

# Ionic Mechanisms in Pulse Irradiated Poly(vinyl chloride) System Containing Stabilizing Additives

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**ABSTRACT:** The pulse radiolysis studies of poly(vinyl chloride), PVC, film containing stabilizers i.e., Tinuvin P, Irgastab PVC 11, and Irganox 1076 have been carried out with the main aim of investigating ionic reactions in these systems. The evidences are presented concerning the formation of ionic transients in model solvents i.e. 2-propanol and *sec*-butyl chloride as well as in PVC film. In PVC-stabilizer system under consideration the additives can contribute to the positive charge transfer processes whereas

Tinuvin P, in addition may scavenge effectively electrons (the rate constant for  $e_{\text{solv}}^-$  scavenging in 2-propanol equals  $5.9 \times 10^9 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ ) influencing the negative charge scavenging by PVC matrix itself and the HCl formation during the radiolysis of PVC. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 562–567, 2007

**Key words:** poly(vinyl chloride); pulse radiolysis; stabilizers; Tinuvin P; Irgastab PVC 11; Irganox 1076; radical ions

## INTRODUCTION

Poly(vinyl chloride), PVC, has a large range of practical applications because of its ability to undergo modification in properties by addition of several types of admixtures, such as plasticizers, stabilizers, etc. The medical applications of PVC products require sterilization to prevent the contamination by microorganisms. The sterilization can be done by ionizing radiation but the irradiation can also influence the degradation of PVC matrix.

The effects of ionizing radiation on PVC have been studied particularly in relation to the influence of additives on physical, chemical, mechanical, and biological properties of the customized PVC system.

A new approach to the commonly accepted radical mechanism of radiation induced PVC degradation has been proposed very recently in our laboratory.<sup>1,2</sup> A short review of literature data devoted to the problem under consideration has been presented therein.<sup>1,2</sup>

The convincing set of evidences has been shown<sup>1,2</sup> for the novel mechanism including ionic reactions as a fundamental stage of physical–chemical events taking place during the radiolysis of PVC system.

Stabilizing additives provide the required stability of the polymeric systems towards heat, light, and ionizing radiation. Lerke and Szymanski<sup>3</sup> have studied the effect of epoxy stabilizers on radiation yield of

hydrogen chloride in gamma irradiated PVC. Świerż-Motyśia<sup>4</sup> found that it was possible to formulate PVC systems containing costabilizers (compounds containing phenol or epoxy amide groups) and as a result an improvement of radiation stability was obtained. Very recently, Vinhas et al.<sup>5,6</sup> found that UV light absorber, Tinuvin P, protected gamma irradiated PVC system against degradation by chain scissions.

The aim of this study is to show the ionic reaction mechanisms involved in the radiation induced transformations of PVC in the presence of stabilizers i.e., Tinuvin P, Irganox 1076, and Irgastab PVC 11 (all commercial names by Ciba, see Experimental). Our aim is to use pulse radiolysis method to find experimental evidences concerning the charge transfer processes that occur in irradiated PVC matrix containing such additives.

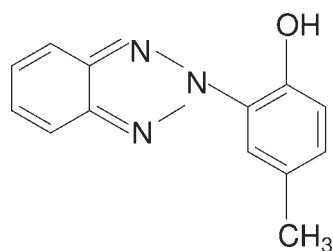
The ionic approach to the mechanism of radiation induced degradation of the PVC would have the great impact on the progress in development of novel PVC formulations. It ought to help in the willful design of the admixtures chemical structure, which could be effective in scavenging of the primary ionic PVC species. It seems to be the way to discover a new type of compounds (plasticizers, stabilizers, etc.) which may influence the degradation of polymer itself as well as the yield of harmful end-products i.e., HCl.

