

## Photodegradable Vinyl Plastics. I. Effect of N-Halogen Additives

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### Synopsis

The addition of small amounts of N-halogen compounds to polystyrene (PS), polypropylene (PP), and polyethylene (PE) enhanced the photodegradability of the resultant plastic films. The effectiveness of the additives varied with their structure and with the polymer. A comparison of N-bromosuccinimide (NBS) with several known photoinitiators showed it to be superior in effectiveness to all but one. Films were irradiated with a 275-watt RS sunlamp for 66-200 hr. Degradation was measured by increase in carbonyl absorbance at  $1750\text{-}1695\text{ cm}^{-1}$  using infrared spectroscopy and by change in viscosity. PS containing NBS underwent a greater molecular weight loss than unmodified PS after UV exposure as determined by viscosity measurements.

### INTRODUCTION

The preparation and use of photodegradable polymers have been investigated recently as a way of alleviating environmental pollution resulting from the disposal of plastic wastes. Two approaches have been used to impart photodegradability to plastics. The procedure used by Guillet<sup>1,2</sup> involves inclusion of carbonyl groups chemically bound in the polymer molecule which, upon absorption of UV light, undergo photochemical changes resulting in polymer decomposition. A second approach, used by Scott<sup>3</sup> and others,<sup>4,5</sup> involves the physical blending of photoactivating additives which subsequently cause degradation of the polymer. Additives employed for this purpose include metal dithiocarbamates,<sup>3</sup> benzophenone,<sup>5,6</sup> other aromatic ketones,<sup>3,6</sup> and metal salts such as stearates, oleates, and acetyl acetonates, etc.,<sup>7</sup> as well as many other types of organic compounds. We now report the use of N-halogen compounds such as NBS as external additives to enhance photodegradation. Because NBS is known to dissociate via free-radical formation,<sup>8</sup> it seemed likely that it could also act as a photoinitiator in the degradation of polymers. In this paper, a number of N-halogen compounds are compared regarding their efficiency in photodegrading PS, PP, and PE.

### EXPERIMENTAL

**Materials.** Commercial PS (Dow-580) was purified by dissolving in chloroform and precipitating with methanol three times. The commercial PS

was also used without purification. Unstabilized PP (Profax 6501) was provided by Hercules, Inc. High-density PE (Alathon 2005-P) and low-density PE (Alathon 20), both without additives, were provided by the du Pont Company. The PP and high-density PE were used as received. The low-density PE pellets were ground to a fine powder before use. All photoinitiator additives were commercially available and were used without purification.

**Film Preparation.** PS powder and additive (generally 1% by weight) were dissolved in chloroform (15–20% w/v) and cast onto a glass plate. The resulting films were 4–5 mils thick. PP and PE films with additives were prepared by adding an acetone solution of the additive to the polymer resin, mixing thoroughly, allowing the acetone to evaporate, and melt pressing the resulting mixture between a sandwich of Mylar sheets and ferrotype chrome plates. The mixture was heated in the press for 30 sec at 350°F without pressure, and then 370 psi pressure was applied for 30 sec. Finally, the hot film was transferred to an unheated press at 4000 psi while cooling. Film thickness was 3–4 mils. In the case of higher melting additives, the temperature of the press was about 10°F above the melting point of the additive. Polymer films  $\frac{3}{4}$  in.  $\times$   $1\frac{3}{8}$  in. were used for both infrared spectroscopy and UV exposure.

**Photodegradation.** The primary method for determining the extent of photodegradation was by measuring the increase in carbonyl absorbance using a Perkin-Elmer infrared spectrophotometer, Model 257. For PS, absorbance was measured at ca. 1750 and 1695  $\text{cm}^{-1}$ . For PP and PE, absorbance was measured at 1715  $\text{cm}^{-1}$ . Intrinsic viscosities of toluene solutions at 30°C of nonirradiated and irradiated PS were determined using an Ubbelohde dilution viscometer. Molecular weight  $M$  was obtained from intrinsic viscosity  $[\eta]$  by the Mark-Houwink equation,  $[\eta] = KM^a$ , where  $K = 0.923 \times 10^{-4}$  and  $a = 0.72$ .

Films were irradiated on a revolving table 9 in. in diameter and 6 in. below a downward-directed 275-watt RS sunlamp. PS and PP samples were exposed for 66 hr and PE samples, for 100–200 hr. By comparing the increase in carbonyl absorbance before and after irradiation, the extent of photo-oxidation was ascertained. The additive effectiveness ratio was determined by dividing the absorbance increase for polymer with additive by the absorbance increase of polymer without additive. This ratio provides a measure for numerically comparing the relative effectiveness of various photoinitiators. An additive effectiveness ratio greater than one indicates that the additive functions as a photosensitizer, whereas a ratio less than one indicates the additive acts as a photostabilizer.

