Naval Research. J.B. and D.C.B. thank BP for permission to publish this paper.

Registry No. Na, 7440-23-5; K, 7440-09-7; poly(1,2-ethenediyl), 26571-64-2.

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The Role of Oxygen in the Photoaging of Bisphenol A Polycarbonate. 2.[†] GC/GC/High-Resolution MS Analysis of Florida-Weathered Polycarbonate

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ABSTRACT: Use of GC/GC/high-resolution mass spectrometry to analyze the $LiAlH_4$ and $LiAlD_4$ reductive cleavage products from a 4-year Florida-aged sample of non-UV-stabilized bisphenol A polycarbonate has confirmed the presence of small amounts of photo-Fries and ring oxidation products along with large amounts of side-chain oxidation products. These results are consistent with a photoaging mechanism in which side-chain and ring photooxidation are initiated by a photo-Fries process and colored photoproducts are derived primarily from ring oxidation.

Introduction

When non-UV-stabilized bisphenol A polycarbonate is exposed outdoors for several years, its surface is observed to become yellow and show evidence of cross-linking, pitting, and cracking. Most early investigations[1-8] on the photoaging of bisphenol A polycarbonate suggested that the key mechanism in this phenomenon is the photo-Fries reaction (Scheme I). More recent work,[9-16] however, indicates that under the influence of longer wavelengths of light—such as experienced during outdoor exposure—photooxidation (Scheme II) is the predominant reaction pathway. In addition, work by Lemaire[13,14] demonstrated that photo-Fries products are themselves easily photooxidized, making it difficult to find evidence of the photo-Fries pathway.

Although the evidence has been less rigorous, ring oxidation has been shown to play a role in the photoaging of bisphenol A polycarbonate. For example, ESCA studies of resin photooxidized under both sunlight ($\lambda > 300$ nm)[11] and Hg arc light ($\lambda > 280$ nm)[10,12] show a decrease of the $\pi \rightarrow \pi$ shake-up ESCA satellite, indicating the loss of aromatic groups. Quantitative FTIR analyses of laser-induced polycarbonate photodegradation[16] indicate a depletion of main-chain aromatic groups and suggest an increase in ring substitution. Oxygen uptake experiments[9] indicate the absorption of up to 12 mol of O_2 per monomer unit and the evolution of 4.6–7.7 mol of $CO + CO_2$ per monomer unit during the photooxidation of thin polymer films using different light sources. These high values cannot be explained by side-chain oxidation and carbonate group hydrolysis alone and indicate that ring oxidation is also occurring. Finally, both outdoor and artificial weathering experiments of the side-chain-free poly-

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[†] The paper cited in ref 9 is considered to be part 1 of this series.

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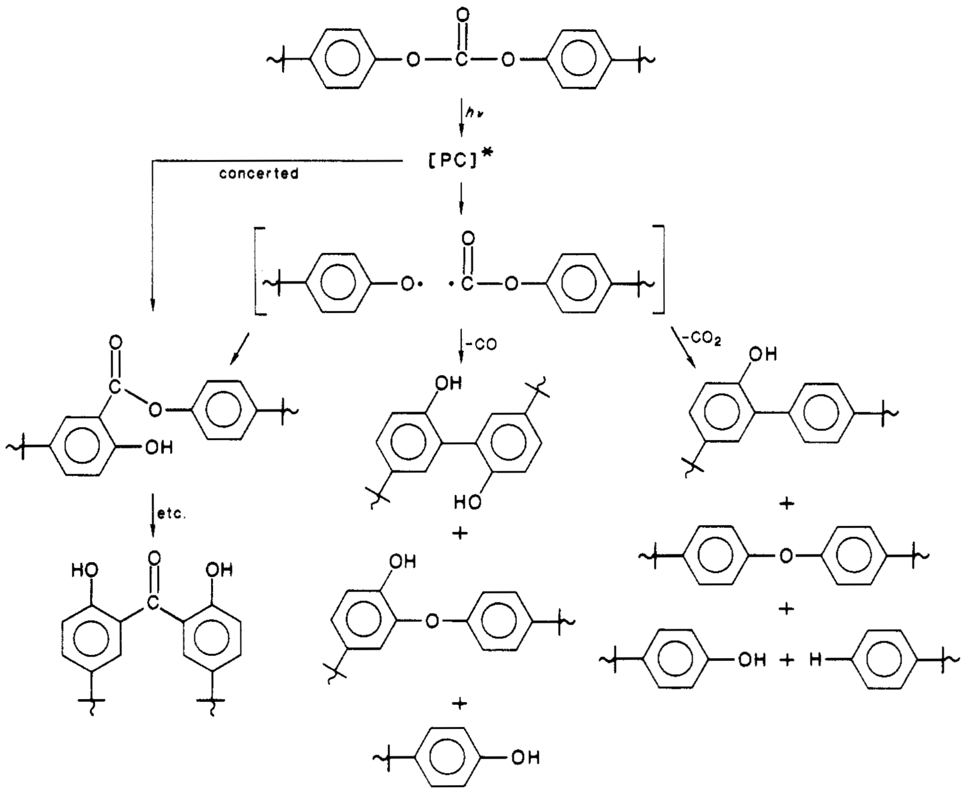
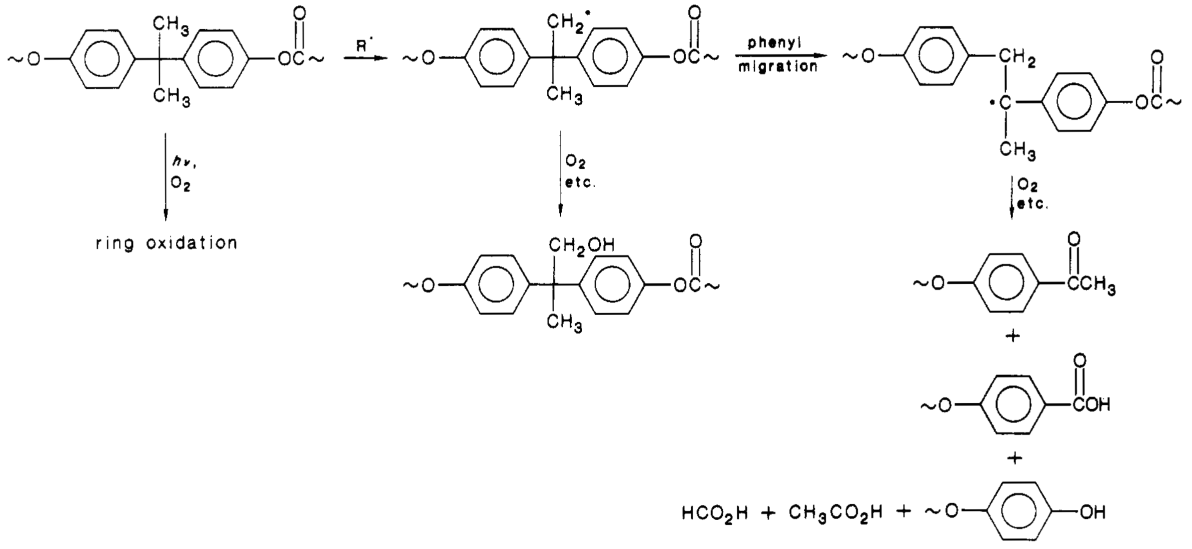
Scheme I
Photo-Fries Pathway