## EXPERIMENTAL

Poly(vinyl chloride), PVC, for medical application, S-70 SM product of Anwil SA (Poland) was used as received. Tetrahydrofuran, THF, HPLC grade, inhibitor free (Aldrich, product no. 27,038-5) was used as

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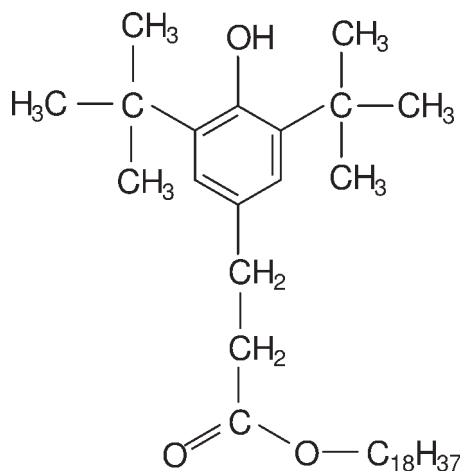
Scheme 1

a solvent for PVC film preparation; 2-propanol, spectroscopic grade (Merck), and *sec*-butyl chloride, G.C 99+% (Aldrich) were used as received. All liquid solutions were deoxygenated by bubbling argon or nitrogen gas for  $\sim 30$  min.

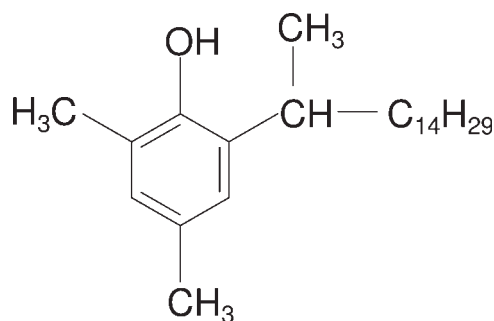
Three compounds, Ciba Specialty Chemical products, were used as a stabilizers i.e., Tinuvin P (2-(2H-benzotriazol-2-yl)-*p*-cresol, product no. 0304832), (Scheme 1), Irganox 1076 (octadecyl-3-(3'5'-di-*tert*-butyl-4'-hydroxy-phenyl)-propionate, antioxidant product no. 0329956 AD), (Scheme 2), and Irgastab PVC 11 (2,4-dimethyl-6-(1-methyl-pentadecyl)phenol, product no. 3882450 AA) (Scheme 3).

PVC-stabilizer films were cast from their THF solutions. The solvent was removed from the sample by evaporation at room temperature and finally the film was kept in a sample holder in vacuum ( $\sim 10^{-4}$  mmHg) for at least 10 h prior to the pulse radiolysis experiment.

The pulse radiolysis measurements were carried out using a linear electron accelerator ELU-6 (USSR made) that delivered pulses of different time scales/doses: 17 ns (dose  $\sim 50$  Gy), 1  $\mu$ s (dose  $\sim 200$  Gy), and 4  $\mu$ s (dose  $\sim 500$  Gy). The home-made styro-foam-copper cryostat through which cold nitrogen was passed and enabled experiments at temperatures down to  $\sim 90$  K. The Hamamatsu R-928 photomultiplier was used as a light detector. The signals were recorded on digitizing scopes either Philips PH



