

Photodegradable Vinyl Plastics. II. Effect of Arylmethyl Halides, Phenyl Halomethyl Ketones, and Haloalkene Additives

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Synopsis

Three classes of active halogen compounds were effective in promoting photodegradation of polystyrene, polypropylene, and polyethylene. The classes are arylmethyl halides, phenyl halomethyl ketones, and haloalkenes. The additives were blended with the polymers and fabricated into films which were irradiated 66–200 hr with a 275-watt RS sunlamp. Photo-oxidation, as determined by IR spectroscopy, was used as a measure of photodegradation. The relationship between the structure of the additive and its effectiveness as a photoinitiator within each of the three classes of compounds is discussed. In general, photoactivated polystyrene was degraded the most, followed by polypropylene and then polyethylene. Viscosity measurements on irradiated polystyrene containing the additives showed significantly greater molecular weight loss than a polystyrene control.

INTRODUCTION

In a previous study,¹ N-halogen compounds, such as N-bromosuccinimide, added to polystyrene (PS), polypropylene (PP), and polyethylene (PE) increased photodegradability of the resulting films. Based on this finding, we thought that other active halogen compounds also might enhance photodegradability. In this investigation, the effectiveness of a series of arylmethyl halides, phenyl halomethyl ketones, and haloalkenes were examined. We were interested in determining the relative effectiveness of these three classes compared to the N-halogen compounds, how structural variations of the additives influenced their activity, and how the stabilities of PS, PP, and PE were affected by a given additive.

EXPERIMENTAL

Film Preparation. Commercial PS (Dow-580) was purified by first dissolving 90 g of the powdered resin in 510 ml chloroform. The resulting solution was poured slowly into a 1-gallon Waring Blendor containing 2 liters vigorously stirred methanol. The finely precipitated powder was filtered, washed with methanol, air-dried, and finally dried in a vacuum oven at 52°C

at water-aspirator pressure. This procedure was repeated three times yielding PS containing no odor of styrene.

PS films were made by combining 3 g purified PS powder, 1–5% by weight of additive, and 17 ml chloroform and shaking on a wrist-action shaker until a solution was obtained. This solution was spread on a 4 × 8 in. glass plate using a film casting knife with a setting of 0.038 in. The plate was suspended above chloroform in a covered tray to retard evaporation as the solvent. A film free of bubbles resulted.² After the plate had dried overnight, it was placed in a tray containing distilled water, and the film floated away from the glass. From the resulting film, which was 0.004–0.005 in. thick, a piece $\frac{3}{4} \times 1\frac{3}{8}$ in. was cut and used for both IR spectroscopy and exposure to UV light. The procedure for preparing films from high-density PE (du Pont Alathon 2005-P) and PP (Hercules Profax 6501) has been described.¹ All additives were commercially available and were used as received.

Photodegradation. Films were irradiated with General Electric 275-watt RS sunlamps. Because the light intensity of these lamps is not uniform with time, the lamps were used between 50 and 500 hr of operating time. The RS sunlamp has been employed by other investigators for studying the photodegradation of plastics,^{3,4} and its characteristics have been compared to various UV light sources.^{5,6} The method used for irradiating films on a revolving table located 6 in. below the sunlamp is a modification of a published procedure.⁷ PS and PP samples were irradiated for 66 hr and PE, for 100–200 hr.

Measurements of carbonyl absorbance before and after irradiation were made with a Perkin-Elmer IR spectrophotometer, Model 257. The increase in carbonyl absorbance was used to determine the extent of photodegradation. The additive effectiveness ratio (AER) was determined by dividing the absorbance increase for polymer with additive by the absorbance increase of polymer without additive. 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. When desired, the additive effectiveness ratio was divided by the per cent additive to provide an index for comparing samples containing different amounts of additive. Intrinsic viscosities of toluene solutions of PS films were determined at 30°C with an Ubbelohde dilution viscometer. Molecular weight M was obtained from intrinsic viscosity $[\eta]$ according to the Mark-Houwink equation $[\eta] = KM^a$.

RESULTS AND DISCUSSION

Effect of Arylmethyl Halides

The IR spectra of irradiated PS, PP, and PE with and without various arylmethyl halide additives are shown in Figure 1. In every case, the polymer with the additive has a significantly greater carbonyl increase than the same polymer without an additive. It can be concluded that the polymers containing these arylmethyl halides have undergone greater photo-oxidation and therefore greater photodegradation than the polymer control. Unlike PP and PE, which have one carbonyl band at 1717 cm^{-1} , PS has two carbonyl bands, one at 1750 and the other at 1695 cm^{-1} . In calculating the carbonyl increase for PS, the combined increases in both bands were utilized.

