

Oxidation of Bisphenol A Polymers

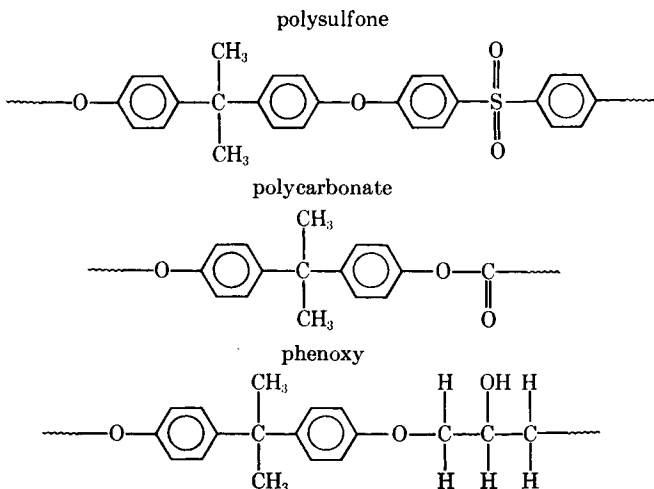
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Synopsis

Polysulfone, polycarbonate, and phenoxy resins were aged under thermal and ultra-violet light conditions. Thermooxidative processes in polysulfone and polycarbonate are of such minor significance as not to impart noticeable losses in these materials below 125°C. In phenoxy, however, thermal oxidation above 100°C results in rapid deterioration of all physical properties. This probably results from the low glass transition temperature of this polymer. Photo-oxidation rapidly degrades polysulfone. This appears to be a consequence of scission at the sulfone link. In polycarbonate, however, the only serious result of short-term irradiation is discoloration. For phenoxy resin, crosslinking through reactions at the hydroxyl group is the principal result of photo-oxidation. In all processes the bisphenol A portion of the three polymers appears to play only a small role.

INTRODUCTION

Three amorphous condensation polymers based on bisphenol A (BPA) (2,2-bis(4-hydroxyphenyl)propane) are of interest to us because they are commercially available and show promise of unusual properties. These polymers are: polysulfone, which is synthesized by reaction of BPA with 4,4'-dichlorodiphenyl sulfone; polycarbonate, prepared by phosgenation of BPA; and phenoxy resin, produced by condensation of BPA with epichlorohydrin.



Work on the degradation of polycarbonate under thermal,^{1,2} ultraviolet light,^{3,4} and high energy irradiation⁵ is extensive. Studies on polysulfone have been restricted to its high-temperature thermal behavior,⁶ although we have recently reported on its degradation in ultraviolet light.⁷ De-

