

# Glass Transitions of Poly(bisphenol-A Carbonate)/ Ultraviolet Light Stabilizer Blends by DSC and TOA

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## Synopsis

Glass transition temperatures are reported for poly(bisphenol-A carbonate) plasticized by 0–12 wt % of the ultraviolet light stabilizers 2-hydroxy-4-methoxy-benzophenone, 2-hydroxy-4-*n*-octoxy-benzophenone, and 2-hydroxy-4-dodecyloxy-benzophenone. Differential scanning calorimetry (DSC) and thermo-optical analysis (TOA) were employed. The glass transition temperatures increased somewhat with shelf time for the room temperature air-dried 1-mil films drawn from methylene chloride solutions. A Bierbaum scratch hardness of 8.8 kg·mm<sup>-2</sup> was observed for a 10-mil poly(bisphenol-A carbonate) film. The effect of load applied to the diamond point (Bierbaum scratch technique) on the shape of TOA transmitted light intensity vs. temperature curves for the resultant scratches was examined. Although the curve shapes are greatly affected, the characteristic TOA temperatures derived therefrom remain essentially unchanged. The glass transition regions are not quite as broad for these polymer/plasticizer blends as they are for compatible polymer/polymer blends.  $T_{\text{TOA}}$ , the temperature at which birefringence disappears in the scratched films, is found identical to  $T_f$  (DSC), the temperature at which the specific heat transition is completed.

## INTRODUCTION

Compounds having the structure 2-hydroxy-4-alkoxy-benzophenone are frequently used as protectants for transparent plastics against degradation by ultraviolet light.<sup>1</sup> Their high extinction coefficients in the near ultraviolet light region and their ability to convert the absorbed energy to heat without chemical change make them good choices as stabilizers. Increasing the chain length of the alkoxy group lowers the melting point of the stabilizer and thereby increases its solubility in a polymer. Also, the volatility and the mobility of the stabilizer in the polymer are decreased. When combined uniformly throughout a glassy polymer such UV stabilizers are normally at such low concentrations that the glass transition temperature is not greatly lowered. However, a more effective and efficient use of these stabilizers is to introduce them at higher concentrations into the surface region of a polymer and leave the bulk of the polymer unchanged.<sup>2</sup> It is then of interest to know the composition and the consequent glass transition temperature of the surface region since diffusion rates and various other physicochemical properties may be strongly affected thereby.

The glass transition temperatures  $T_g$  of homogeneous poly(bisphenol-A carbonate)/UV light stabilizer blends are here examined by differential scanning calorimetry (DSC) and by thermo-optical analysis (TOA). The stabilizers, present in 0.00–0.12 weight fraction concentrations, are the 4-methoxy, 4-*n*-octoxy, and 4-dodecyloxy-substituted 2-hydroxy-benzophenones.

The surface hardness of a polycarbonate film was measured by the Bierbaum scratch test method. The shapes of the transmitted light intensity vs. temperature curves are examined in TOA measurements on scratches produced by various loads on the diamond stylus.

## EXPERIMENTAL

### Materials and Sample Preparations

The poly(bisphenol-A carbonate) used for the blend film casting and for the Bierbaum scratch hardness study was obtained from a 10-mil extruded film. The abbreviation PC will be used for this polycarbonate. Its intrinsic viscosity in chloroform at 25°C was 0.55 dL/g.  $M_n = 12,400$ ,  $M_w = 29,700$ , and  $M_z = 46,800$  were computed from GPC measurements in chloroform using polystyrene calibrants and Mark-Houwink constants  $K = 1.2 \times 10^{-4}$  and  $a = 0.82$  for the "universal calibration." The stabilizers were: 2-hydroxy-4-methoxybenzophenone, UVINUL M-40® (GAF Corp.); 2-hydroxy-4-*n*-octoxybenzophenone, Cya-sorb UV-531® (American Cyanamid Co., Intermediates Department); 2-hydroxy-4-dodecyloxy-benzophenone, Inhibitor DOBP® (Eastman Chemical Products, Inc., Chemicals Division). These will be referred to as HMBP, HOBP, and HDBP with the letters M, O, and D referring to methoxy, *n*-octoxy, and *n*-dodecyloxy, respectively.

To prepare 1-mil blend films, 100 g of the polycarbonate film was dissolved in methylene chloride to give a 20 wt % solution. To 20 mL aliquots of this solution were added sufficient stabilizer to yield 0.0200, 0.0400, 0.0600, 0.0800, 0.1000, and 0.1200 weight fraction stabilizer based on stabilizer plus polycarbonate. 1-mil films were drawn on 5 in.  $\times$  10 in. glass plates from these solutions using a 5 in width, 6-mil gap doctor blade. After 3-5-min drying under an inverted baking dish the films were allowed to air-dry at room temperature shielded from light. The length of drying time after film drawing before DSC and TOA measurements will be indicated for the various film series.

### APPARATUS AND EXPERIMENTAL PROCEDURE

Differential scanning calorimetry data were obtained with a Perkin-Elmer DSC-2 or DSC-2C Calorimeter. The latter model differs from the former only in the addition of a microcomputer data logger and processor. Temperature calibration was performed with indium, tin, lead, and zinc standards. Differential power was calibrated by the heat of fusion of indium (6.80 cal/g). Two heating scans at 20°/min heating rate from 20°C to 200°C were done on each 9-12-mg sample in standard crimped aluminum sample containers. Free cooling (approximately -135°C/min at 150°C and -90°/min at 100°C) from 200°C to 20°C preceded the second heating of the "short term" dried samples. -40°/min cooling from 200°C to 20°C preceded the second heating of the "long term" dried samples. Three temperatures are used to characterize the glass transition. These are the onset temperatures  $T_s$  (DSC) at the intersection of the tangent from below the transition with the tangent through the  $C_p$  vs.  $T$  inflection point, the glass transition temperature  $T_g$  (DSC) at the 0.5  $\Delta C_p$  position of the transition, and the final temperature  $T_f$  (DSC), corresponding to the intersection

of the tangent through the inflection point with the tangent to the curve beyond the transition region. The  $\Delta C_p$  of the transition, measured between the initial and final tangent at  $T_g$ , is also recorded.