## RESULTS AND DISCUSSION

### Infrared Spectroscopy

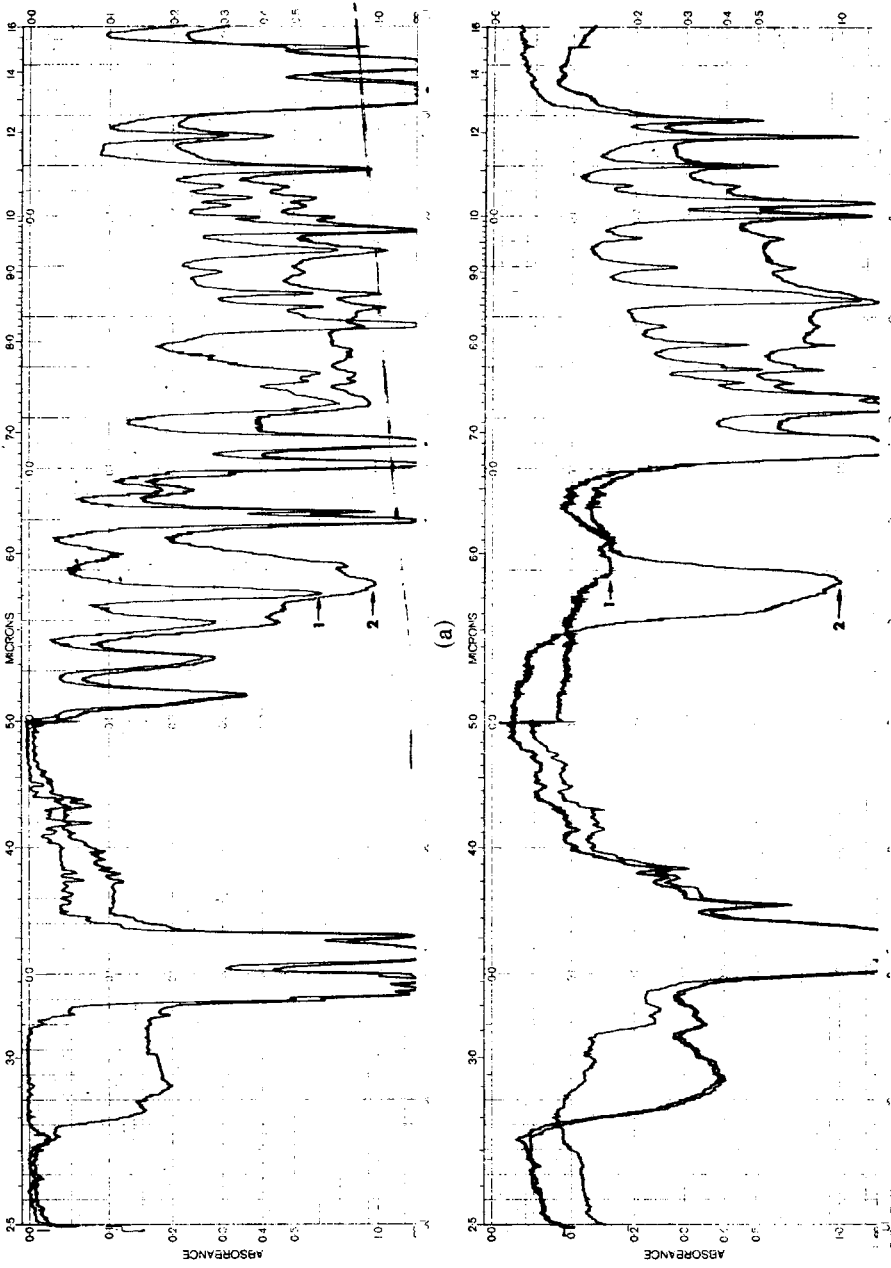
IR spectroscopy has been widely used to study the photo-oxidation of polymers and is especially useful with hydrocarbon polymers because they do not contain interfering oxygen compounds.<sup>9,10</sup> The method used in this investigation was based on a modification of a previously published procedure.<sup>10</sup> Figure 1 shows the infrared spectra of three vinyl polymers containing three