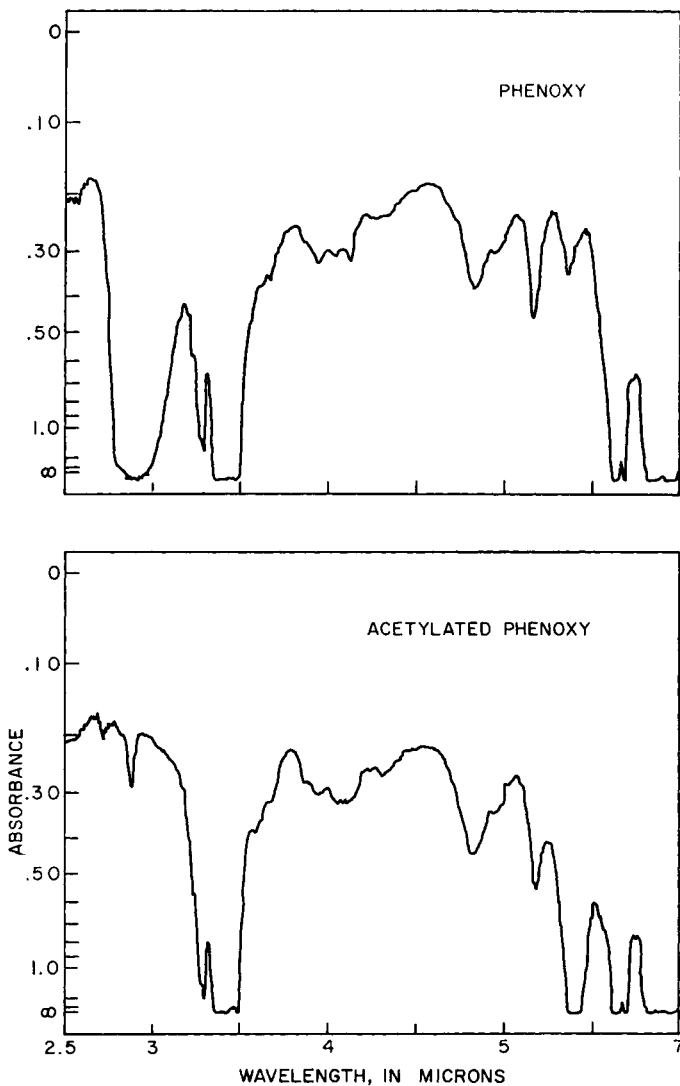


Fig. 1. Infrared spectra of phenoxy and acetylated phenoxy.

scriptions of the degradation of phenoxy have been restricted to ultraviolet light sensitization.⁸ In this report we have summarized our previous work, analyzed some new data, and interpreted the results in terms of the differences in structure of these polymers.

EXPERIMENTAL

Studies were done on commercial plastics, presumed from Soxhlet extraction with methanol to be free of antioxidants. These plastics were cast from chloroform into films 1 mil thick for infrared analysis and 6 mils thick for intrinsic viscosity, gel content, and gas analysis. Infrared spectra were measured on a Beckman IR-8 spectrometer at slow scan (130 $\text{cm}^{-1}/\text{min}$). Intrinsic viscosity measurements were taken with Cannon-Ubbelohde viscometers on chloroform solutions of polysulfone and phenoxy at 25°C and on *p*-dioxane solutions of polycarbonate at 25°C. The constants derived by Wineman⁹ were used to relate intrinsic viscosity of polycarbonate to molecular weight. A Waters Associates model 100 gel permeation chromatograph was used to obtain the weight-average molecular weight data. Gel content was determined by extraction with chloroform in a Soxhlet apparatus. Samples for gas analyses were sealed in quartz break-seal tubes either at 10^{-3} mm Hg pressure or with oxygen at atmospheric pressure. Mass spectrometric analysis of volatiles was done by Gollob Analytical Service, Inc. Elemental analyses of aged samples were performed by the Midwest Microanalytical Laboratory.

Oxygen uptake measurements were done according to the method of Hawkins and co-workers¹⁰ in an all-glass reaction tube on 10-mil compression-molded films. Tensile property measurements were made using an Instron tester on injection-molded type L (ASTM D1822) tensile impact specimens for heat aging and on similarly shaped specimens milled from 10-mil compression-molded film for ultraviolet light aging. Yellowing measurements were made according to ASTM D1925.

The function of the hydroxy group was examined by exposing a 6-mil chloroform-cast phenoxy film for 30 min to an equilibrium vapor concentration of acetyl chloride at 50°C. The treated sample was kept at 50°C for 4 hr in nitrogen at approximately 200 mm pressure to allow reaction of acetyl chloride and evolution of HCl. The recovered sample had an infrared spectrum which was free from hydroxyl absorption and contained intense carbonyl absorption (Fig. 1). This material, after being photo-oxidized, was examined for gel.

RESULTS AND DISCUSSION

Thermal Oxidation

The oxygen uptake test is an effective method for assessing the thermo-oxidative stability of plastics. It is found that for autocatalytic and certain linear processes flexural failure occurs in plastics that have consumed approximately 10 cc of oxygen per gram of material.¹¹ Application of this test for predicting the service lifetime of polymeric materials is particularly reliable when supplemented by other evaluation methods. For instance, criteria for failure are loss in tensile elongation of 50% or the appearance of carbonyl and hydroxyl absorptions in the infrared spectra of suitable materials.

Attesting to its thermal stability, polysulfone absorbed less than 4 cc of oxygen per gram of polymer when held at 140°C for 9000 hr. The oxygen uptake data are reinforced by results of other methods. For example, infrared spectra of polysulfone remain unchanged through 10,000 hr of polymer exposure at 125°C. Furthermore, polysulfone samples retained 75% original elongation after exposures for 17,000 hr at 82°C.

