Weathering of Polystyrene Foam on Exposure in Air and in Seawater

ANTHONY L. ANDRADY* and JAN E. PEGRAM

Research Triangle Institute, P.O. Box 12194, Research Triangle Park, North Carolina 27709

SYNOPSIS

Expanded extruded polystyrene foam was exposed outdoors in air and floating in seawater. The degradation of the materials was determined by ultraviolet spectroscopy, gel permeation chromatography, and measurement of yellowness, viscosity, and tensile properties. The samples underwent extensive yellowing, reduction in average molecular weight, and embrittlement in the exposed surface layer. Furthermore, the rate of deterioration was shown to be faster in seawater than in air, possibly due to the removal by the seawater of the outer protective yellow-colored layer formed during early exposure to sunlight.

INTRODUCTION

Weathering and light-induced degradation of polystyrene has been studied by several researchers. Early work has been reviewed by Titus,[1] Priebe,[2] Weir,[3] and more recently, Rabek.[4] In spite of its widespread use, virtually no research is reported on the weathering of polystyrene foam.

Expanded polystyrene in molded or extruded products is widely used in the packaging industry. Consequently, these products are an important component of urban litter as well as municipal solid waste, and their degradation mechanism is therefore of current interest. Polystyrene foam has also been reported as a major constituent of marine plastics debris[5,6] and is reported to be ingested by several species of birds,[7,8] turtles,[9] and other marine animals. While the negative physiological effects of plastics ingestion are not completely known, a growing body of data[10-13] on the subject suggests long-term effects on the animals. Degradation of polystyrene foam is therefore of special interest in view of the recent technical and legislative interest in plastics waste in the marine environment.

A large body of research literature is devoted to understanding the initiation process in polystyrene photodegradation. In-chain peroxides formed during polymerization,[14] main-chain ketone functionalities,[15] polystyrene–oxygen charge transfer complexes,[16] and terminal phenyl alkyl ketone groups[17] have been suggested as possible centers of initiation. Polystyrene itself does not absorb ultraviolet light of wavelength longer than 280 nm.

Another area of interest is the yellowing reaction observed when polystyrene is irradiated with monochromatic light[18] or sunlight.[19] The mechanism of the yellowing reaction caused by ultraviolet radiation remains essentially unresolved, and a variety of chromophores responsible for the phenomenon have been proposed.[20-24] Savides et al.[18] have studied the effectiveness of using commercial antioxidants in controlling the discoloration. They found synergistic effects using benzotriazole type light absorbers and 2,4,6-tri-t-butylphenol antioxidants.

As pointed out by Weir,[3] most previous studies have been concerned with wavelengths not typical of terrestrial sunlight. This severely limits the applicability of the findings to changes that take place in the outdoor weathering of polystyrene. Furthermore, relatively few studies have addressed the phenomenon of yellowing. No data on weathering of polystyrenes under marine conditions have been reported.

The present work is a comparative study of changes in physical and mechanical properties ob-

tained when expanded extruded polystyrene laminates are naturally weathered in air and while floating in seawater.

EXPERIMENTAL

Commercially available expanded extruded polystyrene foam trays (used in retail packaging of meats) were used for the study. Film samples were extruded using Styron 685, a general-purpose polystyrene resin.

Outdoor Exposure

Polystyrene foam samples were exposed at a coastal location in Beaufort, North Carolina. One set of foam samples was stapled on to a wooden platform and exposed horizontally on the roof of a laboratory building. A second set was exposed floating in seawater. Seawater was continuously pumped through a shallow tank at the beach to maintain a water level of 12–18 in. at all times. Floating the samples within the tank minimized accumulation of debris on the samples while providing biologically active fresh seawater. Samples from each set were removed once every 2 months (dried under ambient conditions in the case of wet samples) and stored in the dark under ambient temperature until tested. The monthly mean temperatures and rainfall in the Beaufort area for the duration of exposure (12 months), as reported by the National Weather Service, are as follows:

	1	2	3	4	5	6	7	8	9	10	11	12
Air temperature (°F)	45.9	45.0	51.4	59.4	70.7	72.9	81.1	80.6	66.9	62.3	58.8	49.9
Water temperature (°F)	50.4	49.8	50.5	61.9	72.7	77.0	81.3	79.5	82.4	62.4	61.0	
Rainfall (in.)	7.39	3.57	5.10	3.16	1.10	2.61	4.45	9.53	7.52	2.86	6.34	1.91

Temperature extremes during the exposure period were 40–87°F in seawater and 19–100°F in air.

