-2-phenoxybenzoate as a function of photolysis time (a) before photolysis and (b) after 1 h, (c) after 50 h, and (d) after 125 h of photolysis.



**Figure 11** UV-visible absorption spectra of polycarbonate (sample A) film as a function of photolysis (Rayonet with 300 nm lamps) time: (a) untreated film; (b) film subjected to 10 min heat treatment at 300°C in air.

mally treated polycarbonate after 10 min (typical of that produced in industrial processing) is small and has only a minor, but still discernible, effect on the overall photodegradation process of polycarbonate. Polycarbonate samples exposed to high temperatures for longer periods of time may produce a more pronounced effect on the photostability. Thus, although the typical temperature (300°C)/time (10 min) profile used herein does not lead to a significant increase in the photolability of polycarbonate, the techniques demonstrated in this article can clearly be utilized to evaluate bigger changes that harsher conditions might result in.

## CONCLUSIONS

Thermal treatment of polycarbonate both in air and in nitrogen leads to structured emission arising from a mixture of thermal degradation products. Thermal rearrangement products of polycarbonate are mainly responsible for the structured emission. Fluorescence analysis readily indicates the presence of dibenzofuran and phenyl-2-phenoxybenzoate-type thermal degradation products produced after very short thermal exposure times. Although long-term photolysis of phenyl-2-phenoxybenzoate-type products might lead to some unexpected increase in the photolability of polycarbonate, we stress that a typ-

ical mild thermal treatment of polycarbonate has only a minor effect on its photodegradation.

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## REFERENCES

1. A. Davis and J. H. Golden, *J. Chem. Soc. (B)*, 45 (1968).
2. K. B. Abbas, *Polymer*, **21**, 936 (1980).
3. A. Davis and J. H. Golden, *J. Chem. Soc. (B)*, 40 (1968).
4. CH. Bailly, M. Daumerie, R. Legras, and J. P. Mercier, *J. Polym. Sci. Phys. Ed.*, **23**, 345 (1985).
5. B. M. Kovarskaya, *Sov. Plast.*, **10**, 12 (1962).
6. M. H. Chipalkatti and J. Laski, *Polym. Mater. Sci. Eng.*, **64**, 131 (1991).
7. J. S. Riffle, E. Shchori, A. K. Banthia, R. G. Freelin, T. C. Ward, and J. E. McGrath, *J. Polym. Sci. Polym. Chem. Ed.*, **20**, 2289 (1982).
8. J. D. Webb and A. W. Czanderna, *Macromolecules*, **19**, 2810 (1986).
9. G. G. Guilbault, R. F. Chen, Govindjee, G. Papageorgiou, E. Rabinowitch, and E. L. Wehry, in *Practical Fluorescence*, G. G. Guilbault, Ed., Marcel Dekker, New York, 1973, Chap. 1.
10. C. E. Hoyle, H. Shah, and G. L. Nelson, *J. Polym. Sci. Part A Polym. Chem.*, **30**, 1525 (1992).

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