In the same oxygen uptake test, polycarbonate absorbed 10 cc of oxygen in 5500 hr at 140°C. However, extrapolating from an Arrhenius plot to the 70°C normal upper limit Bell System service temperature and without allowing for the dilution of oxygen in air, polycarbonate would retain useful properties for 500,000 hr (approximately 60 yrs). Infrared spectra of polycarbonate remained unchanged through 5000 hr of polymer exposure at 125°C. In addition, polycarbonate test bars retained 91% original elongation after 26,000 hr at 82°C.

Finally, phenoxy in the oxygen uptake test at 140°C absorbed 10 cc of oxygen in less than 300 hr. This value probably overestimates the autocatalytic breakdown point because phenoxy tends to give off a considerable volume of gas in oxygen at 140°C. The most obvious reason for this dramatic change relative to the other BPA polymers is the very low T_g (approximately 98°C) for phenoxy. At 140°C the rubbery condition of the system must allow a much more rapid gas diffusion and consequently a faster consumption of oxygen. A similar situation exists in ABS resins and crystalline polyethylenes where "rubbery phase" oxidation is rapid compared to the rest of these composites.^{10,12} An infrared spectrum of a phenoxy film exposed 5000 hr at 90°C had no significant absorption increase in the carbonyl region (5.6–5.8 μ). However, phenoxy tensile bars retained less than 40% original elongation after less than 2500 hr at 82°C in air. Furthermore, the intrinsic viscosity of these aged samples dropped from an original value of 0.41 dl/g to 0.33 dl/g. A chain scission reaction not involving carbonyl formation must be responsible for the instability of phenoxy resins on thermal oxidation.

The thermal aging data on the three BPA polymers show that polysulfone is unaffected and polycarbonate is serviceable in the 80–140°C temperature range. Both materials rate high among thermoplastics in thermo-oxidative stability, being inferior only to poly(ethylene terephthalate) and fluorinated polymers.¹¹ Phenoxy is poor thermally not only because of its low glass transition temperature, but also because of its marked tendency toward chain scission. In view of the stability of the other BPA polymers, it seems reasonable to identify this behavior with the hydroxy alkyl ether portion of the phenoxy chain.

Photo-Oxidation

The three BPA polymers had maxima in their ultraviolet spectra near 2800 Å. This coincides with the low end of the RS sunlamp ultraviolet spectral energy output¹³ and therefore can be considered responsible for polymer degradation. Tahara,³ for instance, found that irradiation

above 2800 Å caused chain scission in polycarbonate. Our postirradiation inspection, however, showed no gross changes in the ultraviolet spectra of the sol portions of the three BPA polymers. Energy absorption through polymer impurities, particularly those imparting yellow color to these polymers, must also contribute to polymer breakdown processes.

Our attempts to follow the change in the composition of evolved gases from irradiated BPA polymer samples was complicated by the very small volume of secondary gases—methane, ethane, hydrogen, water, and sulfur dioxide—and equilibration of the primary gases—carbon monoxide and dioxide. All polymers evolved carbon monoxide and dioxide, methane, ethane, and hydrogen on irradiation in both oxygen and under vacuum. Phenoxy and polycarbonate gave off water on photo-oxidation and polysulfone emitted sulfur dioxide on vacuum irradiation. The degradation process must therefore involve in each case random bond breaking. The evolution of the oxides of carbon (Table I) varies somewhat from one polymer to the other. We must suppose that there is an equilibration of these oxides favoring carbon monoxide in vacuum and carbon dioxide in oxygen. The results for polycarbonate, then, are consistent in vacuum with a carbonate-bond breaking process followed by evolution of carbon dioxide, and in air with secondary oxidation processes involving the methyl groups and terminating in the expulsion of both oxides from aldehydic and carboxylic degradation products. With polysulfone under vacuum, the relatively

TABLE I
Relative Volumes of CO and CO₂ Evolved from BPA
Polymers Irradiated with RS Sunlamp