The film samples were exposed in Miami, Florida (July–October 1988), mounted on standard racks at an angle of 45° facing south.

Yellowness Measurements

Yellowness measurements were made using a Macbeth 1500 colorimeter with an integrating sphere. The specular component of light was excluded and the ultraviolet light included in the measurements. A white ceramic tile was used as the backing material. The ASTM yellowness index was calculated on the basis of the CIE standard illuminant C.

The yellowness index (ASTM D1925-70) was calculated from the tristimulus values X, Y, and Z using the formula

$$\text{Yellowness index} = \frac{100(1.28X - 1.06Z)}{Y}$$

Ultraviolet Spectroscopy

Direct absorbance measurements on the polystyrene films were carried out using a Spectronic 1201 spectrophotometer. Absorbance values were read at 1-nm intervals in the region of large absorbance changes.

Tensile Property Measurements

An Instron tester (model 1122) was used to determine the tensile properties of the polystyrene foam. A gauge length of 4.0 cm and a crosshead speed of 20 mm/min were used. A gauge length of 12.5 cm and a crosshead speed of 10 mm/min were used in the case of polystyrene film samples.

Viscosity Measurements

An Ubbelohde viscometer was used to determine the viscosities of foamed polystyrene samples dissolved in chloroform. The intrinsic viscosity $[\eta]$ in deciliters per gram was calculated using the following equation:

$$[\eta] = (1/c)[2(\eta_s - \ln \eta_r)]^{1/2}$$

where η_r is the relative viscosity, η_s is the specific viscosity, and c is the concentration in g/100 mL.

Gel Permeation Chromatography

A Waters GPC system consisting of a model M6000A pump, a series of five columns, and a model R401 differential refractometer detector was used. Columns were Ultrastyragel with a pore size ranging from 10^6 to 10^2 Å.

Fourier Transform Infrared Spectroscopy

Reflectance spectra for polystyrene foam exposed 8 months in air as well as unexposed were obtained on an Analect FTIR spectrometer model FX-6200.

RESULTS AND DISCUSSION

Polystyrene foam samples exposed outdoors in air underwent rapid yellowing on the exposed surface. Table I gives the values of yellowness indices obtained for the various samples. The b parameter in the L,a,b color coordinate system is positive and the a parameter negative. Both increase with the yellowness index. This indicates increased yellow-green color of the sample as opposed to a mere decrease in lightness being responsible for the observed increase in yellowing with exposure. Yellowing is accompanied by an increase in the absorbance in ultraviolet region of the spectrum of polystyrene. While this effect can be qualitatively observed in reflectance spectra of weathered polystyrene foam, it is clearly seen in absorbance spectra of polystyrene films exposed outdoors (Fig. 1). The data is in agreement with previous observations[25] for polystyrene irradiated at 254 nm. The absorbance at a given

wavelength increases as a function of the duration of exposure.

Yellowing was evidently a surface reaction and was accompanied by eventual embrittlement of the affected layer, allowing it to be easily removed by gentle abrasion. As light penetrates the foam, loss of radiation due to scattering occurs at air–polymer interfaces; it is thus reasonable to expect the direct effects of photoreactions to be confined to the surface in the case of polystyrene foam. However, surface studies on photooxidized polystyrene films also show a high degree of surface reaction not typical of the bulk of reacted polymer, suggesting local surface oxidation to be typical of polystyrene film as well.[26] The yellowness index of the exposed surfaces of foam material increased approximately linearly with the duration of exposure for up to 6 months exposure but thereafter decreased. Davis and Sims[19] report a linear increase in Yellowness with the time of exposure for general-purpose polystyrene exposed in Arizona. The present data for polystyrene foam show a higher degree of yellowing for approximately comparable durations of exposure at a North Carolina location receiving less sunlight than Arizona. Furthermore, the present results also show a decrease in the yellowing during the 6–12-month period of exposure by as much as 20% of the maximum value.