Scheme 2

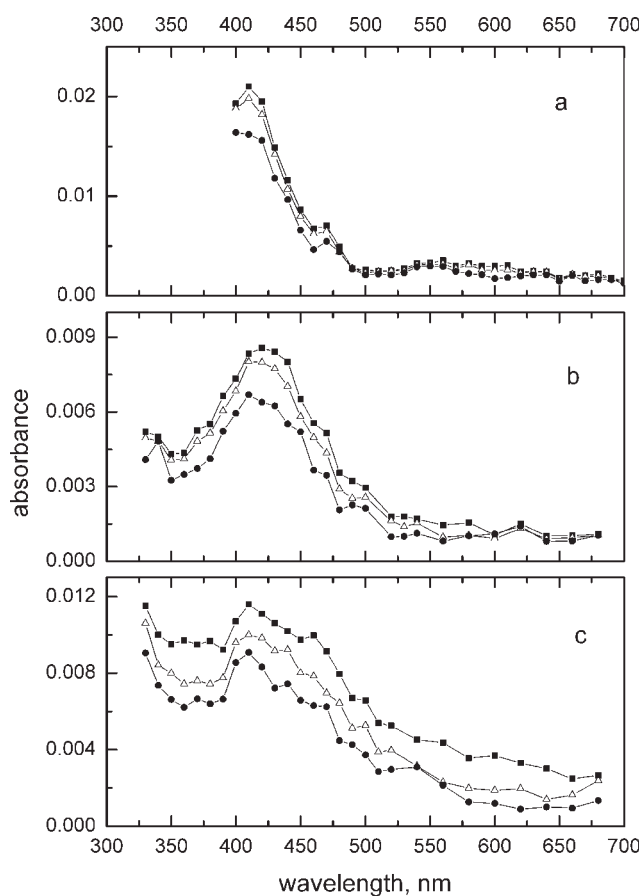


Scheme 3

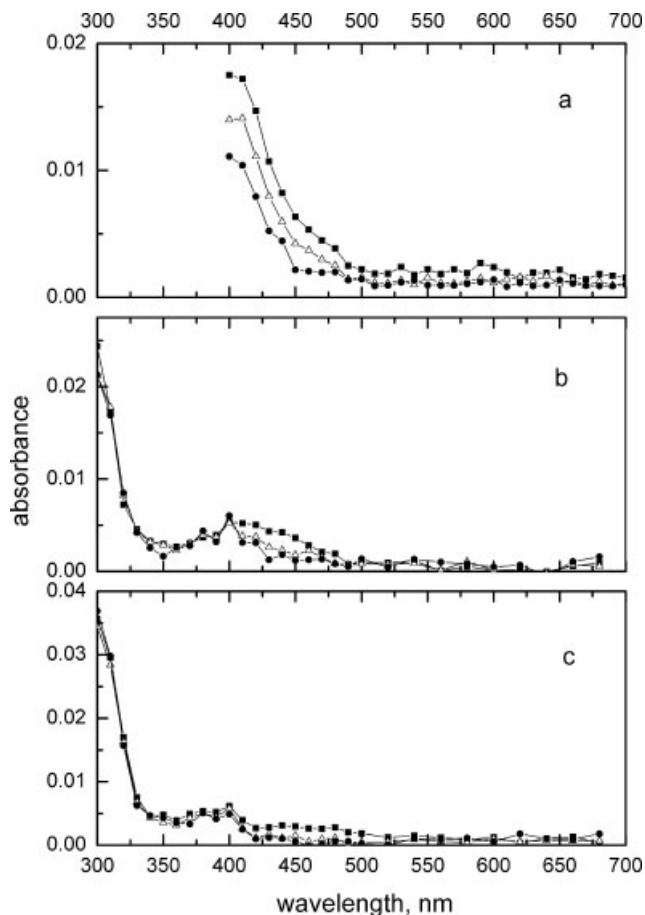
3320 or Tectronix TDS 540 and transferred via interface to IBM-PC computer for storage and analysis. More details concerning detection system and the accelerator can be found elsewhere.<sup>7</sup>

## RESULTS AND DISCUSSION

The influence of temperature on the pulse radiolysis spectra of PVC films containing stabilizing additives is shown in Figures 1 and 2.



**Figure 1** The low temperature transient absorption spectra of PVC film containing: (a) Tinuvin P (2.4% by weight, thickness 0.46 mm, 110 K); (b) Irgastab PVC 11 (2% by weight, thickness 0.43 mm, 96 K); (c) Irganox 1076 (2.3% by weight, thickness 0.48 mm, 96 K). ■-10  $\mu$ s;  $\Delta$ -100  $\mu$ s; ●-1 ms after the 4  $\mu$ s electron pulse.



**Figure 2** The room temperature transient absorption spectra of PVC film containing: (a) Tinuvin P (2.4% by weight, thickness 0.44 mm, 293 K); (b) Irgastab PVC 11 (2% by weight, thickness 0.43 mm, 294 K); (c) Irganox 1076 (2.3% by weight, thickness 0.48 mm, 294 K); ■-10  $\mu$ s;  $\Delta$ -100  $\mu$ s; ●-1 ms after the 4  $\mu$ s electron pulse.

Figure 1 shows the UV-VIS absorption spectra of PVC films doped with Tinuvin P, Irgastab PVC 11, and Irganox 1076 irradiated at low temperatures.