different N-halogen additives before and after irradiation. In all cases, photo-oxidation is indicated by major increases in the carbonyl region ( $1750\text{--}1690\text{ cm}^{-1}$ ) and in the hydroxyl region ( $3600\text{--}3300\text{ cm}^{-1}$ ). Acids, aldehydes, ketones, hydroxy compounds, and hydroperoxides have been reported as groups responsible for these absorptions.<sup>9</sup> The spectra after irradiation for PS with or without additives differed from those of PP and PE in that two carbonyl bands were present with PS, but only one carbonyl band was present for the aliphatic polymers. In the upper spectrum of Figure 1, the two carbonyl bands are present at  $1730\text{ cm}^{-1}$  and  $1695\text{ cm}^{-1}$ . This is in accord with other observations on photodegraded PS in which several bands have been reported.<sup>11</sup> In calculating the increase in carbonyl absorbance for PS, both bands have been used, whereas for PP and PE, only one band has been used. Consequently, the additive effectiveness ratios are generally greater for the PS samples than for samples of the other two polymers. The results of irradiating PE and 1% N-iodosuccinimide for both 100 hr and 200 hr are shown in the lower spectrum of Figure 1. These time intervals were chosen to determine if the extent of degradation would greatly increase on longer exposure. In this case doubling exposure time resulted in somewhat less than double the carbonyl increase.

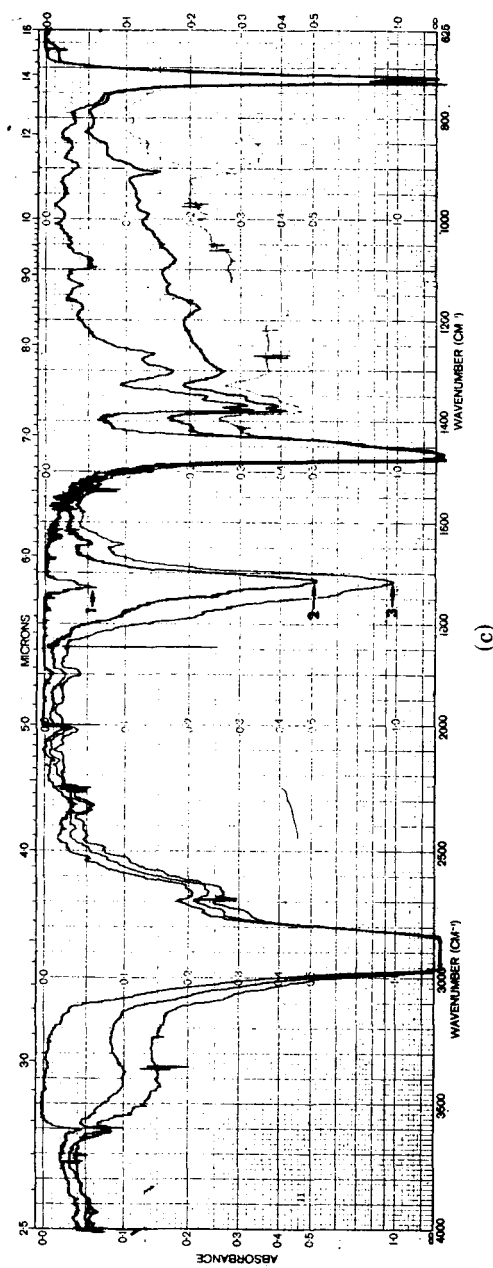
### Effect of Additives

The results of irradiating various vinyl polymers containing 1% of a series of N-halogen additives are shown in Table I. As previously mentioned, the additive effectiveness ratios are greater for the aromatic PS samples than for the aliphatic polymers. The table also shows that PP generally is degraded more than PE. This would be expected because the tertiary hydrogen atoms in PP are more labile than the methylene hydrogen atoms in PE. Low-density and high-density PE were degraded to approximately the same extent as indicated by the data in Table I and in unpublished data.

Several conclusions can be drawn relating the structure of the additives to their effectiveness. First, the more N-halogen groups between carbonyl groups in the structure, the more effective is the additive. Thus for both PP and PE, trichloroisocyanuric acid, which has three N—Cl groups, is the most effective additive. Also, 1,3-dibromo-5,5-dimethylhydantoin is more effective in PS and PP than its 3-monobromo analog. Secondly, the order of activity of the N—X group is N—I > N—Br > N—Cl. Thus, in PE (HD), NIS > NBS > NCS; and in both PS and PP, NBS > NCS. One would also expect this order considering that the bond energies follow the reverse order, N—Cl > N—Br > N—I.<sup>12</sup> Thus, the N—I, bond which has the lowest bond energy, would be broken most easily and would therefore be the most reactive. We are currently studying the UV photolysis of N-halogen compounds in polymers by electron spin resonance. Free-radical concentration was significantly greater in irradiated polymers incorporating N-halogen additives than in irradiated unmodified polymers. It thus appears likely that at least the N-halogen succinimides probably are cleaved by UV light into free radicals which then promote a chain photo-oxidation according to well-established mechanisms. Finally, the superiority of NBS over both NCS and N-bromo-