Table I Yellowing, Deterioration, and Changes in Molecular Weight of Polystyrene Foam Exposed Outdoors[a]

| Duration (months) | Color | | | | Thickness of Lower Layer (cm) | | M_n[GPC] $\times 10^3$ | | M_w[GPC] $\times 10^3$ | |
	L	a	b	YI	Seawater	Air	Seawater	Air	Seawater	Air
0	92.7	−0.08	−0.13	−0.01	0.418	0.418	117.3	117.3	241.8	241.8
2	88.57	−2.99	12.59	23.11	0.221	0.349	109.0	102.8	228.7	221.6
	88.29	−3.11	13.01	23.93						
	88.77	−3.13	13.31	24.40						
4	89.04	−3.78	14.99	27.16	0.164	0.308	106.3	91.0	228.0	213.5
	88.33	−3.79	15.60	28.49						
	88.88	−3.74	15.14	27.54						
6	87.23	−3.83	17.26	32.29	0.168	0.234	93.8	78.7	270.7	195.0
	89.18	−3.96	16.24	29.46						
	88.19	−3.73	16.11	29.71						
8	—	—	—	—	0.229	0.217	75.0	71.4	182.6	184.2
10	87.20	−3.50	13.64	25.19	0.155	0.214	58.8	68.0	165.6	171.8
	86.53	−3.30	12.56	23.34						
	87.53	−3.42	13.03	23.93						
12	83.94	−3.03	14.06	27.46	—	0.219	—	63.9	—	160.4
	84.62	−3.03	13.00	25.00						
	84.77	−2.99	13.56	26.17						

[a] Symbols: M_n, number average molecular weight; M_w, weight average molecular weight; YI, yellowness index.
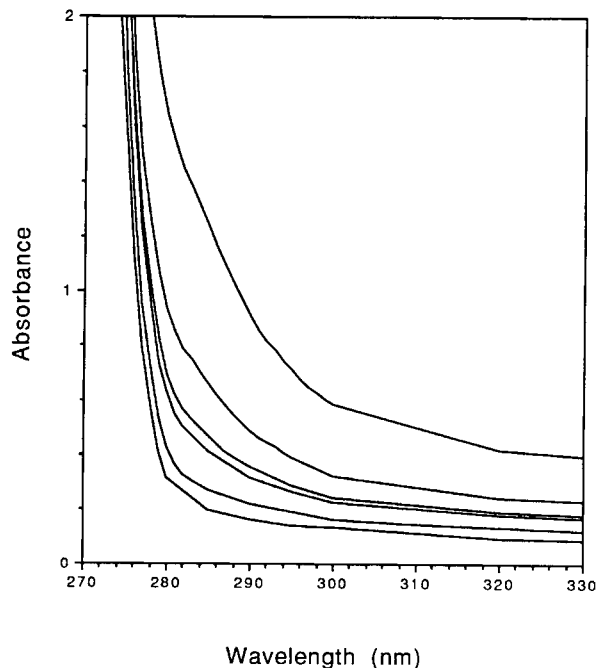
Figure 1   Absorbance spectra of polystyrene films exposed outdoors. Left to right: 0, 1, 3, 5, 7, and 9 weeks of exposure.

Such a decrease was not obtained in the previously reported study[19] and is likely to be obtained with foams only. The decrease is probably a result of the slow loss of the yellowed brittle layer due to rain and wind rather than to a bleaching reaction at longer exposure times. In fact, thickness measurements of the nonembrittled lower layer of exposed samples (shown in Table I) support this view and show the thickness of the sample to decrease with time of exposure until it is reduced by nearly 50% at the end of 1 year.

Yellowness indices of samples exposed floating in seawater could not be conveniently measured due to the extensive surface fouling of the samples. Most surfaces, including plastics, undergo facile fouling[27] when exposed to seawater for even a few weeks. However, it was easy to visually observe yellowing in exposed areas and to remove by gentle abrasion the affected surface layer. The thickness of the remaining nonembrittled layer, presumably unaffected by the light-induced degradation process, decreased more rapidly for samples exposed in seawater than for those exposed in air. The reason for the faster deterioration of polystyrene in seawater is not entirely clear.

However, some fraction of the yellowed surface layer does dissolve in water. Water extracts of the yellowed surface absorb UV light (290–330 nm),

suggesting that this layer might protect the underlying polymer from photodegradation by absorbing the active ultraviolet light. In fact, Tryon and Wall[28] followed the yellowing reaction of polystyrene films by measuring the absorbance at 340 nm. The samples exposed in seawater were possibly protected from photodegradation to a lesser extent than those exposed in air, since the yellowed surface layer is washed away by seawater and abraded off gradually, exposing fresh layers of sample to the radiation. Consequently, the sample in water might be expected to undergo faster degradation relative to that in air. This is consistent with the observation that the embrittled layer obtained at a given duration of exposure tends to be thicker in the case of samples exposed in seawater compared to those exposed in air (Table I).