Scheme II
Photooxidative Pathway[a]



[a] Also produced: hydroperoxides, esters, anhydrides, CO_2, CO, H_2, and H_2O.

carbonate made from bis(3-hydroxyphenyl) ether (*m*-BPO PC) demonstrated that it photoyellowed approximately 3 times faster than the bisphenol A polycarbonate.[17] This indicates that, at least in the case of *m*-BPO PC, ring oxidation is the source of photoyellowing and suggests that ring oxidation probably plays an important role in the photoyellowing of bisphenol A polycarbonate as well.

While the above work has done much to explain the origins of the photoaging of bisphenol A polycarbonate, a number of important questions remain unanswered, such as the identity of the yellow photoproducts, the nature of the cross-linking reactions, and the relative importance of side chain vs. ring oxidation. In an effort to clarify these points, an in-depth analytical study was made of a photoaged, non-UV-stabilized commercial sample of bisphenol A polycarbonate using GC/GC/high-resolution mass spectrometry (GC/GC/Hi-Res MS).

Experimental Section

Materials. The bisphenol A polycarbonate sample used in this study was a non-UV-stabilized Lexan 101-112 grade polycarbonate (Lexan is a registered trademark of the General Electric Co.) in the form of a 4 × $^1/_8$ in. molded disk which had been weathered 4 years in Florida. The resin had an $[\eta]$ of 0.57 dL/g ($CHCl_3$), was end-capped with phenol, and contained 0.1 wt % of a phosphite/epoxy heat stabilizer system. Samples of the photoaged surface were isolated by manually scraping the yellowed surface with a curved scalpel to obtain thin (~10 μm) yellow shavings of polymer. A sample of resin cut from the interior of the disk was used as an unweathered control.

Tetrahydrofuran (Burdick & Jackson Lab, Inc., LC Grade) was purified and dried by distilling it under nitrogen with sufficient sodium (40% dispersion in mineral oil sold by Alfa Products) to form a blue complex with benzophenone. GC/MS analysis and UV spectroscopy indicated that the resulting distillate was pure except for the presence of a trace of benzene.

Lithium aluminum hydride (LAH), 95$^+$% purity, and **lithium aluminum deuteride** (LAD), 98 atom % D, were purchased from the Aldrich Chemical Co.

5-(α,α-Dimethyl-*p*-hydroxybenzyl)salicylic acid (*o*-carboxybisphenol A) was purchased from the Aldrich Chemical Co. (Catalog no. 14,9098) as were Gold Label grade samples of *o*- and *p*-cresol.

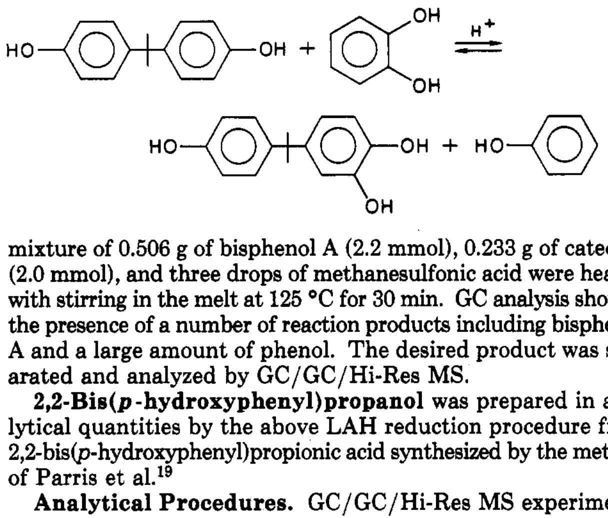
Reductive Hydrolysis Procedure. Theoretically 3 mol of LAH are required to reductively cleave 4 mol of an aromatic carbonate as shown in eq 1. In practice, an ~4-fold excess of

$$3\mathrm{LiAlH_4} + 4\mathrm{ArOC({=}O)OAr} \xrightarrow{\mathrm{THF}} \xrightarrow[\mathrm{workup}]{\mathrm{H_2O}} 4\mathrm{CH_3OH} + 3\mathrm{Al(OH)_3} + 3\mathrm{LiOAr} + 5\mathrm{HOAr} \qquad (1)$$