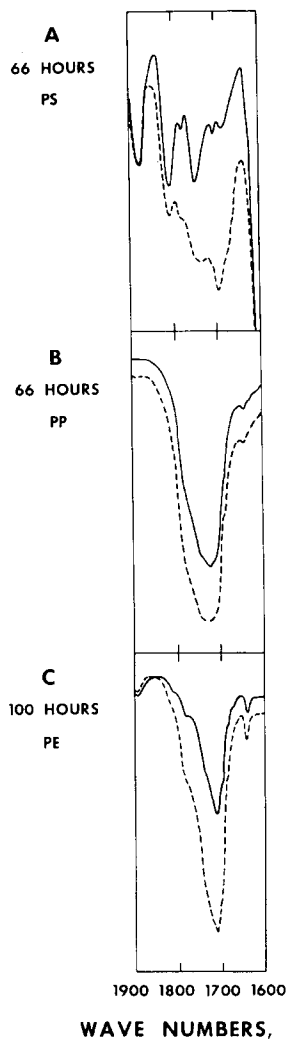


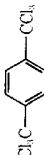
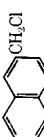


Fig. 1. IR spectra of vinyl polymers with and without additives after irradiation with UV sunlamp. (A): (—) PS; (.....) PS + 5% $\phi_3\text{CBr}$. (B): (—) PP; (.....) PP + 1% $\phi_2\text{CCl}_2$. (C): (—) PE; (.....) PE + 5% $p\text{-Cl}_3\text{C}\phi\text{CCl}_3$.

In Table I are shown the results of irradiating vinyl polymers containing arylmethyl halides in which the structures of the additives have been systematically altered. This was done to correlate structural variation with additive effectiveness. The higher the AER, the more readily the additive can induce photodecomposition in the polymer. Also, dividing AER by per cent additive enables additives to be compared independent of concentration. First, it should be noted that with both PS and PE, generally 2–5% additive was required to yield ratios greater than unity. Because the N-halogen additives studied previously¹ were effective at the 1% level, we conclude that as a class the arylmethyl halides are not as effective as the N-halogens. With PP, 1% additive was generally adequate to give polymer blends with ratios greater

TABLE I
Effect of Arylmethyl Halides on the Photodegradation of Vinyl Polymers^a

Name	Additive Structure	Polystyrene			Polypropylene ^b			Polyethylene		
		% Additive	AER ^c	$\frac{\text{AER}}{\% \text{ Additive}}$	AER	$\frac{\text{AER}}{\% \text{ Additive}}$	% Additive	AER	$\frac{\text{AER}}{\% \text{ Additive}}$	
Benzyl chloride	$\phi\text{CH}_2\text{Cl}$	5	1.05	.210	.745	—	—	—	—	
Chlorodiphenylmethane	$\phi_2\text{CHCl}$	5	2.44	.488	1.02	—	—	—	—	
Dichlorodiphenylmethane	$\phi_2\text{CCl}_2$	2	2.29	1.15	1.66	5	.673	.135		
Chlorotriphenylmethane	$\phi_3\text{CCl}$	1	1.46	1.46	1.40	3	2.09	.697		
Triphenylmethane	$\phi_3\text{CH}$	5	2.65	.530	1.07	—	—	—	—	
Benzyl bromide	$\phi\text{CH}_2\text{Br}$	3	3.23	1.08	1.13	—	—	—	—	
Bromodiphenylmethane	$\phi_2\text{CHBr}$	2	4.05	2.03	1.37	3	1.81	.603		
Bromotriphenylmethane	$\phi_3\text{CBr}$	5	4.80	.960	1.36	5	1.77	.354		
Benzal bromide	ϕCHBr_2	—	—	—	.630	5	1.28	.256		
α,α,α -Trichlorotoluene	ϕCCl_3	5	2.12	.424	1.35	5	1.04	.208		
α,α,α -Trifluorotoluene	ϕCF_3	5	.959	.199	1.22	—	—	—	—	
α,α' -Dibromo- <i>o</i> -xylene		3	3.70	1.23	1.43	5	.654	.131		
α,α,α' -Tetrabromo- <i>o</i> -xylene		2	3.71	1.86	1.37	5	3.00	.600		
1,2-Dibromo-1,2-diphenylethane	$\text{Br}-\text{CH}-\text{CH}-\phi$	5	2.18	.436	1.30	5	1.82	.364		
$\alpha,\alpha,\alpha',\alpha',\alpha'$ -Hexachloro- <i>p</i> -xylene		5	3.14	.628	1.33	5	3.30	.660		
Dodecylbenzyl chloride	$\text{C}_{12}\text{H}_{25}-\text{CH}_2\text{CH}_2\text{Cl}$	2	.992	.496	1.44	5	3.24	.648		
1-Chloromethylnaphthalene		5	3.33	.666	1.30	—	—	—	—	
Polymer control	(no additive)	0	1.00	—	1.00	0	1.00	—	—	