The FTIR examination of the yellowed surface layer of foam samples revealed extensive changes in functional groups at the surface during outdoor exposure. Figure 2 shows a difference spectrum (top spectrum) obtained from unexposed material (bottom spectrum) and polystyrene exposed for 8 months in air (middle spectrum) using a scaling
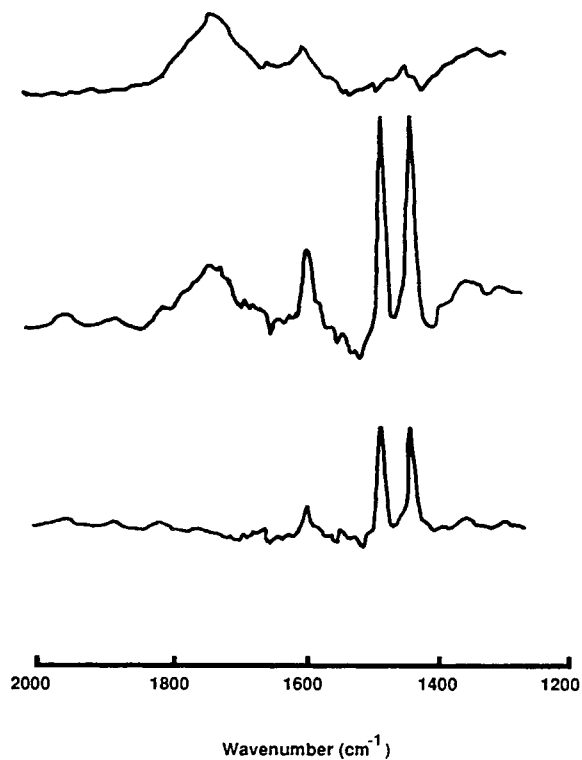

Figure 2   Reflectance FTIR spectra of polystyrene foam. Top to bottom: difference spectrum, exposed 8 months in air, unexposed. Note carbonyl group absorption at 1730 cm⁻¹.

WEATHERING OF POLYSTYRENE FOAM **1593**

factor such that the 1491-cm^{-1} band is set as the baseline value. The spectrum shows the development of two strong absorption bands, one at 1730 cm^{-1} and one at 1600 cm^{-1}, with yellowing. The former is indicative of ketone group formation, which is consistent with general mechanisms of polystyrene oxidation.[29] The band at 1600 cm^{-1} might be due to a C=C group conjugated with a phenyl group or a β diketone structure. The latter has been proposed as a possible end group formed during polystyrene photooxidation.[22] Surprisingly, there was no increase in the bands corresponding to hydroxyl groups, as suggested in the previous work.[23]

A consequence of light-induced degradation in polystyrene foam is the reduction of the average molecular weight of the polymer as a result of photolytic chain scission.[30] Changes in the molecular weight of polystyrene foam as monitored by gel permeation chromatography and solution viscosity are shown in Tables I and II. While the yellowing is mostly restricted to the embrittled surface layer of polystyrene foam, the lower seemingly unaffected layer also undergoes some degradation. The original number average molecular weight of the outer embrittled layer of polystyrene foam was reduced by 86% on exposure outdoors for a 12-month period.

The lower layer lost 45% of the initial number average molecular weight during the same exposure period. Both GPC measurements and viscosity measurements on the lower nonembrittled layer clearly show significant changes in the molecular weight of the material. This is expected in the case of a free-radical degradation process where the radicals can easily "move" about the polymer matrix via hydrogen abstraction.

Figure 3 is based on gel permeation chromatographic determination of number average molecular weights for the two sets of samples exposed in air and in seawater. These determinations were carried out on a lower unembritted layer of samples. Since the rate of change in thickness of the samples is not the same for two conditions of exposure, the comparison implied in the figure is, strictly speaking, not appropriate. Essentially, the number average molecular weight of the embrittled material is regarded as not contributing to the average molecular weight of exposed samples. However, the qualitative features of the analysis are interesting.

