Color Stabilization of Poly(vinyl Chloride) Against High-Energy Electron Irradiation

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Synopsis

Color stability in irradiated PVC may be achieved by (1) structural modification to block dehydrochlorination, (2) addition of radiation protectors, or (3) addition of radical scavengers. This study explores the latter approaches. Twenty-six compounds representing a variety of structural types were screened for their effectiveness as measured by subsequent color development. Fifteen of the compounds imparted partial or complete postirradiation stability. Possible stabilizer mechanisms are discussed.

INTRODUCTION

Poly(vinyl chloride) undergoes rapid discoloration on exposure to high-energy electrons, gamma radiation, and ultraviolet light.[1] Proposed mechanisms suggest that irradiation gives rise to polymer alkyl radicals which initiate radical-chain dehydrochlorination, yielding visibly colored conjugated long-chain polyenyl radicals. Oxygen exposure reduces the polyenyl-radical population, leaving more stable polyenes.[2] Two features of this process combine to limit the use of PVC in some applications: (1) discoloration will be most severe where radiation intensity is highest, namely, at the surface, and (2) high extinction coefficients of long-chain polyenes in the visible region account for the observed intense discoloration of PVC at very low levels of polyene concentration.

In seeking materials which will inhibit polyene growth in irradiated PVC, and which are effective in this capacity at relatively low concentrations, we have taken as starting points the previously observed color stability of PVC irradiated in concentrated tetrahydrofuran (THF) solution[3,4] and the well-known stabilizing activity of aromatics.[5,6] Compounds tested included cyclic ethers and sulfides of varying ring size, linear ethers, and a variety of aromatics. Maintenance of stabilizer concentrations at high temperatures dictated the choice of solids, high-boiling liquids, and naturally retained solvents. Color developments following irradiation were monitored by ultraviolet-visible spectroscopy. Electron-spin resonance studies on several of the more effective stabilizer–PVC systems have provided information on stabilizer interaction.

EXPERIMENTAL

Prospective stabilizers were incorporated into a commercial-grade, unstabilized high molecular weight PVC by mechanical grinding or by solvent casting. Grinding took place either dry or in warm methanol to ensure better dispersion, after which the mixtures were dried. Films were then pressed between Mylar-lined plates for 10–11 min total heating time, to a maximum of 144–147°C at 12,000 lbs. pressure. Solvent-cast films were evaporated in nitrogen; solvents were first distilled over CaH_2 in nitrogen. Films for ESR studies were cast from THF and dried under nitrogen at room temperature. THF, initially unstabilized, was distilled over CaH_2 in dry nitrogen prior to use; retained THF in the films was removed by heating at 100°C at 10^{-4}–10^{-5} torr. Breakdown and eventual recovery of the vacuum with the films at 100°C indicated an end to outgassing of residual THF. Stabilizer retention for molded and solvent-cast films was checked by infrared spectroscopy confirming stabilizer presence in most films. In several cases, characteristic IR absorptions could not be observed because of intense PVC absorption, and stabilizer retention had to be assumed. In compounds I-1, 3, 4, 5, 10, and 11, retention was based on weight increase after solvent casting, and for compounds III-25 and 26, retention was assumed.

Film specimens were irradiated in nitrogen at room temperature to 6 Mrad total dose with 1 MeV electrons, stored in nitrogen overnight and in air for two days. UV-visible spectra, recorded on each film before irradiation, after irradiation and storage in nitrogen, and after storage in air, provided a measure of color development. Films for the ESR studies were irradiated in vacuo at liquid nitrogen temperature in sealed quartz tubes.

UV-visible spectra were obtained with Cary Model 15 and 14 spectrometers; infrared spectra, with a Perkin-Elmer Model 21 and ESR signals with a Varian V4500. Optical density at 7000 Å was arbitrarily assigned the value 0.1 for UV-visible surveys. Changes in this region are slight for large changes elsewhere in the spectrum. For low and intermediate values of optical density, the error is negligible.