Thermooptical data were taken in the manner originally described<sup>3</sup> with some minor equipment and procedure modifications. Polymer films scratched with a steel stylus were mounted in a Mettler FP21 Hot Stage heated at  $10^\circ/\text{min}$  by a Mettler FP2 Controller in a Zeiss Standard WL Triocular Polarizing Microscope. Transmitted light through the birefringent scratch region of the film between crossed plane polarizer and analyzer was received by a photocell. Its intensity was presented as a proportional voltage to a Hewlett-Packard 700A X-Y Recorder, and a perceived light intensity (arbitrary units) vs. temperature (time) plot was recorded. Three characteristic temperatures were taken from the TOA curves in the glass transition region where the transmitted light intensity changes from a high value to a near-zero value. The tangent intersections and midpoint location yielding the characteristic temperatures are analogous to those yielding the DSC characteristic temperatures. The TOA temperatures are designated  $T_s$  (TOA),  $T_{\text{med}}$  (TOA), and  $T_{\text{TOA}}$ . The perceived light intensity depends in a very complex manner on the degree and nature of the birefringence induced by the scratching, on the color orders and photocell spectral response, and on the scratch depth and geometry. To determine whether the characteristic transition temperatures were sensitive to variation in the perceived intensity vs. temperature curve form, resort was made to a more controlled method of scratch formation as described in the following paragraph.

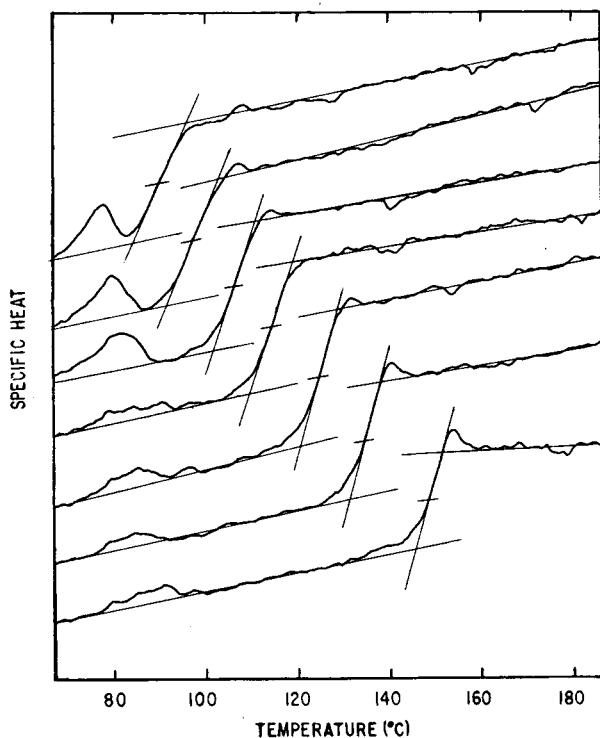


Fig. 1. DSC curves for PC/HDBP blend films 337 days after film formation. First heating at  $20^\circ/\text{min}$ . HDBP wt % ranges from 9 (bottom curve) to 12 (top curve) in 2% increments. Data are normalized to equal weight samples. Vertical scale and placements are arbitrary.

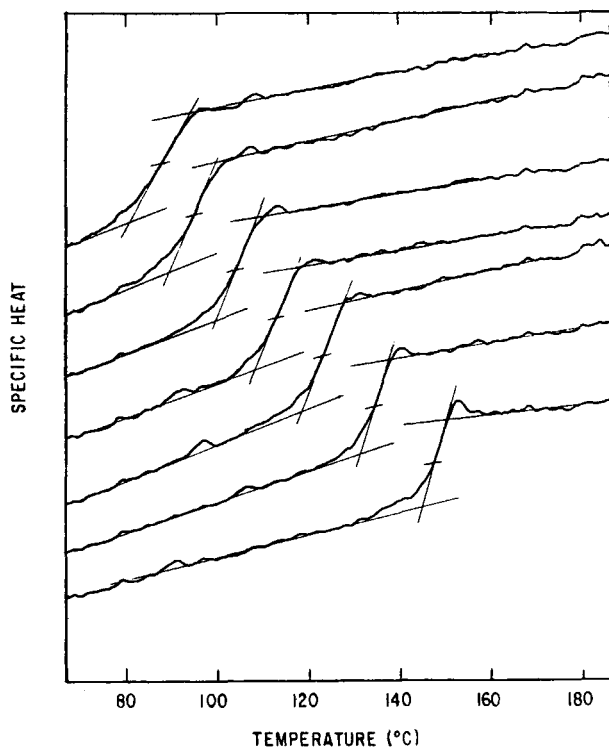


Fig. 2. DSC curves for PC/HDBP blend films 337 days after film formation. Second heating at 20°/min after -40°/min from 200°C to 40°C. HDBP wt % ranges from 0 (bottom curve) to 12 (top curve) in 2% increments. Data are normalized to equal weight samples. Vertical scale and placements are arbitrary.

The Bierbaum scratch hardness technique<sup>4-6</sup> was used to produce scratches in PC film surfaces. The films were cemented to glass slides with epoxy cement and scratched by transporting them on a microscope stage under a cut diamond cube mounted vertically on a diagonal and weighted with chosen loads. The film stage was transported at approximately 0.25–0.30 mm/s by manual operation of a worm gear drive. Six scratches spaced at 250  $\mu\text{m}$  center-to-center were scribed by the diamond point. Scratch widths were measured by transmitted light in an MM6 Leitz Microscope (Method A, Ref. 6). Scratch profiles were examined by epoxy potting of the scratched surface, cross-sectioning, polishing, and photographing at 750 $\times$  magnification.