In general, for random scission in the absence of concurrent crosslinking the degree of polymerization changes with time according to the following equation for moderate extents of degradation[31]:

Table II Summary of Tensile and Viscosity Data for Polystyrene Foam Exposed Outdoors

Duration (months)	Tensile Strength[a] (kg/cm^2)		Tensile Strength[b] (kg/cm^2)		Intrinsic Viscosity[d]
	Mean	SD[c]	Mean	SD[c]	
Samples Exposed in Air					
0	3.89	0.50	3.89	0.50	0.859
2	4.31	0.34	5.16	0.40	0.778
4	3.46	0.59	4.70	0.80	0.709
6	2.45	0.27	4.37	0.48	0.648
8	2.39	0.27	4.60	0.52	0.637
10	2.61	0.14	5.09	0.27	0.627
12	2.37	0.27	4.53	0.51	0.593
Samples Exposed in Seawater					
2	2.88	0.21	5.45	0.40	0.802
4	1.13	0.71	5.50	1.82	0.766
6	1.09	0.17	3.20	0.44	0.673
8	1.22	0.29	2.22	0.54	0.621
10	0.69	0.09	2.13	0.22	0.557

[a] Tensile strength calculated using the initial area of cross section.
[b] Tensile strength calculated using the area of cross section based on residual unembrittled layer.
[c] Standard deviation based on 4–6 test pieces.
[d] Intrinsic viscosity in dL/g. Foam samples obtained from entire cross section of exposed samples.
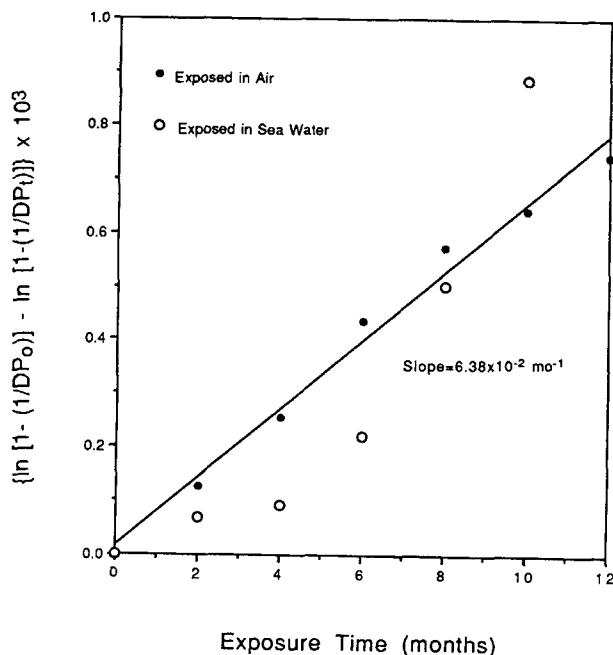
Figure 3 [ln(1 − 1/DP$_0$) − ln(1 − 1/DP$_t$)] vs. time based on GPC molecular weight data for polystyrene foam exposed in air and at sea.

$$1/[DP]_{n,t} - 1/[DP]_{n,0} = kt \qquad (1)$$

where t is time and k is a rate constant. For higher degrees of degradation the preceding equation becomes

$$\ln(1 - 1/[DP]_{n,0}) - \ln(1 - 1/[DP]_{n,t}) = kt \qquad (2)$$

Assuming photodegradation to be the sole mechanism for molecular weight reduction, the rate constant k is given by

$$k = \Phi I/[n_0] \qquad (3)$$

where n_0 is the initial concentration of main chain links, I is the average number of quanta absorbed per unit volume per second, and Φ is the quantum efficiency of the scission process. As shown in Figure 3, the plot of data according to Eq. (2) is linear for results pertaining to exposure in air. Those for exposure in seawater are initially linear with a rate constant lower than that observed with samples exposed in air. This is to be expected in view of the known slower degradation of common thermoplastics when exposed floating in seawater compared to the degradation of those exposed in air.[32,33] At exposure times exceeding about 4 months,* the curves

* The data is likely to have shown nonlinearity at an even shorter duration of exposure if the polystyrene from the embrittled, yellowed surface layer had been included in the material used for molecular weight determination.

deviate from linearity, suggesting a large increase in the k value. This increase is possibly due to the gradual removal of the embrittled yellow layer that filters out the harmful ultraviolet radiation, continually exposing new material to light.