Polymer	Exposure condition	Time of irradiation, hr	Relative CO volume	Relative CO ₂ volume
Polycarbonate	vacuum	6	4	11
	"	24	7	17
	"	100	22	46
	O ₂	6	22	34
	"	24	130	90
	"	100	300	940
Polysulfone	vacuum	24	5	4
	"	100	15	9
	"	500	28	18
	O ₂	24	32	36
	"	100	140	220
	"	500	480	1600
Phenoxy	vacuum	6	9	1
	"	24	18	2
	"	100	80	7
	"	1000	420	48
	O ₂	24	150	72
	"	100	360	1500
"	1000	1200	6000	

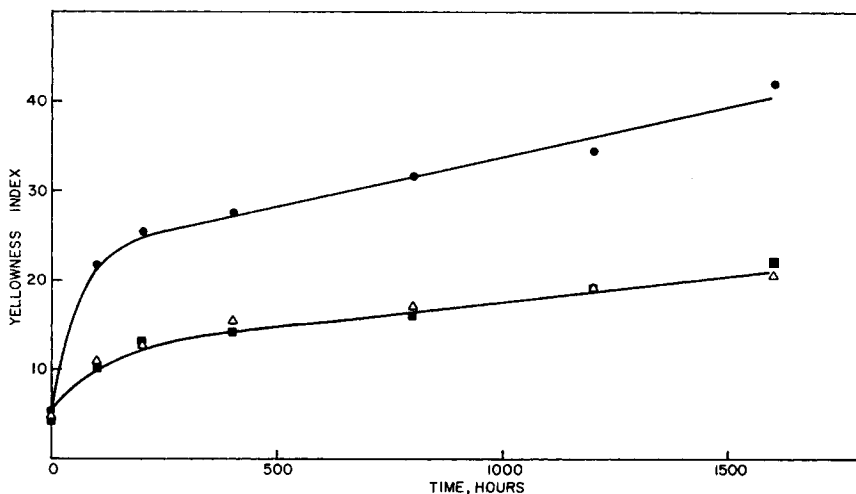
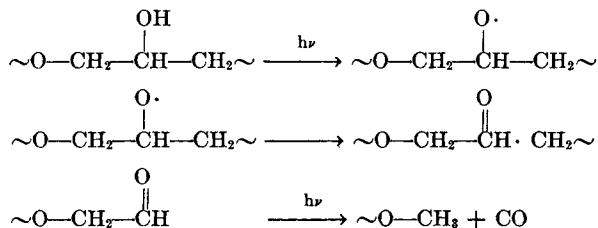


Fig. 2. Photo-oxidative yellowing in the BPA polymers. ●) Polysulfone; ■) phenoxy; Δ) polycarbonate.

small quantity of the carbon oxides isolated indicate that preoxidation of the polymeric sample perhaps in processing provides the aldehydic and carboxylic groups necessary to yield these gases. In oxygen the reaction must be the same as the secondary process for polycarbonate. Phenoxy is characterized by a surprisingly high evolution of carbon monoxide under vacuum. Evidently, the hydroxy alkyl ether portion of the chain readily reverts to a carbon monoxide yielding form, i.e.:



A mechanism of this type is supported by the chain scission observed and the tendency of the polymer to gel to a lesser extent under vacuum. In oxygen, phenoxy tends to favor the secondary process in polycarbonate, but to a greater degree (about a factor of two).

Irradiation of polysulfone in air causes, along with gas evolution, a decrease in molecular weight, consistent with a random chain scission mechanism.⁷ More important, however, is the isolation of a low molecular weight chloroform-insoluble, water-soluble organic material. This product is believed to be a highly oxidized short-chain disulfonic acid⁷ which presumably, because of its mobility and reactivity, contains over 90% of the oxygen absorbed by the total polymer. The deep color of this product certainly contributes to the rapid increase in yellowness of polysulfone