## RESULTS AND DISCUSSION

The DSC data are represented by the curves in Figures 1 and 2, and the characteristic temperatures for the glass transition region are listed in Tables IA, IB, IIA, and IIB. The DSC curves are included to indicate marking and to show the dependence of curve shapes on specimen history. The first heating of all the films revealed small sub- $T_g$  maxima in the specific heat vs. temperature curves (Fig. 1). Although these peaks are somewhat sharpened and the maxima are displaced to slightly higher temperatures with increased time at room temperature, the peaks also exist in the solution drawn films whose glass transition

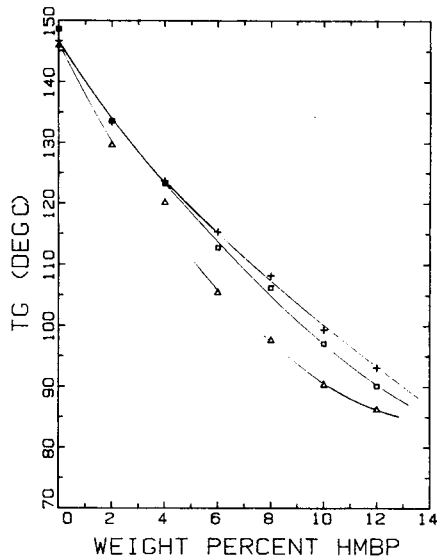


Fig. 3.  $T_g$  (DSC) vs. weight percent HMBP for PC/HMBP blend films. Second heating at  $20^\circ/\text{min}$ . ( $\Delta$ ) 8 days after film formation; ( $\square$ ) 335 days after film formation; (+) 15 days RT + 17 hours at  $80^\circ\text{C}$  under vacuum + 14 days RT after film formation.

data are listed in Table IA. This phenomenon is common to polymer glasses prepared by various procedures<sup>7,8</sup> and has been treated by several investigators as a manifestation of a distribution of relaxation times in the glasses.<sup>9-12</sup>

The effect on  $T_g$  of drying time at room temperature in air is illustrated in Figures 3, 4, and 5 for the second heatings of the three blend systems. The

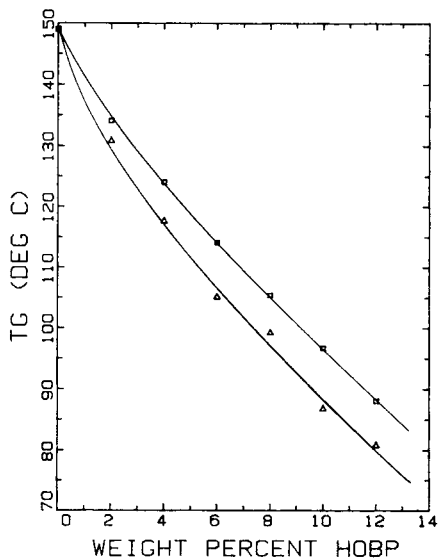


Fig. 4.  $T_g$  (DSC) vs. weight percent HOBP for PC/HOBP blend films. Second heating at  $20^\circ/\text{min}$ . ( $\Delta$ ) 6 days after film formation; ( $\square$ ) 88 days after film formation.

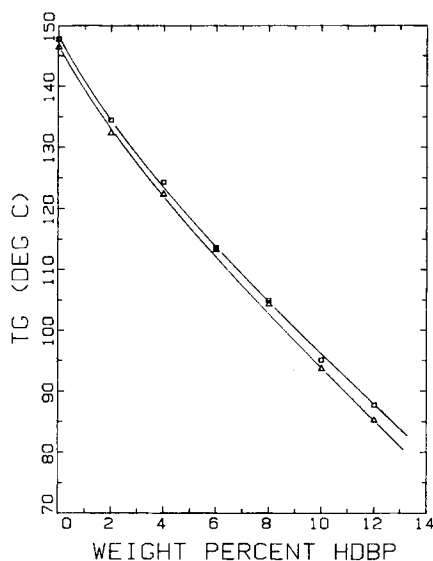


Fig. 5.  $T_g$  (DSC) vs. wt % HDBP for PC/HDBP blend films. Second heating at  $20^\circ/\text{min}$ . ( $\Delta$ ) 13 days after film formation; ( $\square$ ) 337 days after film formation.

TABLE IA  
DSC Data: First Heat,  $20^\circ/\text{min}$

$w$	$T$ ( $^\circ\text{C}$ )			$\Delta C_p$ ( $\text{J}\cdot\text{g}^{-1}\cdot\text{K}^{-1}$ )
	$T_s$ (DSC)	$T_g$ (DSC)	$T_f$ (DSC)	
<u>HMBP<sup>a</sup></u>				
0.00	143.2	147.2	151.3	0.28
0.02	116.7	124.2	131.4	0.24
0.04	117.5	121.8	126.1	0.30
0.06	93.5	102.7	112.9	0.28
0.08	87.0	93.3	100.7	0.26
0.10	84.3	91.2	97.9	0.25
0.12	79.9	85.3	90.3	0.26
<u>HOBP<sup>b</sup></u>				
0.02	125.1	129.8	134.0	0.28
0.04	111.1	117.1	122.0	0.28
0.06	97.3	103.4	108.0	0.27
0.08	87.0	94.7	98.6	0.24
0.10	77.9	84.7	86.0	0.22
0.12	72.4	76.6	79.3	0.22
<u>HDBP<sup>c</sup></u>				
0.00	144.6	148.3	152.2	0.20
0.02	124.9	135.7	147.3	0.30
0.04	119.3	123.8	128.5	0.29
0.06	109.8	115.3	120.6	0.31
0.08	101.8	106.2	110.8	0.28
0.10	92.3	97.8	104.2	0.25
0.12	80.3	87.1	93.7	0.24

<sup>a</sup> 8 days after film formation.