In the case of Tinuvin P system (2.4% by weight), the transient absorption increasing towards shorter wavelengths leveling at  $\sim 400$  nm was detected [Fig. 1(a)]. The weak maximum at 470 nm and a long tail extending towards IR can be observed (compare with Fig. 3).

The low temperature ( $\sim 96$  K) absorption spectra of pulse irradiated PVC samples containing Irgastab PVC 11 [Fig. 1(b)] and Irganox 1076 [Fig. 1(c)] are quite similar. In both cases the transient absorption bands in the range 390–500 nm can be observed with maxima at 420 and 410 nm for Irgastab PVC 11 and Irganox 1076, respectively.

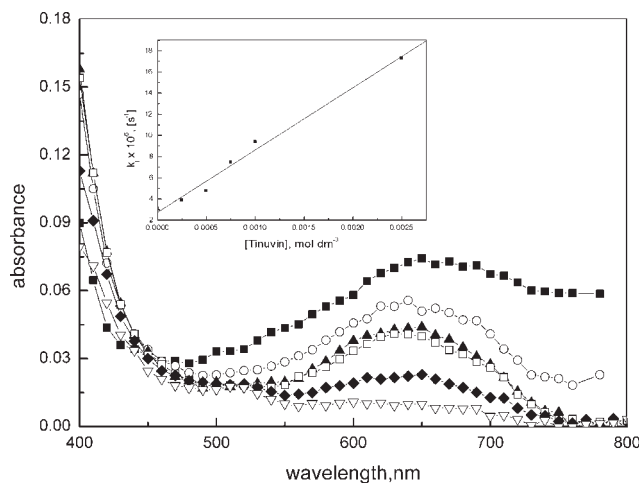
In general, the increase up to room temperature has no appreciable effect in the case of PVC-Tinuvin P system [Fig. 2(a)]. Certainly, the lifetime of the UV band seems to be shorter at higher temperature. At room temperature, in the range of 10  $\mu$ s–1 ms the absorption at

400 nm decreases to  $\sim 63\%$  of the initial value whereas at 110 K the corresponding number equals 75%.

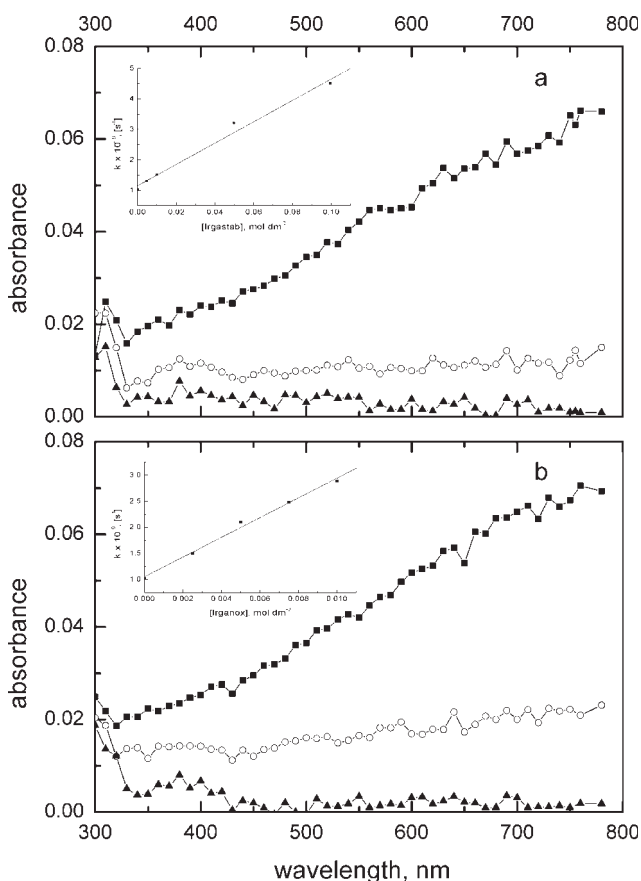
The room temperature absorption spectra of pulse irradiated PVC - Irgastab PVC 11 and PVC - Irganox 1076 systems are again quite similar. In both cases the wide, primary product bands in the range of 390–500 nm disappeared in the time range of 10  $\mu$ s–1 ms. This process seems to be faster for PVC-Irganox 1076 system. New bands with maxima at 380 nm and 400 nm can be found in both matrices. In addition, strong, almost stable absorptions rising towards 300 nm were detected.