RESULTS AND DISCUSSION

A summary of stabilizer data is presented in Table I; spectra for representative compounds of each class are given in Figures 1 to 5. The criterion of stabilizer effectiveness is overall spectral growth in the visible following storage in air. Class I compounds exhibit little or no spectral growth and are visually colorless. Class II compounds show a small spectral growth, appearing slightly colored to the eye, while class III compounds are grossly discolored, differing little from irradiated PVC.

An approximate measure of color development among the various stabilizers is

$$\Delta A_{5000\ \text{Å}}/\bar{X},$$

TABLE I

Group	Compound	Wt %	N₂ storage time, hr	Air storage time, hr	$\dfrac{\Delta A_{5000\,\text{Å}}}{\bar{X}}$
I					
	(1) Tetrahydrofuran	8.5	19.1	49.2	0
	(2) 3-Hydroxytetrahydrofuran	5.4	25.5	68.6	0.71
	(3) 1,3-Dioxolane	7.3	19.8	71.5	0
	(4) 1,4-Dioxane	9.5	19.8	71.6	0
	(5) 1,3-Dioxane	9.2	19.9	71.7	0
	(6) 2-(Tetrahydrofurfuryloxy)-tetrahydropyran	4.9	65.8	48.0	1.3
		2.2	22.2	69.6	7.5
	(7) 2-Hydroxymethyl-1,4-benzodioxan	5.1	65.7	50.9	0.85
	(8) Fluorene	5.2	19.7	75.3	1.3
	(9) Anthracene	5.5	26.1	68.1	0
		1.4	22.2	69.7	3.2
	(10) Tetrahydrothiophene	5.9	25.5	69.7	3
	(11) 1,4-Thioxane	4.9	25.9	70.0	0
II					
	(12) Tetrahydropyran-2-methanol	5.3	21.7	69.4	4.7
	(13) 2-(2-chloroethoxy)tetra-hydropyran	6.0	21.8	69.5	4.4
	(14) Dibenzofuran	5.1	19.8	75.8	7.8
	(15) 2-Hydroxy-4-n-octoxy-benzophenone	4.9	22.2	69.6	5.2
III					
	(16) Poly(vinyl chloride)		25.4	67.9	28
	(17) Epichlorohydrin	6.2	21.6	69.2	34
	(18) Tetrahydrofurfurylamine	6.7	25.8	68.4	25
	(19) Ethylene carbonate	5.4	21.5	69.1	29
	(20) S-Trioxane	4.9	25.6	68.5	23
	(21) Paraldehyde	5.7	26.2	68.0	18
	(22) N-Ethylmorpholine	6.3	25.9	68.3	42
	(23) Oxepane	5.6	26.0	68.2	26
	(24) t-Butyl ether	6.8	22.9	70.0	32
	(25) Polyglycol	5.6	22.4	70.0	—
	(26) Pentamethylene sulfide	4.2	25.6	69.8	—
	(27) p-Dithiane	3.1	25.7	69.9	—

where $\Delta A_{5000\,\text{Å}}$ is the absorbance increase at 5000 Å following irradiation and storage in nitrogen and air, and $\bar{X}$ is the average film thickness. This factor is approximately equivalent to