<sup>b</sup> 6 days after film formation.

<sup>c</sup> 13 days after film formation.

TABLE IB  
 DSC Data: First Heat, 20°/min

$w$	$T$ (°C)			$\Delta C_p$ (J·g <sup>-1</sup> ·K <sup>-1</sup> )
	$T_s$ (DSC)	$T_g$ (DSC)	$T_f$ (DSC)	
<u>HMBP<sup>a</sup></u>				
0.00	144.7	147.1	150.0	0.23
0.02	131.8	134.4	136.0	0.21
0.04	119.9	123.7	128.0	0.35
0.06	111.1	113.8	114.0	0.32
0.08	103.7	106.9	109.3	0.28
0.10	94.0	98.2	100.0	0.31
0.12	88.2	91.7	94.6	0.29
<u>HOBP<sup>b</sup></u>				
0.00	145.8	149.1	152.0	0.25
0.02	132.1	135.5	137.3	0.28
0.04	120.3	123.5	126.0	0.26
0.06	110.2	115.0	117.3	0.30
0.08	101.7	106.0	108.6	0.30
0.10	92.3	97.0	99.6	0.35
0.12	84.9	90.0	92.6	0.23
<u>HDBP<sup>c</sup></u>				
0.00	146.3	149.0	150.6	0.24
0.02	131.8	135.0	138.0	0.29
0.04	121.6	124.6	127.0	0.26
0.06	110.4	114.1	118.0	0.31
0.08	103.0	107.4	109.3	0.28
0.10	92.6	97.2	99.3	0.30
0.12	86.0	91.4	96.0	0.25

<sup>a</sup> 335 days after film formation.

<sup>b</sup> 88 days after film formation.

<sup>c</sup> 337 days after film formation.

greater  $T_g$  depressions in the shorter drying periods are believed due to small residual amounts of methylene chloride. In Figure 3,  $T_g$  data are included for a set of PC/HMBP films which had been room temperature air-dried for 15 days, vacuum-dried for 17 h at 80°C with a slow nitrogen bleed, and then room temperature air-dried for another 14 days. The  $T_g$  for these elevated temperature, vacuum-dried samples are very similar to, but slightly higher than (as much as 3.0° at  $w_2 = 0.12$ ), the  $T_g$  of the 335-day room temperature air-dried films. Although the 17-hour drying at 80°C appears to have eliminated the residual methylene chloride problem, the possibility of slight stabilizer loss (especially of HMBP) indicated long-term, room-temperature drying to be preferable.

The breadth of the glass transition region as judged by  $T_f$  (DSC) -  $T_s$  (DSC) indicates a sharper transition for the long-term dried films than for the short-term dried films. Discarding two extreme values from each data set (i.e., averaging 18 values each in Table IA and Table IIA and 19 values each in Table IB and Table IIB) yields the following averages and standard deviations ( $\sigma$ ):

Series	Avg [ $T_f$ (DSC) - $T_s$ (DSC)]	$\sigma$
short term, first heat	10.5	2.3
short term, second heat	10.3	1.1
long term, first heat	6.2	0.9
long term, second heat	6.6	1.0

TABLE IIA  
DSC Data: Second Heat, 20°/min, after 20–200°C (+20°/min) and 200–20°C (Free Cooling)

<i>w</i>	<i>T</i> (°C)			$\Delta C_p$ (J·g <sup>-1</sup> ·K <sup>-1</sup> )
	<i>T<sub>s</sub></i> (DSC)	<i>T<sub>g</sub></i> (DSC)	<i>T<sub>f</sub></i> (DSC)	
<u>HMBP<sup>a</sup></u>				
0.00	142.4	145.9	149.1	0.25
0.02	124.7	129.6	134.5	0.23
0.04	114.7	120.1	125.3	0.24
0.06	99.9	105.4	111.3	0.26
0.08	92.3	97.6	103.1	0.24
0.10	85.2	90.3	95.3	0.20
0.12	81.1	86.2	91.1	0.25
<u>HOBP<sup>b</sup></u>				
0.02	126.2	130.8	134.0	0.25
0.04	112.3	117.6	122.4	0.21
0.06	100.0	105.1	109.3	0.22
0.08	93.6	99.2	103.3	0.24
0.10	81.0	86.8	91.3	0.21
0.12	74.8	80.8	85.3	0.24
<u>HDBP<sup>c</sup></u>				
0.00	142.8	146.4	150.3	0.23
0.02	123.7	132.3	141.3	0.25
0.04	117.5	122.3	127.1	0.23
0.06	108.1	113.2	118.1	0.23
0.08	98.5	104.3	109.9	0.29
0.10	88.3	93.6	100.1	0.24
0.12	78.4	85.2	92.3	0.26

<sup>a</sup> 8 days after film formation.

<sup>b</sup> 6 days after film formation.

<sup>c</sup> 13 days after film formation.

The differences in transition breadth may arise from a distribution of residual methylene chloride concentration in the short-term dried films. It is somewhat surprising, however, if this is the source of increased breadth, that the methylene chloride did not distribute uniformly above  $T_g$  during the first heat. It should be remarked that DSC measurements on the long-term dried films were made with the DSC-2C apparatus while the DSC measurements on the short term dried samples were made with the DSC-2 apparatus.