LAH (or LAD) was utilized to compensate for the presence of adventitious H_2O. Typically ~30 mg of polycarbonate (0.12 mmol) and ~20 mg of LAH (0.53 mmol) in 2 mL of dry, purified THF were magnetically stirred overnight in a closed 2-dram vial to form a thick white paste. The product was worked up by first adding 20 μL of distilled H_2O (1.11 mmol) to the stirred slurry, followed by the addition of several small pieces of dry ice to neutralize the reaction products. Finally, in order to remove the metal salts from the product mixture, the resulting slurry was filtered through a small plug of silica gel in a glass pipette, eluted with dry methanol, and evaporated with a stream of nitrogen. The trimethylsilyl derivatives of the resulting products were prepared by treating the evaporated solutions with *N*,*O*-bis(trimethylsilyl)trifluoroacetamide.

The presence of methanol in the reaction product was confirmed by ^{1}H NMR and GC in a 1-g scale-up of the above procedure. This same reductive procedure was used to prepare samples of model compounds for analysis.

2-(4-Hydroxyphenyl)-2-(3,4-dihydroxyphenyl)propane was prepared by the transalkylation method of Mark,[18] eq 2. A mixture of 0.506 g of bisphenol A (2.2 mmol), 0.233 g of catechol (2.0 mmol), and three drops of methanesulfonic acid were heated with stirring in the melt at 125 °C for 30 min. GC analysis showed the presence of a number of reaction products including bisphenol A and a large amount of phenol. The desired product was separated and analyzed by GC/GC/Hi-Res MS.



(2)

2,2-Bis(*p*-hydroxyphenyl)propanol was prepared in analytical quantities by the above LAH reduction procedure from 2,2-bis(*p*-hydroxyphenyl)propionic acid synthesized by the method of Parris et al.[19]

Analytical Procedures. GC/GC/Hi-Res MS experiments were performed by using a Vg Analytical ZAB mass spectrometer system, which has been described in detail previously.[20] For the current work, the first stage of GC separation was accomplished using a 10-ft × 2-mm i.d. GC column packed with 3% OV1 on 100/120 mesh Gas Chrom Q (Applied Science Laboratories). Samples of about 2-μL volume (50% solids in *N*,*N*-bis(trimethylsilyl)trifluoroacetamide (BSTFA)) were injected at a column temperature of 70 °C, and the column was then temperature programmed from 70 to 290 °C at 10 °C per minute. Ten percent of the effluent from the primary column was split to a flame ionization detector (FID). A typical primary chromatogram obtained in this way is presented as Figure 1. With reference to the primary chromatogram, both the solvent peak and the vast majority of the BPA peak were vented from the instrument, while the rest of the column effluent was diverted to a cold trap and then reinjected onto a second GC column for further separation.

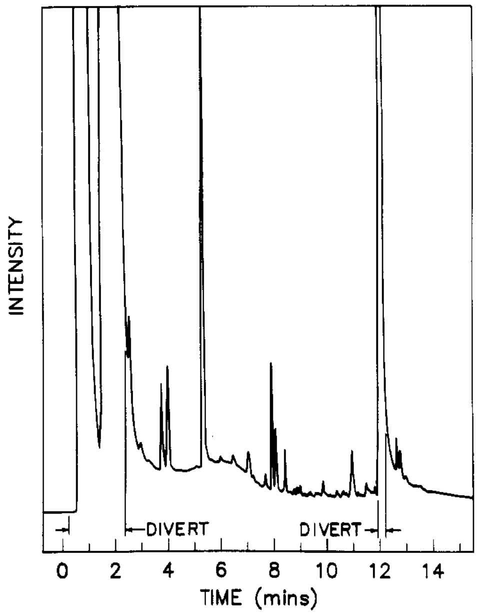


Figure 1. Primary packed column chromatogram of the product mixture showing portions of eluent diverted (vented).

The second stage of GC separation was accomplished by using a J&W Scientific Model DB-1 fused-silica capillary column. The column had a 0.25-μm film thickness and 0.25-mm i.d. The contents of the cold trap were injected at 70 °C, and the oven was temperature programmed from 70 to 290 °C at 8 °C per minute. Both stages of the GC separation utilized helium for the carrier gas. The fused silica capillary was connected directly to the ionization volume of a high-resolution mass spectrometer, and no molecular separator was employed.

The GC interface line temperature was 270 °C and the ion source temperature was 230 °C. The ion source was operated in the electron impact mode at 70-eV electron energy and a trap current of 270 μA. During the course of the secondary chromatogram, mass spectra were acquired continuously at a resolution of 10 000 ($m/\Delta m$, 10% valley definition). Spectra were obtained over the mass range 200–500 amu by using 2.6-s upscans with an interscan delay of 0.4 s. These conditions provided 11 ADC samples per peak at the data system and a mass measurement accuracy consistently better than 2.0 millimass units. Low-resolution mass spectral data ($m/\Delta m$ 1000) were also acquired over the mass range 20–600 amu, which provided the full fragmentation patterns that were used to help make structural assignments. Data were acquired by using a Finnigan-MAT Model 2400C mass spectrometry data system running under SUPERINCOS software. Perfluorokerosene was admitted continuously with the sample to allow high-resolution mass measurement.