$$\sum_i \epsilon_i C_i$$

where the summation is over all polyene lengths absorbing at 5000 Å, ϵ_i is the extinction coefficient, and C_i is the concentration of each polyene species. It is assumed here that the same polyene populations, that is, similar concentration ratios of polyene lengths, exist in all stabilized
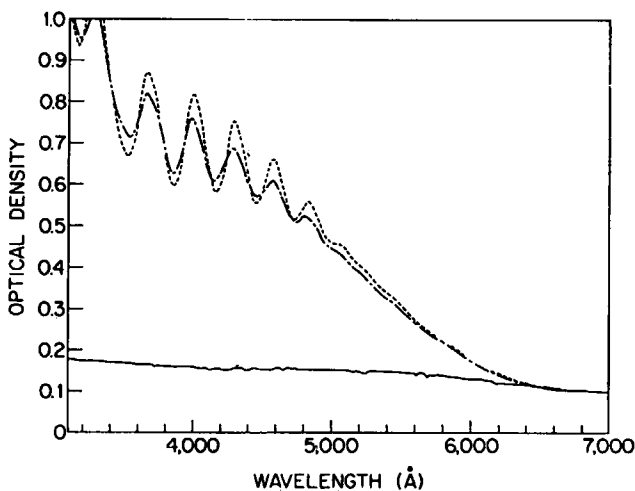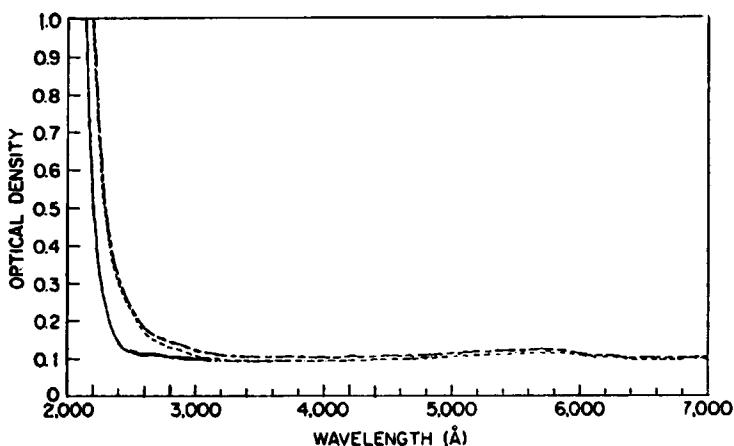
Fig. 1. UV-visible spectra of PVC: (—) control; (- - - - -) irradiated, 6 Mrad, stored in
N₂ for 25.4 hr; (— - — —) stored in air for 67.9 hr.

films and that the sole effect of each stabilizer is to retard the population,
more or less. Spectral contours of the irradiated and aged films support
this assumption. The factor $\Delta A/\bar{X}$ is therefore proportional to polyene
concentration present in the degraded films, providing a valid relative
comparison of color among the stabilizers studied. In terms of this
factor, class I compounds fall in the range 0–1.3, class II, in the range
4.4–7.8, and class III, in the range 18–42, with 28 as the value for PVC.

It is noted that a more general measure of total polyene development for
PVC would be $\int_{7000}^{2000} I\,d\nu$, thereby yielding total absorption regardless of
local intensity variations. With the assumption of a constant relative

Fig. 2. UV-visible spectra of PVC + 7.3% 1,3-dioxolane: (—) control; (- - - - -) ir-
radiated, 6 Mrad, stored in N₂ for 19.8 hr; (— - — —) stored in air for 71.5 hr.
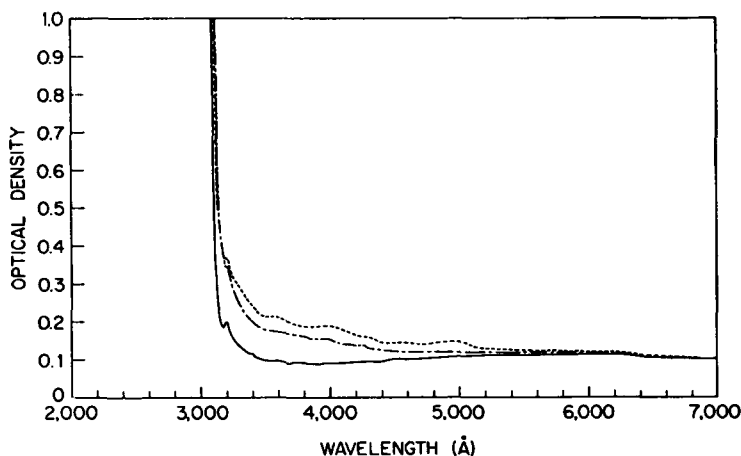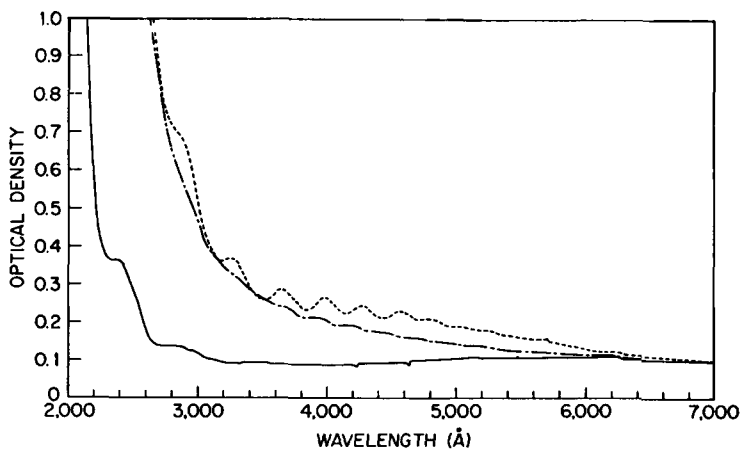
Fig. 3. UV-visible spectra of PVC + 5.2% fluorene: (—) control; (- - - - -) irradiated, 6 Mrad, stored in N₂ for 19.7 hr; (— - —) stored in air for 75.3 hr.