Several expressions have been derived to relate glass transition temperature to composition for polymer/small molecule and polymer/polymer blends. Although the glass transition is a nonequilibrium, kinetic phenomenon, the formalism of Ehrenfest second-order transitions has led to a glass transition/composition relation for polymer/polymer blends which can be specialized into the various previously proposed relations.<sup>13,14</sup> It should be noted that, in part, the entropic arguments leading to the relation rely upon the long-chain character of both constituents in the blend. Application of the expression to polymer/small molecule blends is a further extension. The Couchman equation relating the blend glass transition temperature  $T_g$  to the component weight fractions ( $w_1$ ,  $w_2$ ), glass transition temperatures ( $T_{g1}$ ,  $T_{g2}$ ), and specific heat increments at the glass temperatures ( $\Delta C_{p1}$ ,  $\Delta C_{p2}$ ) is<sup>13</sup>

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



TABLE IIB

DSC Data: Second Heat, 20°/min, after 20–200°C (+20°/min) and 200–20°C (Free Cooling)

<i>w</i>	<i>T</i> (°C)			$\Delta C_p$ (J·g <sup>-1</sup> ·K <sup>-1</sup> )
	<i>T<sub>s</sub></i> (DSC)	<i>T<sub>g</sub></i> (DSC)	<i>T<sub>f</sub></i> (DSC)	
<u>HMBP<sup>a</sup></u>				
0.00	146.2	148.6	150.0	0.22
0.02	130.5	133.6	136.5	0.24
0.04	119.4	123.2	126.0	0.26
0.06	109.0	112.7	114.6	0.23
0.08	102.7	106.2	109.0	0.24
0.10	93.3	97.1	98.0	0.22
0.12	85.4	90.1	93.3	0.25
<u>HOBP<sup>b</sup></u>				
0.00	145.6	149.0	150.6	0.23
0.02	131.1	134.1	136.6	0.20
0.04	119.6	124.0	126.0	0.22
0.06	109.8	114.1	117.3	0.24
0.08	101.3	105.4	107.9	0.20
0.10	91.8	96.7	99.3	0.25
0.12	82.7	88.1	90.3	0.25
<u>HDBP<sup>c</sup></u>				
0.00	144.8	147.7	150.5	0.23
0.02	131.0	134.4	137.5	0.23
0.04	119.8	124.3	128.0	0.24
0.06	109.6	113.5	116.0	0.24
0.08	100.7	104.9	107.3	0.23
0.10	90.7	95.1	98.6	0.23
0.12	81.7	87.7	91.3	0.24

<sup>a</sup> 335 days after film formation.<sup>b</sup> 88 days after film formation.<sup>c</sup> 337 days after film formation.

With  $T_{g1}/T_{g2}$  approximately equal to 1, eq. (1) reduces the form of the Wood copolymer equation<sup>15</sup>

$$T_g = \frac{w_1 \Delta C_{p1} T_{g1} + w_2 \Delta C_{p2} T_{g2}}{w_1 \Delta C_{p1} + w_2 \Delta C_{p2}} \quad (2)$$

If the relation<sup>16</sup>

$$\Delta C_{p1} T_{g1} = \Delta C_{p2} T_{g2} \quad (3)$$

is satisfied, eq. (2) further reduces to the Fox relation<sup>17</sup>

$$1/T_g = w_1/T_{g1} + w_2/T_{g2} \quad (4)$$

The present data on polycarbonate (1)–UV stabilizer (2) blends were taken only in the composition range  $0 < w_2 < 0.12$ . This was due to an interest in a practical range of stabilized film composition and a desire to avoid crystallization of the UV stabilizer. These data cannot, therefore, be used to test definitively the relative merits of eqs. (1), (2), and (4) in approximating glass transition vs. composition behavior.  $T_{g1}$  and  $\Delta C_{p1}$  have been measured, but  $T_{g2}$  and  $\Delta C_{p2}$  have not been measured. The believed precision of the second-heat  $T_g$  values for the long-term dried blends (Table IIB), however, encouraged us to examine the degree of their conformance to eqs. (1) and (4), and to examine the significance of the  $\Delta C_{p2}/\Delta C_{p1}$  and  $T_{g1}/T_{g2}$  ratios thus obtained. In subsequent dis-

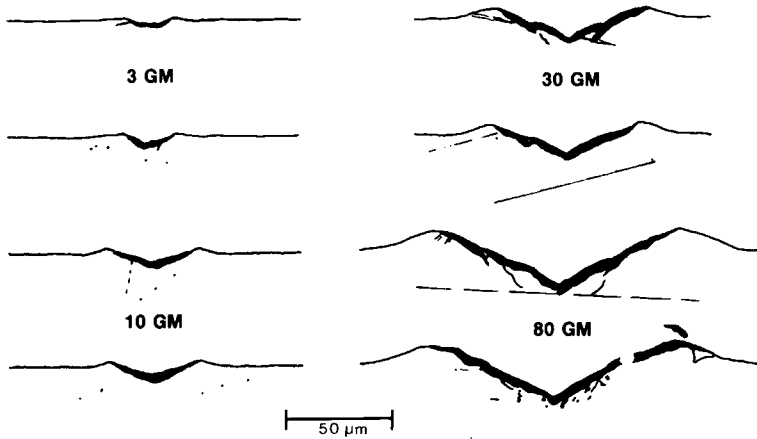


Fig. 6. Profiles of Bierbaum scratches produced at four load levels. 750 $\times$  photomicrographs after epoxy embedment, cross-sectioning, and polishing.

cussion we assume the melting temperatures of the HMBP, HOBP, and HDBP stabilizers to be 62°C, 47°C, and 44°C, respectively.<sup>18</sup>

Equation (1) was applied directly to the  $T_g, w_2$  data sets in the form

$$\ln T_g = \ln T_{g2} - \frac{1}{r} \frac{1 - w_2}{w_2} \ln \frac{T_g}{T_{g1}} \quad (1a)$$

where  $r \equiv \Delta C_{p2}/\Delta C_{p1}$ .  $T_{g1}$  was taken as the observed  $T_g$  ( $w_2 = 0.00$ ) for each data set. The use of eq. (1a) is analogous to the use of eq. (8), Ref. 15. Unfortunately, the most accurate evaluation of  $T_{g2}$  and  $r$  would be obtained from data