For foamed polystyrene, the changes in mechanical properties of the material with duration of outdoor exposure are also an important consideration. It is generally convenient to monitor environmental deterioration of plastics in terms of tensile properties, particularly ultimate extension. The polystyrene foam, however, has a very low extension at break to begin with, and the small changes observed on weathering are difficult to interpret. Changes in tensile strength of the material are, however, of interest. Table II gives values for tensile strength of the complete sample as well as of the lower nonembrittled layer at different durations of exposure. The data again shows the degradation process to be faster when exposure is carried out in seawater rather than in air. In agreement with the viscosity data, it also shows the tensile strength of the lower layer to be affected by the exposure, particularly in the case of exposure in seawater.

Figure 4 shows the variation of intrinsic viscosity of the samples with time of exposure. Particularly in the case of samples exposed in seawater, the viscosities probably are overestimates as some fraction of the embrittled layer will have been lost by dis-
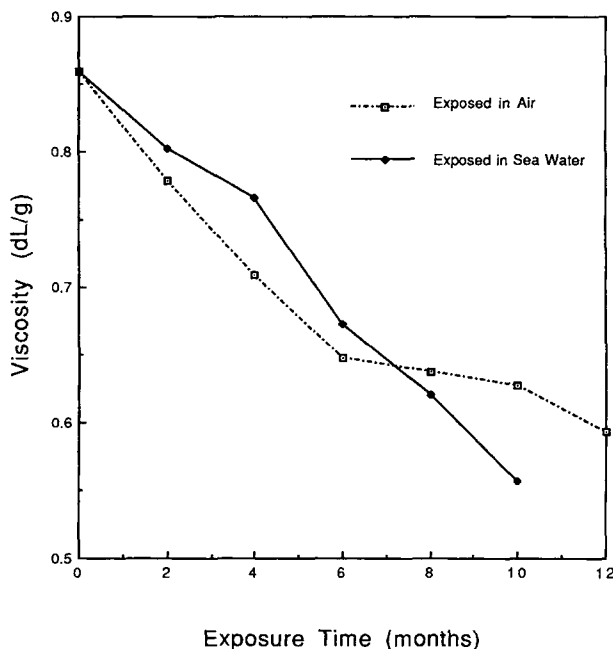

Figure 4 Intrinsic viscosity of polystyrene foam exposed in air and at sea.

solution and water movement. Viscosities steadily decrease with exposure for both samples. In terms of both viscosity and molecular weight measurements, the lower layers of samples exposed in seawater and in air are degraded to about the same extent at about the seventh month.

Interestingly, the rate of degradation of extruded polystyrene films in air is considerably faster than that of the foam. The number average molecular weight of film samples exposed in air dropped by about 64% on exposure for 9 weeks. No data for deterioration of films in seawater is available. But in a preliminary experiment, the polystyrene films exposed outdoors while floating in seawater were completely embrittled and unrecoverable within a month of exposure. This might, however, be in part due to mechanical stresses on the brittle film in addition to possible photodegradation.

CONCLUSIONS

Outdoor exposure of expanded, extruded polystyrene foam in air results in rapid discoloration and embrittlement of the exposed surface. As in the case of polystyrene films, the exposure results in increased UV absorbance and the formation of a possibly protective yellow surface layer, the thickness of which varies with time. The yellowing in the case of polystyrene foam is accompanied by marked changes in the average molecular weight and the tensile strength of the material. The data suggest that while such changes are more marked in the yellowed surface layer, the underlying unembrittled layer is also affected.

Exposure of the material to the outdoor environment while floating in seawater also resulted in similar changes. However, the rate of deterioration of the polystyrene samples, as measured by changes in thickness of unembrittled material, number-averaged molecular weight, solution viscosity, and tensile strength, was found to be faster than that for exposure in air. This is at least in part attributed to the continuous loss of yellowed surface layer in water and the consequent reduction in effective screening of sunlight.