distribution of polyene lengths, this function provides a more sensitive measure of degradation in the early stages.

Stabilizer mechanisms accounting for class I and II effects are best dealt with by distinguishing between aromatic and nonaromatic systems. The effectiveness of many aromatics as radiolytic stabilizers in polymers of all types is well documented.[5,6] We assume that similar mechanisms of excited state interaction and energy dissipation apply here as well. Hence, the stability of PVC containing I-8,9 and II-14,15 is attributed to efficient coupling between the radiation input or polymer excited states and the aromatic systems.

Fig. 4. UV-visible spectra of PVC + 5.3% tetrahydropyran-2-methanol: (—) control; (- - - - -) irradiated, 6 Mrad, stored in N₂ for 21.7 hr; (— — —) stored in air for 69.4 hr.
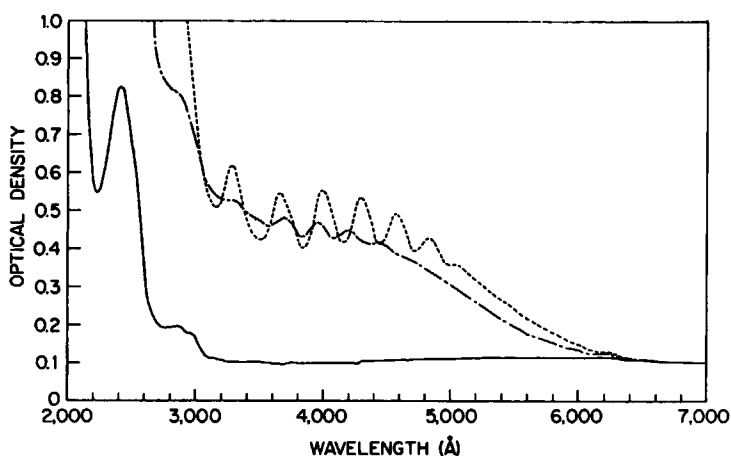
Fig. 5. UV-visible spectra of PVC + 5.4% ethylene carbonate: (—) control; (- - - - -) irradiated, 6 Mrad, stored in N_2 for 21.5 hr; (— – —) stored in air for 69.1 hr

Cyclic ethers other than epoxides appear to be little known as radiolytic stabilizers. Of eleven such systems studied here it was immediately apparent that five- and six-membered rings containing one or two oxygens imparted a high measure of stability, the only exception being tetra-hydrofurfurylamine. However, films compounded with this ether as well as N-ethylmorpholine emerged yellow from the molding process, implying a destabilizing influence of amine groups. Three- and seven-membered rings, rings with three oxygens, and noncyclic ethers exhibited no stabilizing influence. Cyclic sulfides generally were nonstabilizers, although compounds 10 and 11 proved effective. Excluding the latter from the class of pure sulfides leaves tetrahydrothiophene as an isolated cyclic sulfide stabilizer.