TABLE III  
Glass Transition Temperature and Associated Parameters from Linear Regression Fitting of Table IIB Data to Selected  $T_g(w_2)$  Relations. Polycarbonate (1)-UV Stabilizer (2)

	Stabilizer	$T_{g1}$ (°K)	$T_{g2}$ (°K)	$r$	$T_{g1}/T_{g2}$	$T_{g2}/T_{m2}$
A <sup>a</sup>	HMBP	(421.8)	307.3	6.14	1.37	0.92
	HOBP	(422.2)	297.6	5.38	1.42	0.93
	HDBP	(420.9)	265.2	3.56	1.59	0.84
B <sup>b</sup>	HMBP	418.6	181.8		2.30	0.54
	HOBP	419.9	177.7		2.36	0.55
	HDBP	419.6	176.5		2.38	0.56
C <sup>c</sup>	HMBP	418.5	(181.8)	1.55	2.30	0.54
	HOBP	419.8	(177.7)	1.57	2.36	0.55
	HDBP	419.5	(176.5)	1.57	2.38	0.56
D <sup>d</sup>	HMBP	419.1	225	2.23	1.86	(0.67)
	HOBP	420.3	214	2.13	1.96	(0.67)
	HDBP	420.1	212	2.12	1.98	(0.67)
E <sup>e</sup>	HMBP	419.0	218.9	2.12	1.91	(0.653)
	HOBP	420.3	209.1	2.04	2.01	(0.653)
	HDBP	420.0	207.1	2.03	2.03	(0.653)

<sup>a</sup> Eq. (1a).

<sup>b</sup> Eq. (4), Fox relation.

<sup>c</sup> Eq. (1b),  $T_{g2}$  obtained from Fox relation.

<sup>d</sup> Eq. (1b), assumed  $T_{g2} = 0.67 T_{m2}$ .

<sup>e</sup> Eq. (1b), assumed  $T_{g2} = 0.653 T_{m2}$ .

TABLE IV  
Bierbaum Scratch Hardness and TOA Data on Extruded Polycarbonate Film

Load On point (g)	Y-Z width ( $\mu\text{m}$ )	Hardness BSH ( $\text{kg}\cdot\text{mm}^{-2}$ )	$T_s$ (TOA)	$T_{\text{med}}$ (TOA) ( $^{\circ}\text{C}$ )	$T_{\text{TOA}}$ ( $^{\circ}\text{C}$ )
3	18	9.3	150.6	152.0	153.3
10	34	8.7	150.8	152.4	153.9
30	58	8.9	151.4	152.6	153.8
80	96	8.7	151.6	152.8	154.0

in the region  $w_2 \rightarrow 1$ . The results of direct application of eq. (1a) are shown in Table IIIA. The high values of  $r$  and  $T_{g2}$ , and the associated high  $T_{g2}/T_{m2}$  and low  $T_{g1}/T_{g2}$  ratios, result from a perceived large positive curvature of the  $T_g$  vs.  $w_2$  curves and the long extrapolation to  $w_2 = 1.00$ . The perceived curvature  $s$  decreases in the order  $s$  (HMBP)  $>$   $s$  (HOBP)  $>$   $s$  (HDBP).

Fitting the  $T_g, w_2$  data of Table IIB to the Fox equation [eq. (4)] yields the  $T_{g1}$  and  $T_{g2}$  values shown in Table IIIB. The  $T_{g1}$  values, of course, lie near the measured values for the pure polycarbonate films. The  $T_{g2}$  values are similar for the three stabilizers with a slight trend in the expected direction  $T_{g2}$  (HMBP)  $>$   $T_{g2}$  (HOBP)  $>$   $T_{g2}$  (HDBP). Rearranging eq. (1) into the form

$$\ln T_g = \ln T_{g1} + r \frac{w_2}{1 - w_2} \ln \frac{T_{g2}}{T_g} \quad (1b)$$

and accepting the  $T_{g2}$  values obtained by the Fox relation (cf. Table IIIB) one computes the  $T_{g1}$  and  $r$  values listed in Table IIIC. It is noted that  $r = T_{g1}/T_{g2}$ . Since eq. (4) was obtained from eq. (1) by the assumption  $r = T_{g1}/T_{g2}$  after the approximation  $T_{g1}/T_{g2}$  is approximately equal to 1, it is not surprising that the

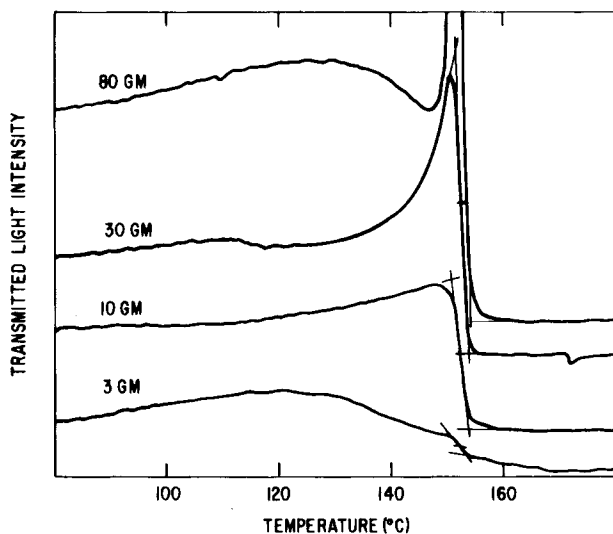


Fig. 7. TOA curves for 10-mil PC film with scratches produced by the Bierbaum technique. Loads on the diamond stylus are indicated. Heating rate is  $10^{\circ}/\text{min}$ . The same vertical scale is used for each curve, but the vertical placements are arbitrary.