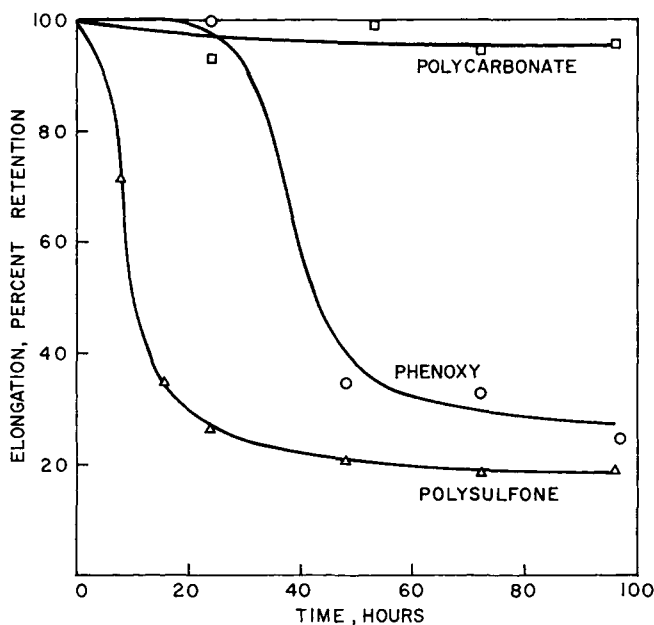


Fig. 3. Effect of photo-oxidation on the elongation of the BPA polymers.

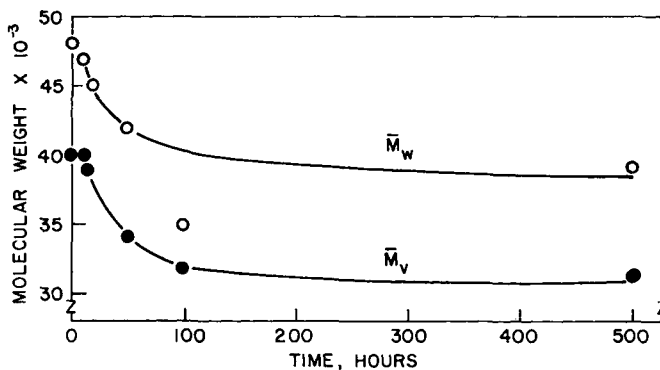


Fig. 4. Effect of photo-oxidation on the molecular weight of polycarbonate.

(Fig. 2) compared to the other BPA polymers. This condition becomes a detriment, particularly where appearance in molded parts, for instance, is a factor. The effect of irradiation on elongation (Fig. 3) for polysulfone is also quite striking. Again the low molecular weight oxidation product must be responsible.

Photo-oxidation of polycarbonate results in a reduction of both viscosity-average and weight-average molecular weights (Fig. 4). The gases evolved indicate that random scission takes place. Just as Tahara³ observed above 2800 Å, irradiation with the RS sunlamp did not produce crosslinking in polycarbonate. Despite the decrease in molecular weight, polycar-

bonate elongation is retained for at least 100 hr (Fig. 3). The amount of carbon dioxide evolved under vacuum indicates that scission takes place predominantly at the carbonate linkage. Degree of yellowing in polycarbonate is lower than in polysulfone by a factor of two and the retention of elongation is at least an order of magnitude better.

Irradiation of phenoxy in oxygen leads to chain scission, as indicated by reduction in intrinsic viscosity, compounded by a rapid crosslinking reaction (Fig. 5). Of the three, phenoxy is the only material that shows cross-link formation under these irradiation conditions. The singularity of this effect excludes the participation of the BPA portion of the chain in the gel-forming reaction. Furthermore, irradiation sufficient to cause a production of 25% gel in the parent polymer was ineffective in forming gel in a

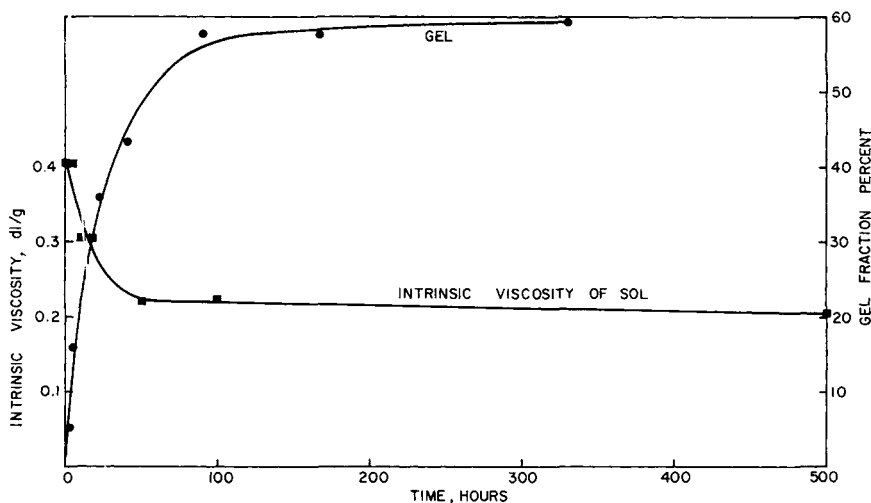


Fig. 5. Effect of photo-oxidation on phenoxy resin.