Results and Discussion

Reductive cleavage of the photoaged polycarbonate was performed in duplicate by using LAH in one case and LAD in the other. In this way one could both cleave the carbonate linkages in the polymer and isotopically label any carbonyl-containing groups in the resin, cf. eq 3 and 4.

$$\mathrm{RC({=}O)OR'} \xrightarrow[\text{2. } \mathrm{H_2O}]{\text{1. LAD}} \mathrm{RCD_2OH} + \mathrm{HOR'} \qquad (3)$$

$$\mathrm{RC({=}O)R'} \xrightarrow[\text{2. } \mathrm{H_2O}]{\text{1. LAD}} \mathrm{RCD(OH)R'} \qquad (4)$$

Comparison of the masses of the LAH and LAD products provides unambiguous evidence that a product is derived by metal hydride reduction. Thus any compound found to contain two D's (relative to the protic analogue) is derived from a carboxylic acid or ester while those containing one D are derived from a ketone or aldehyde. Furthermore, the use of two duplicate hydride reductions that

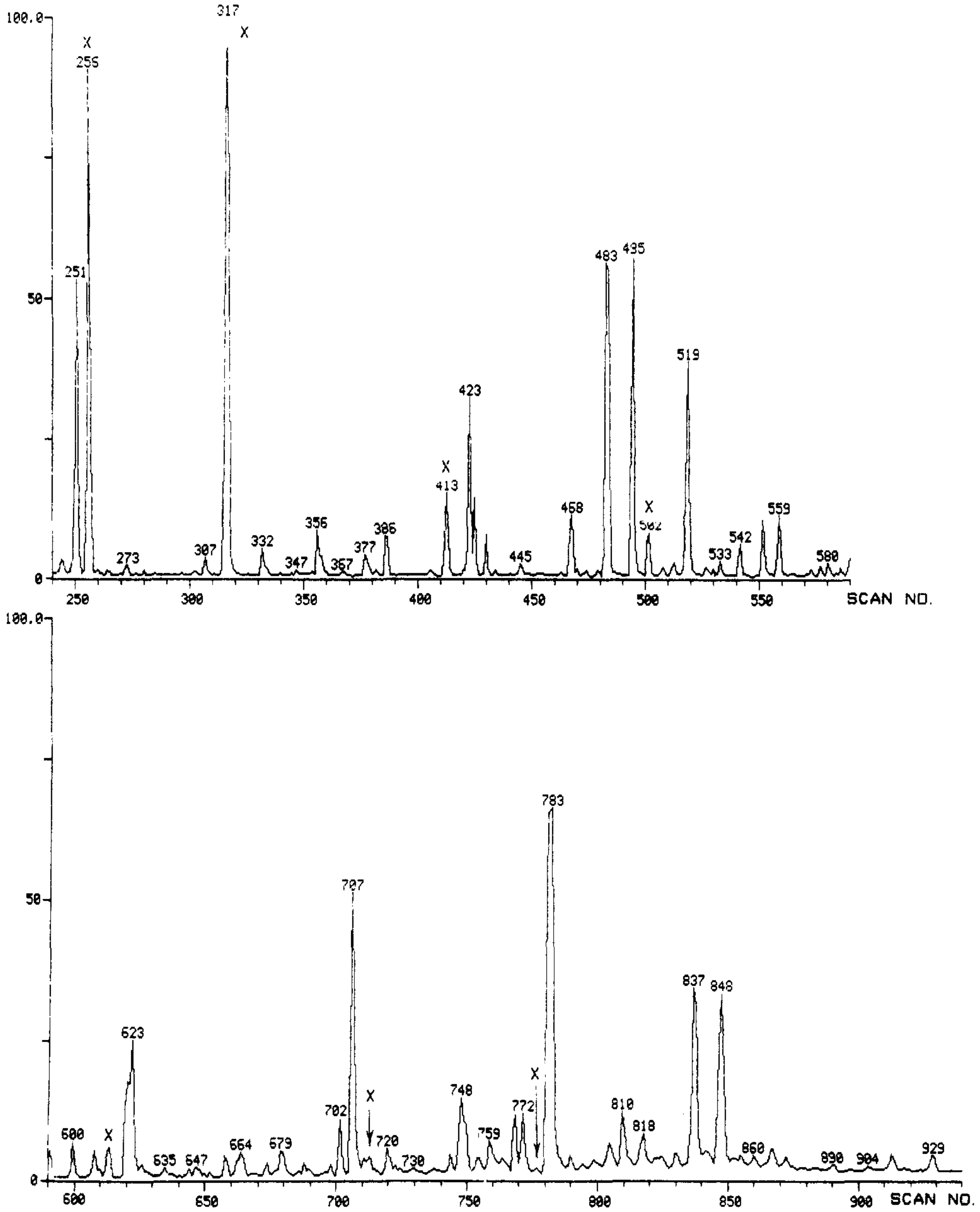
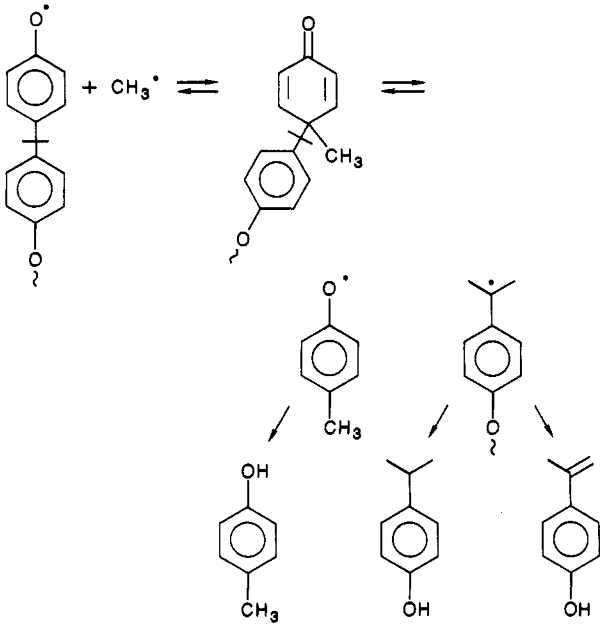