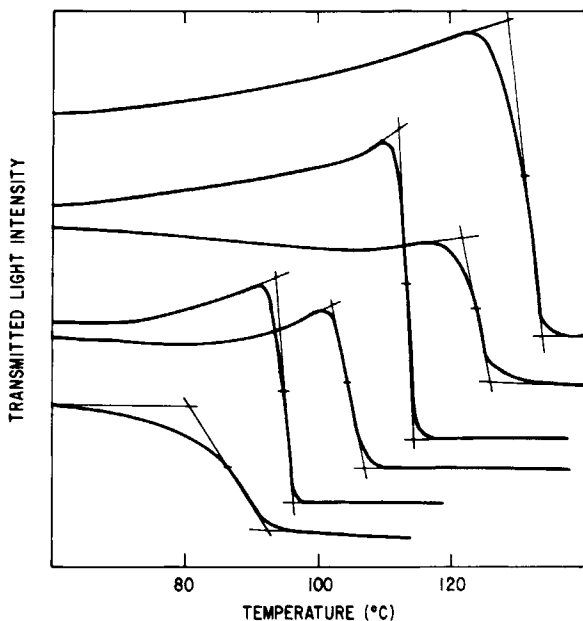


Fig. 8. TOA curves for PC/HMBP blend films. Weight fractions HMBP range from 0.02 (top curve) to 0.12 (bottom curve) in 0.02 increments. Heating rate is  $10^{\circ}/\text{min}$ . The vertical placement of curves is arbitrary.

substitution of  $T_{g2}$  values obtained from eq. (4) back into eq. (1b) does not satisfy eq. (3).

An estimation of the glass transition temperatures of the stabilizers can be made from their melting temperatures. The average ratio of  $T_g/T_m$  for nine mono-alkyl benzenes,<sup>19</sup> phenyl salicylate,<sup>20</sup> and 2-naphthyl salicylate<sup>20</sup> is  $0.669 \pm 0.026$ .<sup>21</sup> Use of this ratio to provide  $T_{g2}$  values yields the  $r$  and the  $T_{g1}/T_{g2}$  ratios shown in Table IIID. These ratios do not quite equal each other and therefore do not quite satisfy eq. (3). However, the correspondence of  $r$  to  $T_{g1}/T_{g2}$  is rather good. One further computation was therefore made. By iteration it was determined  $T_{g2}/T_{m2} = 0.653$  gave a glass transition temperature for HDBP which, when used in eq. (1b), yielded  $r = T_{g1}/T_{g2}$  [i.e., satisfied eq. (3)]. This value of  $T_{g2}/T_{m2}$  is well within the  $2\sigma = 0.052$  range for  $T_{g2}/T_{m2} = 0.67$ . Table IIIE presents the  $r$  and  $T_{g1}/T_{g2}$  results derived from setting  $T_{g2}/T_{m2} = 0.653$  for each of the stabilizers.

The application of the Couchman relations, eq. (1), to the present  $T_g, w_2$  data sets (Table IIB) provides a good fit with reasonable values for the  $T_{g2}$  and  $r = \Delta C_{p2}/\Delta C_{p1}$  parameters. It will be interesting to note when experimental values for  $T_{g2}$  and  $\Delta C_{p2}$  are determined whether the parameter values listed in sections D or E of Table III are in near agreement with the true values.

Profiles of the scratches in the 10-mil PC obtained by the Bierbaum technique using 3-, 10-, 30-, and 80-g loads on the diamond point are shown in Figure 6. Some elastic recovery is in evidence in each profile. With no recovery the angle at the bottom of the scratches should be  $101.54^{\circ}$ . It has not yet been determined whether the recovery occurred shortly after the diamond point traverse or during the epoxy embedding process. The Bierbaum scratch hardness (BSH) is cal-

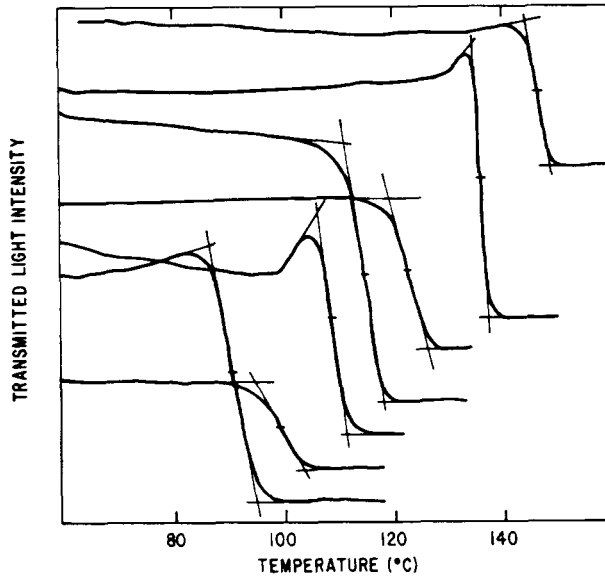


Fig. 9. TOA curves for PC/HOBP blend films. Weight fractions of HOBP range from 0.00 (top curve) to 0.12 (bottom curve) in 0.02 increments. Heating rate is  $10^{\circ}/\text{min}$ . The vertical placement of curves is arbitrary.

culated from the load  $m$  (kg) on the diamond point and the Y-Z scratch width (SW) (mm) as measured by transmitted light (Method A, Ref. 6).

$$\text{BSH} = m/(\text{SW})^2$$

The calculated BSH at the four load levels are listed in Table IV. The three higher loads yield a very constant BSH of about  $8.8 \text{ kg}\cdot\text{mm}^{-2}$ .