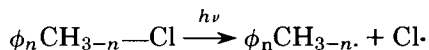
^a Irradiation time for PS and PP: 66 hr; PE: 100 hr; 275-watt RS sunlamp.

^b Weight % additive with PP was 1%.

^c Additive effectiveness ratio (AER) is equal to the increase in carbonyl absorbance for polymer and additive divided by the increase in carbonyl absorbance for polymer only. Increase in carbonyl absorbance was determined by IR at 1750–1695 cm^{-1} before and after irradiation.

than unity. This suggests that arylmethyl halides are more effective photoinitiators in PP than in PS or PE.

A number of other correlations can be made between additive structure and effectiveness based on the data in Table I. In both PS and PP, the more phenyl groups attached to a C—Cl group, the more effective is the additive. Thus, in PS, $\phi_3\text{CCl}$ (1.46) > $\phi_2\text{CHCl}$ (.488) > $\phi\text{CH}_2\text{Cl}$ (.21). In PP, $\phi_3\text{CCl}$ (1.40) > $\phi_2\text{CHCl}$ (1.02) > $\phi\text{CH}_2\text{Cl}$ (.745). These results can be explained by assuming a free-radical photolysis:



where $n = 1, 2,$ or 3 in which the phenylmethyl free radical is more resonance stabilized by three phenyl groups than by one. The longer-lived trityl radical would thus be more capable of initiating photodecomposition in the main polymer chain than a shorter-lived free radical. Varying the number of chlorine atoms attached to the phenylmethyl group gave the following: in PS, $\phi_2\text{CCl}_2$ (1.15) > ϕCCl_3 (.424) > $\phi\text{CH}_2\text{Cl}$ (.210); in PP, $\phi_2\text{CCl}_2$ (1.66) > ϕCCl_3 (1.35) > $\phi\text{CH}_2\text{Cl}$ (.745). With these two polymers, $\phi_2\text{CCl}_2$ was more effective than ϕCCl_3 but with PE, the reverse was true, ϕCCl_3 (.208) > $\phi_2\text{CCl}_2$ (0.135).

A comparison was also made between bromine- and chlorine-containing arylmethyl halides. Because the bond energy for the C—Br bond is less than for the C—Cl bond (65.9 versus 78.5 kcal/mole),⁸ the former bond should be broken more easily, and the arylmethyl bromides might be expected to be more reactive than the arylmethyl chlorides. The data in Table I show that, with certain structures, arylmethyl bromides are superior to arylmethyl chlorides as photoinitiators, but with other structures, the reverse is true. Thus, in PS, $\phi_2\text{CHBr}$ (2.03) >> $\phi_2\text{CHCl}$ (.488); and in PP, $\phi_2\text{CHBr}$ (1.37) > $\phi_2\text{CHCl}$ (1.02); also in both polymers $\phi\text{CH}_2\text{Br}$ is superior to $\phi\text{CH}_2\text{Cl}$. Unexpectedly, however, $\phi_3\text{CCl}$ was more effective than $\phi_3\text{CBr}$ in all three polymer systems. Thus, in PS, $\phi_3\text{CCl}$ (1.46) > $\phi_3\text{CBr}$ (.960) > $\phi_3\text{CH}$ (.530). Triphenylmethane was included for comparative purposes only. Because the C—H bond energy (98.8 kcal/mole) is higher than the C—Cl or C—Br bond energies, $\phi_3\text{CH}$ was predictably less active than its halogen analogs. $\phi_3\text{CCl}$ was slightly more effective than $\phi_3\text{CBr}$ in PP where $\phi_3\text{CCl}$ (1.40) > $\phi_3\text{CBr}$ (1.36) > $\phi_3\text{CH}$ (1.07); in PE, $\phi_3\text{CCl}$ (.697) > $\phi_3\text{CBr}$ (.354). The superiority of $\phi_3\text{CCl}$ over $\phi_3\text{CBr}$ must be due to factors other than bond strength.