completely acetylated polymer (Fig. 1). This clearly shows that the hydroxyl group in phenoxy is responsible for the crosslinking reaction. The yellowness index in phenoxy remains essentially the same as that for polycarbonate through 1500 hr of photo-oxidation (Fig. 2). However, rapid decrease in elongation for phenoxy under the same irradiative conditions occurs at least four times sooner than in polycarbonate. This, however, is two times longer than that for polysulfone (Fig. 3).

Photo-oxidation data on the three BPA polymers indicate surprisingly that polycarbonate, aside from its tendency to yellow, is quite able to retain its physical properties through proportionately long exposure times. The stability difference toward RS irradiation between polycarbonate and the more aromatic polysulfone is in the opposite direction to the finding of Krasnansky and co-workers¹⁴ that ionizing radiation stability increases with increases in aromatic content. The sulfone linkage is probably the key to the instability of polysulfone which, from appearance and property

retention, is the poorest of the three. Phenoxy probably has poor retention of physical properties with irradiation because of the hydroxyl group.

CONCLUSION

Thermal oxidation experiments show that in terms of the test conducted, polysulfone, for all practical purposes, remains unaffected, while polycarbonate is very slowly affected in exposure at or below 140°C. Phenoxy resin, on the other hand, is rapidly degraded, probably because of its relatively low glass transition temperature.

In photo-oxidation, the behavior of these materials relative to one another is significantly different than that in thermal oxidation. Polysulfone, for instance, degrades most rapidly in appearance and in physical properties. Polycarbonate does degrade but is the least affected in this group under our photo-oxidative conditions. Phenoxy loses physical properties rapidly under irradiation, probably because of the tendency for the hydroxyl group to engage in oxidative crosslinking. Yellowing of the material, however, in this series is moderate.

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References

1. A. Davis and J. H. Golden, *J. Chem. Soc. (B)*, 45 (1968).
2. J. Kammermaier, *Kolloid-Z. u. Z. Polym.* **224**, 128 (1967).
3. S. Tahara, *Chem. High Polym. (Japan)*, **23** (253), 303 (1966).
4. T. J. Gedemer, *Appl. Spectrosc.*, **5**, 141 (1965).
5. J. H. Golden and E. A. Hazell, *J. Polym. Sci. A*, **1**, 1671 (1963).
6. W. F. Hale, A. G. Farnham, R. N. Johnson, and R. A. Clendinning, Paper presented at the American Chemical Society, Polymer Division, New York, N.Y., September 1966, *Polymer Preprints*, **7**, 503 (1966).
7. B. D. Gesner and P. G. Kelleher, *J. Appl. Polym. Sci.*, **12**, 1199 (1968).
8. P. G. Kelleher and B. D. Gesner, *J. Appl. Polym. Sci.*, **13**, 9 (1969).
9. P. L. Wineman, in W. F. Christofer and D. W. Fox, eds., *Polycarbonates*, Reinhold, New York, 1962, p. 42.
10. W. L. Hawkins, W. Matreyek, and F. H. Winslow, *J. Polym. Sci.*, **41**, 1 (1959).
11. P. G. Kelleher, *J. Appl. Polym. Sci.*, **10**, 843 (1966).
12. B. D. Gesner, *J. Appl. Polym. Sci.*, **9**, 3701 (1965).
13. R. C. Hirt, R. G. Schmitt, N. D. Searl, and A. P. Sullivan, *J. Opt. Soc. Amer.*, **50**, 706 (1960).
14. V. J. Krasnansky, B. G. Achammer, and M. S. Parker, *SPE Trans.*, **1**, 133 (1961).

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