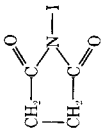


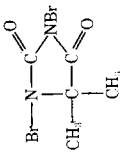
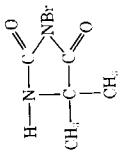

(b)  
Fig. 1 (continued)

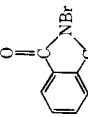
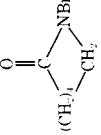


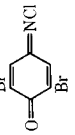
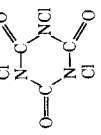


(c)

Fig. 1. (a) IR spectrum of polystyrene and 1% 1,3-dibromo-5,5-dimethylhydantoin: (1) before irradiation; (2) after 66 hr of irradiation. (b) IR spectrum of polypropylene and 1% N-bromosuccinimide: (1) before irradiation; (2) after 200 hr of irradiation. (c) IR spectrum of polypropylene and 1% N-iodosuccinimide: (1) before irradiation; (2) after 66 hr of irradiation.

TABLE I  
Effect of N-Halogen Additives on the Photodegradation of Vinyl Polymers<sup>a</sup>

Additive Name	Structure	Polystyrene		Polypropylene		Polyethylene H.D.		Polyethylene L.D.	
		Carbonyl <sup>b</sup> increase	Add. <sup>c</sup> effec. ratio	Carbonyl increase	Add. effec. ratio	Carbonyl increase	Add. effec. ratio	Carbonyl increase	Add. effec. ratio
N-Iodosuccinimide		—	—	.615	1.33	.496	1.58	.250	1.04
N-Bromosuccinimide		.954	5.42	.912	1.97	.242	.771	.299	1.24
N-Chlorosuccinimide		.563	3.20	.577	1.25	.188	.598	—	—
1,3-Dibromo-5,5-dimethylhy- dantoin		1.453	8.26	.807	1.75	.353	1.12	.332	1.38
3-Bromo-5,5-dimethylhy- dantoin		1.189	6.76	.587	1.27	.408	1.30	—	—
N-Bromoacetamide		.506	2.88	.629	1.36	.332	1.06	—	—

N-Bromophthalimide		.549	3.12	.810	1.75	.247	.787	—	
N-Bromocaprolactam		.724	4.11	.050	.108	.215	.685	—	
N,N-Dichlorourethane		.325	1.85	.705	1.53	.200	.637	—	
N,N-Dichlorobenzene sulfonamide		.383	2.18	.595	1.29	.165	.526	—	
2,6-Dibromoquinone 4-Chloroimide		.539	3.06	.150	.324	.098	.312	—	
Trichloroisocyanuric acid		.460	2.61	2.25	4.87	.582	1.85	—	
Polymer control (no additive)		.176	1.00	.462	1.00	.314	1.00	.241	1.00

<sup>a</sup> Additive concentration, 1% by weight.

<sup>b</sup> Carbonyl increase is the increase in the carbonyl absorbance measured at 1750-1695 cm<sup>-1</sup> by IR before and after irradiation.

<sup>c</sup> Additive effectiveness ratio is equal to the increase in carbonyl absorbance for polymer and additive divided by the increase in carbonyl absorbance for polymer only.

TABLE II  
Comparison of N-Bromosuccinimide with other Photoinitiators in the Degradation of Polystyrene

Additive	Purified polystyrene		Commercial polystyrene	
	Carbonyl increase	Additive effectiveness ratio	Carbonyl increase	Additive effectiveness ratio
N-Bromosuccinimide (NBS), 1%	.882	4.37	.912	1.54
NBS, 0.1%	.218	1.08	.569	.961
NBS, 2%	1.73	8.56	2.93	4.95
1,4-Napthoquinone	.609	3.02	.489 <sup>a</sup>	.826
2,4-Pentanedione, iron(III) derivative	.310	1.54	.754	1.27
Benzophenone	.545	2.70	.772	1.30
4,4'-Bis(dimethyl-amino)benzophenone	.494	2.45	.919	1.55
Cobalt stearate	1.31	6.49	1.25	2.12
Cobalt oleate	.192	.950	—	—
Benzoyl peroxide	.463	2.29	—	—
Benzoyl peroxide (1%) + NBS (1%)	1.36	6.73	—	—
Benzophenone (1%) + NBS (1%)	1.63	8.07	—	—
1,3-Dibromo-5,5-dimethylhydantoin	(1.45) <sup>b</sup>	(8.26)	.788	1.33
Polystyrene control (no additive)	.202	1.00	.592	1.00

<sup>a</sup> 1,2- Rather than 1,4-napthoquinone was used here.