Because of the higher bond energy of the C—F bond (105.4 kcal/mole) compared to the C—Cl bond (78.5), it would be expected that ϕCF_3 would be less reactive than ϕCCl_3 . This was verified in PS where ϕCCl_3 (.424) > ϕCF_3 (.199) and in PP where ϕCCl_3 (1.35) > ϕCF_3 (1.22). In comparing the di- and tetrabromo-*o*-xylenes, one might predict that the tetrabromo would be more effective than the dibromo. This was true for PS where tetrabromo (1.86) > dibromo (1.23), and in PE where tetrabromo (.600) >> dibromo (.131). In PP, however, the tetrabromo (1.37) was slightly less reactive than the dibromo (1.43). Finally, in PS and PE, *p*-Cl₃C ϕCCl_3 containing two Cl₃C— groups is more reactive than ϕCCl_3 with one such group. Thus in PS, *p*-Cl₃C ϕCCl_3 (.628) > ϕCCl_3 (.424), and in PE, *p*-Cl₃C ϕCCl_3 (.660) > ϕCCl_3 (.208), but in PP, *p*-Cl₃C ϕCCl_3 (1.33) and ϕCCl_3 (1.35) are about equal in effectiveness. In general, the effectiveness of the arylmethyl halides as photoinitiators fol-

TABLE II
Effect of Phenyl Halomethyl Ketones on the Photodegradation of Vinyl Polymers^a


Name	Structure	Polystyrene 66 hr ^c		Polypropylene 66 hr		Polyethylene			
		Carbonyl ^b increase	AER ^b	Carbonyl increase	AER	Carbonyl increase	AER		
2,4'-Dibromoacetophenone		.818	4.05	1.06	2.58	.345	1.20	.712	2.25
α,α -Dichloroacetophenone	$\phi\text{C}(\text{C}\text{Cl}_2)\text{C}(=\text{O})\text{H}$.434	2.15	.580	1.41	.345	1.20	.894	2.83
α -Bromo- α -phenyl- acetophenone	$\phi\text{C}(\text{C}\text{H})\text{C}(\text{Br})\text{C}(=\text{O})\text{H}$.513	2.54	Film too brittle		.225	.784	.574	1.82
2-Chloro-4'-phenyl- acetophenone		.271	1.35	.501	1.22	.232	.809	—	—
α,α' -Dibromodibenzyl ketone	$\text{Br}-\text{C}(\text{C}\text{H})-\text{C}(\text{Br})-\text{C}(=\text{O})-\text{H}$.701	3.47	1.57	3.82	.373	1.30	.387	1.23
2-Bromo-1,3-diphenyl- 1,3-propanedione	$\phi\text{C}(\text{C}\text{H})-\text{C}(\text{Br})-\text{C}(=\text{O})-\text{H}$.675	3.34	.554	1.35	.410	1.43	—	—
Polymer control (no additive)		.202	1.00	.411	1.00	.287	1.00	.316	1.00

^a Additive concentration, 1% by weight.

^b See Table I, footnote c.

^c Irradiation time.

TABLE III
Effect of Haloalkenes on the Photodegradation of Vinyl Polymers^a

Name	Additive	Structure	Polystyrene			Polypropylene			Polyethylene			
			Carbonyl increase	AER	$\frac{\text{AER}}{\% \text{ Additive}}$	% Additive	Carbonyl increase	AER	$\frac{\text{AER}}{\% \text{ Additive}}$	Carbonyl increase	AER	$\frac{\text{AER}}{\% \text{ Additive}}$
1,4-Dibromo-2-butene		$\text{BrCH}_2\text{CH}=\text{CH}-\text{CH}_2\text{Br}$.939	3.82	.764	5	.584	1.31	.282	.285	1.10	.220
2,3-Bis(bromethyl)-1,4-dibromo-2-butene		$(\text{BrCH}_2)_2\text{C}=\text{C}(\text{CH}_2\text{Br})_2$	1.34	5.45	1.09	5	.720	1.61	.322	.678	2.61	.522
Hexachloropropene		$\text{Cl}_3\text{C CCl}=\text{CCl}_2$.534	2.17	.434	1	.577	1.29	1.29	.198	.762	.152
Hexachlorocyclopentadiene			1.32	5.37	1.08	3	.688	1.54	.513	.264	1.02	.204
Cinnamyl bromide		$\phi\text{CH}=\text{CH}-\text{CH}_2\text{Br}$.997	4.05	.810	3	.506	1.14	.380	.286	1.10	.220
Cinnamyl chloride		$\phi\text{CH}=\text{CH}-\text{CH}_2\text{Cl}$.598	2.43	.486	3	.432	.970	.323	.230	.885	.177
Polymer control		(no additive)	.246	1.00	—	0	.446	1.00	—	.260	1.00	—

^a 5% additive was used with PS and PE.

lows expected considerations of bond energies and resonance stabilization of free radicals. There are enough exceptions, however, that care must be exercised in making predictions regarding the activity of any particular additive.