ESR studies on unstabilized PVC and PVC containing cyclic ether and aromatic additives provided only qualitative information. The well-known[7] ESR spectrum of PVC irradiated at 77°K and stored at 77°K, 195°K, and 293°K was observed. Of the stabilized materials, two types of interaction were apparent. PVC–THF yielded low-temperature spectra nearly identical to PVC alone, that is, a well-resolved multiplet of six peaks, decaying somewhat after storage at 195°K. Following storage at 318°K, the PVC–THF signal decayed nearly to zero, whereas PVC alone exhibited an unresolved signal of far greater intensity. These results are consistent with a radical mechanism whereby alkyl radicals initially situated on the PVC backbone at low temperatures react directly with THF by hydrogen transfer when the temperature is such as to permit sufficient mobility of the system. In order to account for the loss of ESR signal, further radical reactions within the THF rings must be postulated and will be discussed below. Fluorene and 2-hydroxymethyl-1,4-benzodioxan additives yielded a totally different response. An unsymmetrical unresolved signal resulted immediately in both cases at

77°K, again decaying substantially at room temperature. Insofar as the 77°K signal did not at all resemble that of PVC, we conclude that the primary radiolytic effect either appears in the aromatic stabilizers or is transferred to them.
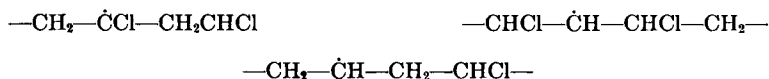
Cyclic ethers may function in a variety of ways. The oxiranes (epoxides) can function as HCl acceptors,
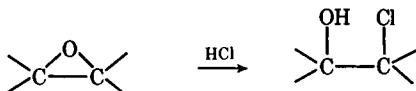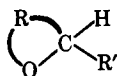

while higher cyclic ethers may act in a manner analogous to the HX antioxidants,
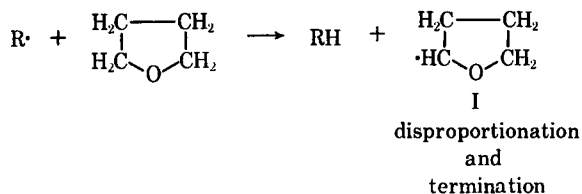
where R· is any of the following radicals:

—CH₂—ĊCl—CH₂CHCl   —CHCl—ĊH—CHCl—CH₂—

—CH₂—ĊH—CH₂—CHCl—

This hydrogen-transfer reaction should be particularly facile with those cyclic ethers possessing a tertiary hydrogen on the α-carbon atom,

and the data in Table I show that this structural feature is present in many of the class I and class II stabilizers. One can speculate about the possibility of further dehydrogenation of species such as compound I by transfer of hydrogen atoms to other R· radicals leading to aromatic or quasi-aromatic systems. If this mechanism is valid, then substances such as tetralin (II) might be expected to be radiolytic stabilizers in PVC as the driving force toward aromatic stability promotes hydrogen donation:
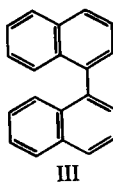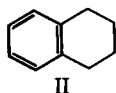
In the case of tetralin, a further reaction converts it to 1,1-binaphthyl (III) in the presence of polyhalo compounds.[8] The resulting aromatic systems

then could stabilize in a manner analogous to anthracene. In other words, the original stabilizer is being converted to a second type of stabilizer while it is performing its function as a hydrogen donor.

CONCLUSIONS

Color stability in irradiated poly(vinyl chloride) is achieved by addition of radical scavengers such as the cyclic ethers and by primary energy absorbers as certain aromatics. Structural requirements for radical scavengers include hydrogen(s) on the α-carbon in five- and six-membered cyclic ethers. All indications point to a potentially large number of substituted cyclic ethers and aromatics which may function as radiolytic stabilizers.

An extension of these results into areas of wider applicability requires answers to the following: (1) Will these materials function as UV or thermal stabilizers in PVC, and (2) will they stabilize other polymers in like manner? The radical chain mechanism for dehydrochlorination in PVC is common to both UV and electron-induced dehydrochlorination, leaving open the possibility that radiolytic stabilizers will be effective UV stabilizers. Recent experimental results indicate the effectiveness of class I cyclic ethers as color stabilizers in the presence of GE type RS sunlamp light, in air. However, if activation of the cyclic ethers occurs during irradiation with 1 MeV electrons, one would not expect stabilization against ultraviolet light above about 2200 Å by the same mechanism, where available energy is insufficient for activation.

References

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