Figure 2. Capillary gas chromatogram of the product mixture. (Peaks labeled X are due to primary column bleeding of stationary phase.)

yield the same products provides increased confidence in the determination.

The capillary GC of the product mixture is shown in Figure 2, and a summary of the high-resolution mass spectral analysis of the peaks in Figure 2 is listed in Table I. Those compounds also present in the control sample are so indicated in Table I. The high-resolution masses reported are for the protic analogues. As can be seen, nearly three dozen products of bisphenol A polycarbonate were identified, most of which had never been previously found. Structural determinations by mass spectrometry are fundamentally limited by the information content of each individual mass spectrum. The information content is itself limited by the degree of fragmentation which in turn is highly structure dependent. In GC/MS experiments, GC retention time may be used to further confirm structure when standards are available. Accordingly, the structural assignments in Table I are associated with varying degrees of confidence as a function of the information available. In those cases where standards or library spectra were available, structural assignments have been made with relatively high confidence. When a molecular ion and abundant fragments were both present, it has often been possible to make very reasonable assignments even in the absence of standards. This was greatly facilitated by the universal application of high-resolution measurements, which provided elemental compositions. However, as is typical for aromatic compounds, many components provided mass spectra consisting only of a molecular ion and few fragments. Such spectra have quite low information content. In such cases, "speculative" structures have been proposed, based solely on elemental composition and on a knowledge of the chemistry involved. Candidate structures have been required to be chemically reasonable, to have obvious pathways to whatever fragments may be observed, and to be free of obvious fragmentation pathways to ions which have *not* been observed. These requirements have been tested by using well-known principles of organic mass spectrometry and with reference to the spectra of other related substances in the sample for which standards are available. In those cases where standards existed, we have also routinely established that the gas chromatographic retention times agree. If standards were unavailable and not easily synthesized, we have required that proposed structures have retention times which are generally consistent with the retention times found for related known substances. Nevertheless, in spite of these tests, many of the structures must remain genuinely speculative until they can be confirmed by other spectroscopic data or by the preparation of additional synthetic standards.

Along with each structural designation, an attempt was made to assign the mechanistic pathway by which each compound was formed, i.e., ring oxidation (RO), ring attack (RA), side-chain oxidation (SCO), and photo-Fries (PF) (see Schemes I and II). The ring attack pathway has previously not been considered important but appears necessary to explain the formation of several of the alkylated phenols identified, e.g., eq. 5. A similar mechanism has been postulated to explain the formation of 2,6-dimethylphenol and 2,4,6-trimethylphenol during the pyrolysis of poly(2,6-dimethyl-1,4-phenylene) ether.[21]

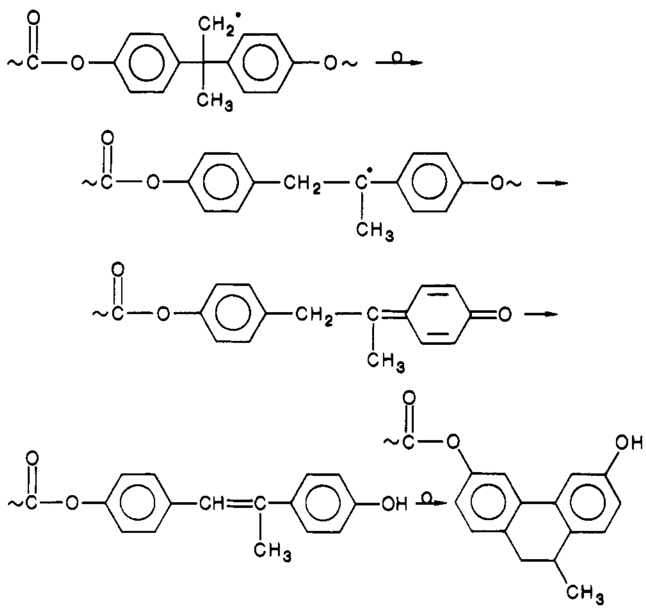


(5)

Overall, the results shown not only confirm the previous work showing the importance of side-chain oxidation in outdoor aged bisphenol A polycarbonate[9,10,13] but, for the first time, present hard evidence for the occurrence of the photo-Fries and ring oxidation during natural weathering. For example, the formation of the compounds analyzed in scans 664, 818, and 867 are best rationalized as being formed via a photo-Fries reaction, while compounds analyzed in scans 559, 608a, 608b, 658, 707, 713, 744, 830, 837a, 837c, and 872 are best explained by a ring oxidation pathway. Admittedly, many of the structural assignments made of these products are only speculative (and are so indicated), especially those compounds we propose as arising from ring oxidation. Nonetheless, a number of assignments have been confirmed by comparison with authentic samples, e.g., compounds corresponding to scans 837a, 848, and 867.