<sup>b</sup> From Table I.

phthalimide parallels the superiority of NBS as an allylic brominating agent compared with these same reagents.<sup>8</sup>

### NBS Compared to Other Photoinitiators

It has been shown that NBS is a good photoinitiator for the degradation of PS. Further experiments were conducted to obtain answers to the following questions: (1) What effect does the purity of the PS have on its photodegradation? (2) What is the effect of varying the concentration of NBS? (3) How does NBS compare to other known photoinitiators? (4) Does NBS operate synergistically with other photoinitiators? Answers to these questions are provided by the data in Table II. As mentioned in the experimental section, the purified PS was obtained from the commercial PS by three precipitations with methanol from chloroform solution. Table II shows that, although the carbonyl increase was greater for the commercial PS than for the purified PS control, purified PS with additives always gave higher additive effectiveness ratios than the corresponding commercial PS with additive. Hence, the commercial PS probably contained some component which inhibited the effect of the photoinitiating additive. The odor of styrene was easily



TABLE III  
Effect of NBS on Viscosity and Molecular Weight of Polystyrene

	Before irradiation		After 66 hr of irradiation <sup>a</sup>	
	$[\eta]$ <sup>b</sup>	$\bar{M}_v$ <sup>c</sup>	$[\eta]$	$\bar{M}_v$
Purified polystyrene	1.818	917,500	.997	400,000
Purified polystyrene + 1% NBS	1.573	752,000	.277	67,500
Commercial poly- styrene	2.202	1,201,000	.548	173,700
Commercial polysty- rene + 1% NBS	2.178	1,181,000	.175	35,000

<sup>a</sup> 275-watt RS sunlamp.

<sup>b</sup> Intrinsic viscosity.

<sup>c</sup> Viscosity-average molecular weight.

detected in the commercial PS but was absent in the purified PS. It was suspected that styrene might be causing the inhibition in additive activity. Analysis of the commercial and purified PS using UV spectroscopy by a previously established method<sup>13</sup> showed 2.1% styrene in the commercial and 0.15% styrene in the purified sample. Samples of purified PS were then prepared containing 1% and 5% styrene; but because these samples photodegraded essentially like purified PS alone, styrene was eliminated as causing the difference. Possibly, the commercial PS contains an antioxidant and/or UV inhibitor which is removed in the purification process, but this matter was not pursued further.

The concentration of NBS was varied between 0.1% and 2% (Table II). At the 0.1% level in purified PS, the additive effectiveness ratio was only slightly above the control, indicating that at this level the additive is not very effective. At the 2% level, the ratio was about double that at the 1% level. Hence, the effectiveness of the additive appears to be proportional to concentration. Additives which enhance photodegradation are generally used in the range of 0.1–10%. By increasing the concentration of NBS in the PS, the extent of degradation would obviously increase.

A comparison of NBS at the 1% level in both purified and commercial PS (Table II) with other photoinitiators at the 1% level showed NBS to be equal to or better than all others, except cobalt stearate. This indicates that NBS is quite efficient as a photoinitiator. In allylic bromination benzoyl peroxide is often used with NBS to facilitate breakdown into free radicals. As indicated by Table II, NBS did not show a synergistic effect when combined with either benzoyl peroxide or benzophenone in PS. However, 1% NBS plus 1% benzoyl peroxide in PP gave an additive effectiveness ratio 1.5 times greater than the sum of its parts. In PE these two additives showed no synergism.

### Molecular Weight Change in Polystyrene

To provide another indication of degradation, viscosity measurements were made on solutions of selected PS films to determine changes in molecular weight. Table III shows that all four PS samples underwent severe reduction in molecular weight after 66 hours of irradiation. Furthermore, the molecu-

lar weight loss was greater for both the purified and commercial PS containing NBS than the PS samples without NBS. Also, the irradiated PS films with NBS were much darker yellow and more severely cracked than their counterparts without NBS. It is presumed that vinyl polymers containing N-halogen additives would undergo a similar photodegradation on exposure to sunlight, resulting in a friable powder that would soon disappear in the environment.

The authors wish to thank Rudolf Bermann for IR and viscosity determinations and Dr. Anthony C. Waiss, Jr., for his helpful comments and encouragement. Reference to a company or product name does not imply approval or recommendation of the product by the U.S. Department of Agriculture to the exclusion of others that may be suitable.

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