Effect of Phenyl Halomethyl Ketones

In Table II are listed several phenyl halomethyl ketones which differ structurally from the arylmethyl halides in that they contain a carbonyl group between the aromatic ring and the carbon-halogen group. Hence, it was of interest to determine how these two classes of compounds would compare as photoinitiators. The expectation was that the phenyl halomethyl ketones would be more reactive than the arylmethyl halides because of the inductive effect of both the phenyl and carbonyl groups on the carbon-halogen bond. The data in Table II show that the phenyl halomethyl ketones are superior to the arylmethyl halides, and are roughly equivalent in activity as photoinitiators to the N-halogens. Of the three polymers tested in Table II, PS was degraded the most, followed by PP and then PE. The ratios obtained for PE after 200 hr are roughly double those for PE after 100 hr showing that within this time interval, degradation appears to vary linearly with time. With all three polymers, the bromine-containing phenyl ketones are generally more effective than the chlorine-containing phenyl ketones.

Effect of Haloalkenes

All of the compounds listed in Table III have one common structural feature: a chlorine or bromine atom on a carbon atom adjacent to a double bond. Such compounds are known to be reactive because cleavage of the carbon-halogen bond produces a species that is resonance stabilized by the double bond. When employed at the 5% level, the haloalkenes generally gave ratios greater than unity. They are therefore comparable in activity as photoinitiators to the arylmethyl halides, and are not as effective as the phenyl halomethyl ketones.

The additive most effective in both PS and PE is 2,3-bis(bromomethyl)-1,4-dibromo-2-butene. This activity is probably due to the four C—Br bonds present in the molecule, any of which can be photolyzed to yield a reactive photoinitiating radical. The analogous dibromobutene, which has only two C—Br bonds, is less active. A comparison of the hexachloropropene with the hexachlorocyclopentadiene shows the latter is more effective in all three polymers because it has two double bonds which can stabilize the free radical formed by photolysis of the allylic C—Cl bond. As expected, cinnamyl bromide was more effective than cinnamyl chloride, thus supporting the same trend shown previously that a bromine-containing compound is generally a better photoinitiator than the analogous chlorine compound.

Because of the aromatic ring present in the cinnamyl halides, at least five resonance forms are possible for the resulting free radical, three of which are shown:

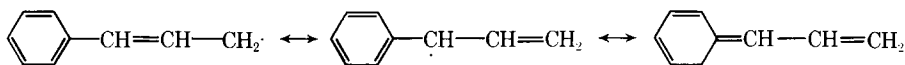


TABLE IV
Effect of Various Additives on Viscosity and Molecular Weight of Polystyrene

Sample	Before Irradiation		After 66 hr sunlamp	
	$[\eta]^a$	\bar{M}_v^b	$[\eta]$	\bar{M}_v
Polystyrene (control)	1.818	917,500	.997	400,000
Polystyrene + 2% $\alpha,\alpha,\alpha',\alpha'$ - tetrabromo- <i>o</i> -xylene	2.291	1,271,000	.325	84,550
Polystyrene + 1% α,α' - dibromodibenzyl ketone	2.155	1,165,000	.277	67,400
Polystyrene + 5% 2,3- bis(bromomethyl)-1,4- dibromo-2-butene	2.177	1,174,000	.147	28,000

^a Intrinsic viscosity.

^b Viscosity-average molecular weight.

This delocalization of the electrons conveys stability to the free radical and hence greater reactivity.

Viscosity and Molecular Weight of Polystyrene

In addition to IR spectroscopy for determining photodegradation, viscosity measurements were made on selected PS samples before and after irradiation to determine molecular weight changes. In Table IV are shown viscosity and molecular weight data on PS containing a member of each of the three classes of additives. Compared to the control, the samples of PS containing the additives have undergone significant changes in viscosity and molecular weight. These findings support the view that photo-oxidation is often accompanied by severe molecular weight loss. Hence, under the experimental conditions used, these three classes of halogen additives were effective in enhancing the photodegradation of vinyl polymers.

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