The occurrence of ring oxidation best explains the yellow discoloration that always occurs during the photooxidation of bisphenol A polycarbonate. While specific darkly colored compounds have not as yet been identified, the empirical formulas obtained for many of these "ring oxidation" products indicate the presence of a high degree of reactive unsaturated groups that could be easily oxidized to colored products. In addition, multi-hydroxylated benzene systems, such as the catechol derivative of scan 837a, are quite prone to further oxidation to darkly colored products.

Scheme III
Potential Identity and Source of $C_{21}H_{30}O_2Si_2$



It is well-known that the photolysis of bisphenol A polycarbonate in the absence of oxygen also leads to colored products.[3,10,15] The extent of this photoyellowing is dependent on the wavelength of light used and at shorter wavelength ($\lambda < 314$ nm) can be greater than in the presence of oxygen.[15] The chemistry of this anaerobic color formation is only partially known but appears to be mainly due to the formation of colored photo-Fries products, e.g., dihydroxybenzophenone and diphenoquinones derived from phenoxy coupling products[6] (see Scheme I). Since our present results indicate that, at the longer wavelengths experienced in outdoor weathering, the concentrations of products from photooxidation far outweight those from the photo-Fries reaction, it seems unlikely that anaerobic photoyellowing processes play an important role in polycarbonate outdoor photoyellowing. Nonetheless, in order to confirm this, we are currently exposing polycarbonates samples to sunlight under aerobic and anaerobic conditions.

The finding of compounds that are best explained by a photo-Fries pathway is of particular mechanistic interest. Previously, we postulated[9] that the photo-Fries reaction, while not a major pathway in the outdoor aging of bisphenol A polycarbonate, is a key source of initiating radicals during the early stages of the reaction before the concentration of more photoreactive products becomes significant. The fact that evidence for the occurrence of the photo-Fries process was not previously found in outdoor aged samples[9,11,15] can be explained by the work of Lemaire,[13,14] who demonstrated that photo-Fries products, if formed, were themselves easily photodegraded. Thus, the finding of trace amounts of these products is in accord with the radical initiator role of this reaction in the early stages of bisphenol A polycarbonate weathering.

An intriguing and not unreasonable structural assignment for the compound analyzed in scan 872 is the silylated derivative of 4,4′-dihydroxy-α-methylstilbene or its 3,6-dihydroxymethylphenanthrene rearrangement product. This would support the proposal by Pryde[15] that this stilbene structure is responsible for the appearance of an ~320-nm band in the UV spectra of bisphenol A polycarbonates that had been irradiated with light of wavelengths greater than 337 nm as illustrated in Schemes II and III.

Table I
High-Resolution Mass Spectral Results from Weathered Bisphenol A Polycarbonate