To identify the origin of the transient species generated in PVC matrix containing the stabilizers under consideration, one has to assess the ability of these additives to scavenge charges i.e., electrons and positive holes.

Using 2-propanol as a solvent, the room temperature rate constants of  $e_{\text{solv}}^-$  reaction with Tinuvin P, Irgastab PVC 11, and Irganox 1076 were found to be equal to  $5.9 \times 10^9 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$  (Fig. 3, insert),  $3.5 \times 10^7 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$  [Fig. 4(a), insert], and  $1.9 \times 10^8 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$  [Fig. 4(b), insert], respectively. Comparing these values with the rate constant of  $e_{\text{aq}}^-$  with vinylchloride<sup>8</sup> i.e.,  $2.5 \times 10^8 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$  one can suggest that Tinuvin P may only compete with the PVC matrix in reaction with electrons. The mechanism of  $e_{\text{solv}}^-$  reaction with Tinuvin P seems to be quite complex. During the first 500 ns, the electron absorption band disappeared as can be observed in the 750–800 nm range where the tail of  $e_{\text{solv}}^-$  absorption is observable. At the same time, the primary product-anion absorption band ( $\lambda_{\text{max}} \sim 640$  nm) can be detected in the time scale up to  $\sim 50 \mu$ s [Figs. 3



**Figure 3** The room temperature transient absorption spectra of 2-propanol-Tinuvin P ( $2.6 \times 10^{-3} \text{ mol dm}^{-3}$ ) system; taken 50 ns (■), 100 ns (○), 500 ns (▲), 1  $\mu$ s (□), 10  $\mu$ s (◆), 40  $\mu$ s (▽) after the 17 ns electron pulse. Inset: The dependence of 1-st order rate constants of  $e_{\text{solv}}^- +$  Tinuvin P reaction versus Tinuvin P concentrations, measured at 750 nm.

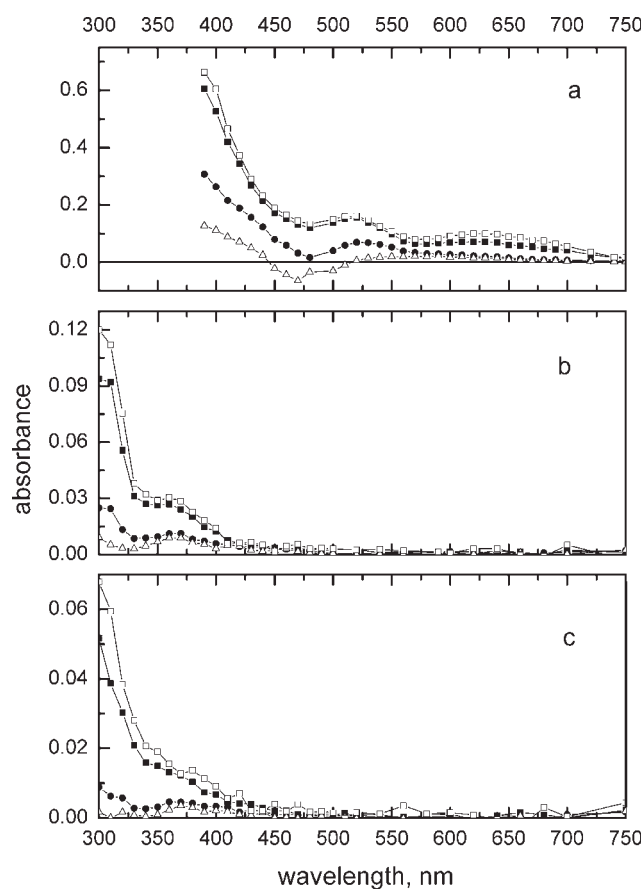


**Figure 4** The room temperature transient absorption spectra of 2-propanol solutions containing: (a) Irgastab PVC 11,  $2 \times 10^{-3} \text{ mol dm}^{-3}$  and (b) Irganox 1076,  $2 \times 10^{-3} \text{ mol dm}^{-3}$  taken at 100 ns (■), 500 ns (○), 5  $\mu\text{s}$  (▲), after the 17 ns electron pulse. Insets: The dependence of 1-st order rate constants of  $e_{\text{solv}}^-$  + suitable solute reaction versus its concentrations, measured at 750 nm.