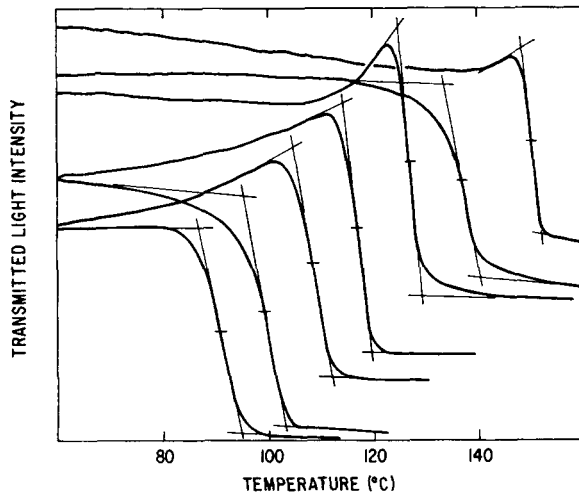


Fig. 10. TOA curves for PC/HDBP blend films. Weight fractions HDBP range from 0.00 (top curve) to 0.12 (bottom curve) in 0.02 increments. Heating rate is  $10^{\circ}/\text{min}$ . The vertical placement of curves is arbitrary.

TOA curves are shown in Figure 7 for the scratched films having profiles illustrated in Figure 6. The overall curve shapes are quite sensitive to the load applied in the Bierbaum technique. However, the characteristic temperatures for the transition (cf. columns 4–6, Table IV) are essentially unaffected. There is possibly a slight trend toward higher values with increasing load for the observed  $T_s$  (TOA) and  $T_{med}$  (TOA). The observed constancy of the transition temperatures despite scratch formation differences encourages greater confidence in the  $T_s$  (TOA),  $T_{med}$  (TOA), and  $T_{TOA}$  values obtained for films scratched by a steel stylus in a less controlled manner.

Figures 8, 9, and 10 present the TOA transmitted light intensity vs. temperature curves of the three series of PC/UV light stabilizer blend films. The compositions and characteristic transition temperatures are listed in Table V. The  $T_{TOA} - T_s$  (TOA) differences are in general less than the  $T_f$  (DSC) -  $T_g$  (DSC) differences, although comparable to the latter for the long-term dried films. Due to the variation in shape of the TOA curves,  $T_{TOA}$  will be the only characteristic temperature examined in some detail. Comparisons will be made with  $T_s$  (DSC),  $T_g$  (DSC), and  $T_f$  (DSC) for the long-term dried films.

In the earliest study of compatible polymer/polymer blends  $T_{TOA}$  was found to be about 10–14° higher than  $T_s$  (DSC). Subsequent polymer/polymer blend studies<sup>22–24</sup> disclosed  $T_{TOA} - T_s$  (DSC) to be as great as 20°, but the 10–14° difference was more commonly observed. The breadth of the glass transition is somewhat greater in compatible polymer/polymer blends than in polymer/low-molecular-weight-plasticizer blends. In the present study  $T_{TOA} - T_s$  (DSC) values lie in the 2.7–8.9° range for first heat PC/HMBP films, 2.7–9.5° range for first heat PC/HOBP films and 6.0–11.1° range for first heat PC/HDBP films. The  $T_{TOA} - T_g$  (DSC) differences for these films are -1.5–2.1°, -0.6–4.8°, and 3.3–6.5°, respectively. Similar comparisons can be made for  $T_{TOA}$  with  $T_s$  (DSC) and  $T_g$  (DSC) second heat values. The differences are slightly greater than in the comparisons with the DSC first heat values.

$T_{TOA}$  correlates best with  $T_f$  (DSC). Examination of Table IB and Table V reveals very good correspondence of these characteristic temperatures. The final disappearance of the stress/strain-induced birefringence in the scratched films coincides with the completion of the specific heat increase in the transition. This indicates a one-to-one relation between the polymer chain motions, giving rise to stress relaxation and to the increased specific heat of the nonglassy polymer. Future examination of this relation should employ DSC and TOA measurements on films having identical preparation and thermal histories.

The thermo-optical transition temperatures may be fitted to the Fox relation form [eq. (4)] to give

$$\text{HMBP: } 1/T_{TOA} = 0.002398 + 0.00290w_2 \quad (5)$$

$$\text{HOBP: } 1/T_{TOA} = 0.002380 + 0.00293w_2 \quad (6)$$

$$\text{HDBP: } 1/T_{TOA} = 0.002358 + 0.00298w_2 \quad (7)$$

As was noted in the fit of  $T_g$  (DSC) data (Table IIIB) the Fox relation gives a moderately good fit at finite  $w_2$ , but some underestimate of the characteristic temperature at  $w_2 = 0$ . The present study has established relations for glass transition temperatures and thermo-optical transition temperatures as functions of composition for three polycarbonate/UV stabilizer systems. Application of

TABLE V  
Thermo-optical Data on PC/UV Stabilizer Blend Films (10°/min)

$w$	$T$ (°C)		
	$T_g$ (TOA)	$T_{med}$ (TOA)	$T_{TOA}$
<u>HMBP<sup>a</sup></u>			
0.02	128.6	130.7	134.1
0.04	121.4	123.8	125.8
0.06	111.2	112.8	114.7
0.08	102.2	104.6	106.9
0.10	93.8	95.1	96.7
0.12	81.2	86.2	92.8
<u>HOBP<sup>b</sup></u>			
0.00	144.2	146.1	148.5
0.02	133.9	135.5	137.5
0.04	119.3	122.3	125.0
0.06	111.8	114.7	117.2
0.08	104.7	106.5	109.2
0.10	93.0	97.2	101.8
0.12	85.9	89.4	93.2
<u>HDBP<sup>c</sup></u>			
0.00	148.3	150.0	152.3
0.02	133.2	136.7	140.1
0.04	124.7	126.8	129.7
0.06	114.2	116.8	119.5
0.08	104.8	108.5	112.3
0.10	95.4	99.4	103.7
0.12	86.9	91.0	95.2

<sup>a</sup> 27 days after film formation.

<sup>b</sup> 28 days after film formation.

<sup>c</sup> 28 days after film formation.

scratch hardness test techniques has permitted refinement and control of the TOA birefringent scratch formation. During constant rate heating the temperature at which the specific heat transition is completed has been found to coincide with the temperature at which stress/strain-induced birefringence disappears.

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