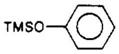
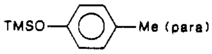
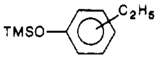
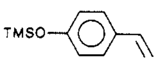
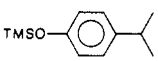
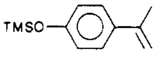
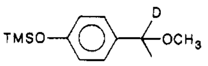
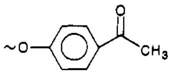
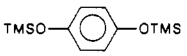
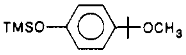
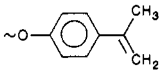
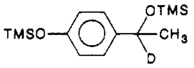
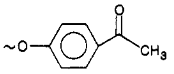
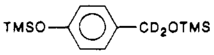
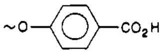
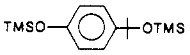
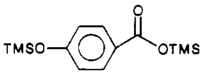
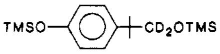
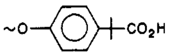
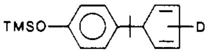
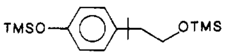
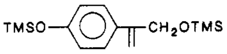
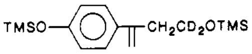
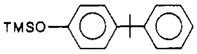
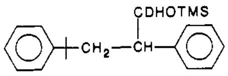
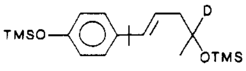
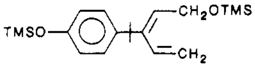
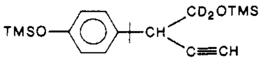
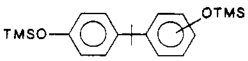
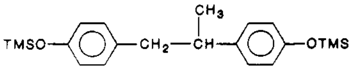
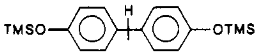
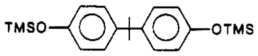
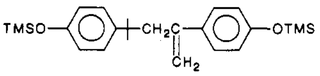
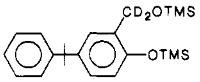
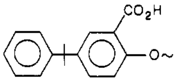
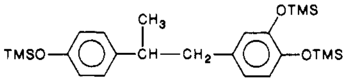
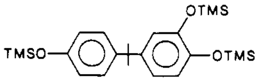
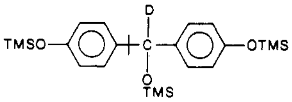
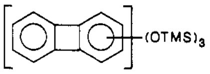
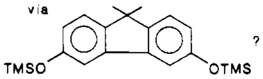
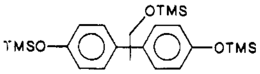
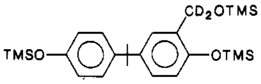
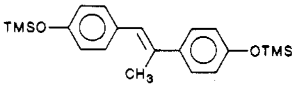
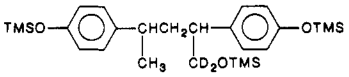
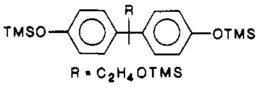
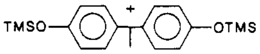
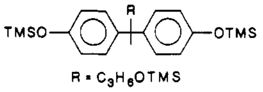
scan[a]	most abundant MS peaks[b]	parent mass ($M^{\bullet +}$)	parent peak hi-res formula[a]	rel yield[d]	struct assignment[e]	likely formatn path	probable source/comments
250[h]	(low res)	166	$C_9H_{14}OSi$	high			end cap
307	(low res)	180	$C_{10}H_{16}OSi$	low		RA	matches authentic sample
356	(low res)	194	$C_{11}H_{18}OSi$	low		SCO	
377	(low res)	192	$C_{11}H_{16}OSi$	low		SCO	
386	208	208.1288	$C_{12}H_{20}OSi$	low		RA	
423a[h]	206	206.1122	$C_{12}H_{18}OSi$	high		RA	
423b	209,224	224.1230	$C_{12}H_{19}DO_2Si$	med.		SCO	
445	239,254	254.1154	$C_{12}H_{22}O_2Si_2$	low		SCO	
468	223, 206, 207, 238	238.1404	$C_{13}H_{22}O_2Si$	med.		RA	
483	267, 282, 251	282.1977	$C_{14}H_{25}DO_2Si_2$	high		SCO	
495	268, 267, 253, 223, 237	268.1322	$C_{13}H_{22}D_2O_2Si_2$	high		SCO	
519	281, 207, 206, 296, 265	296.1597	$C_{15}H_{28}O_2Si_2$	high		SCO	
552	267, 223, 282	282.1102	$C_{13}H_{22}O_3Si_2$	med.		SCO	incomplete redctn
559	207, 223, 295, 310	310.1770	$C_{16}H_{28}D_2O_2Si_2$	med.		RO	
608a	207, 257, 272, 213	272.1610	$C_{17}H_{23}DOSi$	low		RO	speculative assignment
608b	207, 324, 223, 253, 309	324.1953	$C_{17}H_{32}O_2Si_2$	low		RO	speculative assignment
623	281, 294, 206, 265	294.1461	$C_{15}H_{26}O_2Si_2$	med.		FF	prob. a mixture, speculative assignment
658	308, 293, 219, 267	308.1631	$C_{16}H_{26}D_2O_2Si_2$	low		RO	speculative assignment
664	269, 284	284.1573	$C_{18}H_{24}OSi$	low		SCO	
679	207, 205, 309, 233	324.1909	($C_{21}H_{27}DOSi$)[g]	low		SCO	likely from IPP dimer impurity
707	231, 246, 257, 319, 272, 347, 362, 335, 219, 207	362.2087	$C_{20}H_{33}DO_2Si_2$	high		RO	speculative assignment
713	207, 231, 362, 244	362.2079	$C_{20}H_{34}O_2Si_2$	low		RO	speculative assignment
744	207, 348, 267, 245	348.1957	$C_{19}H_{30}D_2O_2Si_2$	low		RO	speculative assignment
748[h]	207, 358, 372, 334	372.1935	$C_{21}H_{32}O_2Si_2$	med.			*o,p*-BPA, also found in blank
759a	357, 372, 344, 267	372.1941	$C_{21}H_{32}O_2Si_2$	low		SCO	speculative assignment

Table I (Continued)

scan[a]	most abundant MS peaks[b]	parent mass (M$^{\bullet+}$)	parent peak hi-res formula[a]	rel yield[d]	struct assignment[e]	likely formatn path	probable source/comments
759b	343, 358	358.1741	$C_{20}H_{30}O_2Si_2$	low		SCO	
783[h]	357, 372, 207, 341, 387	372.1931	$C_{21}H_{32}O_2Si_2$	high			residual BPA
810[h]	397, 207, 348, 412, 231	412.2258	$C_{24}H_{36}O_2Si_2$	low			IPP dimer also found in blank
818	371, 267, 207, 386, 297	386.2090	$C_{22}H_{32}D_2O_2Si_2$	low		PF	
830	445, 460, 207, 370, 223	460.2278	$C_{24}H_{40}O_3Si_3$	low		RO, SCO	speculative assignment
837a	445, 460, 279, 429, 295	460.2277	$C_{24}H_{40}O_3Si_3$	high		RO	matches authentic sample
837b	279, 207, 223, 473, 488	488.2588	$C_{26}H_{43}DO_3Si_3$	low		SCO	via IPP dimer
837c	386, 371	386.1733	$C_{21}H_{30}O_3Si_3$	low		RO	via  ?
848	357, 281, 341, 371, 445, 460	460.2285	$C_{24}H_{40}O_3Si_3$	high		SCO	matches authentic sample
867	459, 207, 281, 267, 474	474.2439	$C_{25}H_{40}D_2O_3Si_3$	low		PF	matches authentic sample
872	370	370.1769	$C_{21}H_{30}O_2Si_2$	low		SCO	speculative assignment
904	473, 488	488.2594	$C_{26}H_{42}D_2O_3Si_3$	low		SCO	speculative assignment from IPP dimer
913	357, 223, 398, 474, 459	474.2446	$C_{25}H_{42}O_3Si_3$	low		SCO	357 strongest peak due to 
929a	357, 223, 343, 488	488.2609	$C_{26}H_{44}O_3Si_3$	low		SCO	
929b	487, 502	502.2764	$C_{27}H_{46}O_3Si_3$	low			