REFERENCES

1. J. Titus, Weatherability of Polystyrene, *Plastic Report*, **38**, (1969).
2. E. Priebe, K. Stange, and K. W. Steiner, *Kunst.*, **60**, 617 (1970).
3. N. A. Weir, *Developments in Polymer Degradation*, N. Grassie, Ed., Applied Science Publishers, London, 1982, Vol. 4 p. 189.
4. J. F. Rabek, *Mechanisms of Photophysical Processes and Photochemical Reactions in Polymers*, Wiley, New York, 1987, p. 510.
5. M. L. Dahlberg and R. H. Day, in *Proceedings of the Workshop on the Fate and Impact of Marine Debris*, R. S. Shomura and H. O. Yoshida, Eds., U.S. Department of Commerce, NOAA, Honolulu, Hawaii, 1985, pp. 198–212.
6. A. T. Pruter, *Mar. Pollut. Bull.*, **18**(6B), 305–310 (1987).
7. P. G. Ryan, *Mar. Environ. Res.*, **23**, 175–206 (1987).
8. M. Gochfeld, *Environ. Pollut.*, **4**, 1–6 (1973).
9. G. H. Balazs, in *Proceedings of the Workshop on the Fate and Impact of Marine Debris, November 27–29, 1984*, R. S. Shomura and H. O. Yoshida, Eds., U.S. Department of Commerce, Honolulu, Hawaii, 1985, pp. 387–429.
10. R. W. Dickerman and R. G. Goelet, Northern Gannet Starvation after Swallowing Styrofoam, *Mar. Pollut. Bull.*, **14**(4), 145–148 (1987).
11. K. Hjelmeland, G. H. Pedersen, and E. M. Nissen, *Mar. Bio.*, **98**, 331–335 (1988).
12. P. G. Ryan, *Mar. Pollut. Bull.*, **19**(3), 125–128 (1988).
13. P. G. Ryan, *Condor*, **90**, 446–452 (1988).
14. G. A. George and D. K. C. Hodgeman, *J. Polym. Sci., Polym. Symp.*, **55**, 195 (1976).
15. G. Geuskens, The Photo-oxidation of Polystyrene: A Review of Solved and Unsolved Problems., Int. Conf. on Advances in the Stabilization and Controlled Degradation of Polymers (Prepr.), June, Luzern, Switzerland (1980).
16. B. Ranby, J. F. Rabek, and Z. Joffe, presented at Conference on Degradability of Polymers and Plastics, London, November (1973).
17. G. A. George, *J. Appl. Polym. Sci.*, **18**, 419 (1974).
18. C. Savides, J. A. Stretanski, and L. R. Costello, in *Stabilization of Polymers and Stabilizer Processes*, R. F. Gould, Ed., Advances in Chemistry Series No. 85, American Chemical Society, Washington, D.C., 1968, p. 187.
19. A. Davis and D. Sims, *Weathering of Polymers*, Applied Science Publishers, Essex, England, 1983, p. 208.
20. J. B. Lawrence and N. A. Weir, *Chem. Commun.*, **9**, 273 (1966).
21. J. Kubica and B. Waligora, *Europ. Polym. J.*, **13**, 325 (1977).
22. O. B. Zapolskij, *Vysokomol. Soedin.*, **7**, 615 (1965).
23. J. F. Rabek and B. Ranby, *J. Polym. Sci.*, **12**, 273 (1974).
24. N. Grassie and N. A. Weir, *J. Appl. Polym. Sci.*, **9**, 975 (1965).
25. G. Geuskens, D. Baeyens-Volant, G. Delaunois, Q. Lu-Vinh, W. Piret, and C. David, *Europ. Polym. J.*, **14**, 291 (1978).

26. J. Peeling and G. T. Clark, *Polym. Degrad. Stabl.*, **3,** 177 (1981).

27. C. E. Fisher, V. J. Castelli, S. D. Rogers, and H. R. Bleile, in *Marine Biodeterioration: An Interdisciplinary Study,* J. D. Costlow and R. C. Tipper, Eds., Naval Institute Press, Annapolis, Maryland, 1984, pp. 261–299.

28. M. Tryon and L. A. Wall, *J. Phys. Chem.,* **62,** 697 (1958).

29. J. F. McKellar and N. S. Allen, *Photochemistry of Man-Made Polymers,* Applied Science Publishers, Essex, England, 1979.

30. C. David, D. Baeyens-Volant, G. Delaunois, Q. Lu Vinh, W. Piret, and G. Geuskens, *Europ. Polym. J.,* **14,** 501 (1978).

31. H. H. G. Jellinek, *Appl. Polym. Symp.,* **4,** 41–54 (1967).

32. A. L. Andrady, Paper presented at Second International Conference on the Fate and Impact of Marine Debris, Honolulu, Hawaii, April (1989).

33. J. E. Pegram and A. L. Andrady, *Polym. Deg. Stabl.,* **26,** 333 (1989).