[a] GC peaks due to more than a single component are designated by a, b, c, etc. [b] In the cases of spectra with >200-amu peaks, only >200-amu peaks are reported. [c] If the peak from LAD treatment contains D, then the D-containing empirical formula is given. [d] Key: high (>50% of peak 495), medium (20–49% of peak 495), low (<20% of peak 495). [e] Structures assigned by correspondence of MS with that in computer library and/or logical deduction from MS fragmentation pattern and most likely pathways of formation. TMS corresponds to a trimethylsilyl group. [f] Key: RO, ring oxidation; RA, ring attack; SCO, side-chain oxidation; PF, Photo-Fries. [g] Determined from parent peak minus 15 Hi-Res measurement. [h] Compound also present in the control obtained from the interior of the photoaged sample.

The combination of a two-stage gas chromatograph with a high-resolution mass spectrometer to obtain elemental compositions for trace and ultratrace components is unique. Such a special technique is required because of the need to have both a large capacity for a major component (BPA) and high gas chromatographic resolution to resolve the complex mixture of photooxidation products. Attempts to carry out this analysis by using a single stage of GC separation fail because only a few hundred nanograms of the major component (bisphenol A) can be injected. Injection of the milligram-size aliquots used here results in completely unacceptable chromatograms due to overloading. This restriction on the quantity of BPA that can be injected effectively places an upper limit on the quantity of each trace impurity which is available for mass spectrometric analysis. As a result, in a single-stage GC analysis, these substances do not reach the mass spectrometer in sufficient quantity to allow high-resolution measurements. Attempts to use only a packed GC system for the separation would fail to provide the gas chromatographic resolution necessary for such a complex mixture. In the technique employed here, the sample is analyzed first on a packed column which allows milligram-size injections. The interfering major component (BPA) is largely vented, and only the minor components are collected and rechromatographed. The second stage of chromatography is performed with a high-resolution capillary so that excellent chromatographic resolution is obtained. Much larger quantities of each impurity reach the mass spectrometer and high-resolution measurements are possible on substances which are present at levels of only about 100 ppm relative to BPA.

A shortcoming of this GC/GC/MS technique involves the potential loss of trace impurities which exactly coelute with BPA and therefore are discarded before the second stage of analysis. This problem can in principle be partly overcome by performing multiple experiments using different liquid phases for the primary separation because, in theory, the same two materials are unlikely to coelute on two different liquid phases. This approach is, of course, not entirely effective. However, it should be noted that the same difficulty is inherent in all of the potentially competing approaches to this analysis such as LC/GC/MS.

Conclusions

Use of GC/GC/high-resolution mass spectrometry to analyze the $LiAlH_4$ and $LiAlD_4$ reductive cleavage products from a 4-year Florida-aged sample of non-UV-stabilized bisphenol A polycarbonate has confirmed the presence of small amounts of photo-Fries and ring oxidation products along with large amounts of side-chain oxidation products. These results are consistent with a photoaging mechanism in which side-chain and ring photooxidation are initiated by a photo-Fries process and colored photoproducts are primarily derived from ring oxidation.

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Registry No. BPA PC (SRU), 24936-68-3; BPA PC (homopolymer), 25037-45-0.

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Gas Permeability of a Polystyrene–Polybutadiene Block Copolymer with Oriented Lamellar Domains

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ABSTRACT: Permeability coefficients were measured for several gases in a polystyrene–polybutadiene block copolymer possessing a highly oriented lamellar microstructure. The effective permeability of this material was strongly dependent on the direction of domain orientation in the sample film. Permeation in samples whose lamellae were aligned parallel to the permeation direction was described in terms of a three-phase model which incorporates the permeability of the block copolymer interfacial regions.

The control of gas permeation through polymeric materials is a primary concern in the development of technology for gas separations, packagings, and coatings. New possibilities for permeability regulation are presented by block copolymers,[1] which can combine two (or more) polymer components with different transport properties into a microphase-separated system with advantageous morphological characteristics. Morphological features of block copolymers which may affect gas transport include the small size (ca. 10 nm) and narrow size distribution of domains, the extent and direction of orientation of the domains, a high internal surface/volume ratio, and diffuse interfacial regions which can constitute a significant volume fraction of the material. Fundamental relationships between block copolymer morphology and gas permeation are needed to indicate how changes in the size, shape, and orientation of a block copolymer's microdoamins can be utilized to alter and control its gas permeability and permselectivity.

Few studies of gas transport in block copolymers have been published, and direct measurement of permeability coefficients in these materials has been reported[2,3] only rarely. In addition, virtually all experimental investigations relating gas transport to block copolymer morphology have been conducted by using block copolymers whose domains were randomly oriented[4] or whose orientation was not known or specified.

In this study we examine the permeation of various gases through a polystyrene–polybutadiene block copolymer possessing a well-defined, highly oriented lamellar microstructure. The anisotropic nature of this material allows investigation into the dependence of permeability on the direction of domain orientation. In addition, the relatively simple, well-ordered morphology facilitates the study of

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