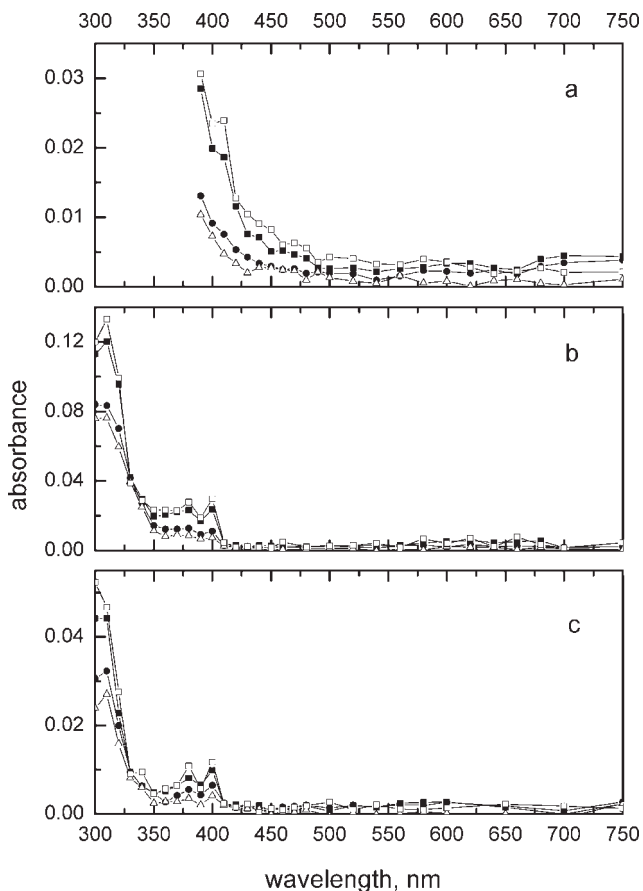
and 5(a)]. The secondary transient product with characteristic absorption maximum,  $\lambda_{\text{max}} \sim 520 \text{ nm}$  [Figs. 3 and 5(a)] decayed in millisecond time scale and seems to be associated with Tinuvin P end decomposition [Fig. 5(a) negative absorption]. Nakagawa<sup>9</sup> found evidences, that hydroxybenzotriazol in alcohol solutions can react with  $e_{\text{solv}}^-$  and anion is generated with negative charge localized on nitrogen. Simultaneously the  $>\text{N}-\text{OH}$  bond is broken leading to the  $\cdot\text{OH}$  radical formation. The recombination of benzotriazol anion with protonated solvent cation may generate benzotriazol molecule. One has to assume the formation of the benzotriazol in our system too, the compound reactive towards  $e_{\text{solv}}^-$  in alcohol solvent. The spectrum of benzotriazol anion in gamma irradiated methyltetrahydrofuran glass at 77 K can be characterized by wide band with maximum at 674 nm and UV absorption below 400 nm.<sup>10</sup>

The kinetic data for Irgastab PVC 11 and Irganox 1076 obtained presently can be compared with the rate constant of  $e_{\text{aq}}^-$  and *p*-cresol<sup>11</sup> i.e.,  $4.2 \times 10^7$

$\text{mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ . In pulse irradiated 2-propanol solutions containing these two additives, the disappearance of  $e_{\text{solv}}^-$  absorption in visible range was detected in about 100 ns time scale (Fig. 4) and simultaneously the traces of anion product formation were also observed. The transient UV bands of anion-products in 2-propanol for Irgastab PVC 11 and Irganox 1076 can be undoubtedly found in microseconds ( $\mu\text{s}$ ) time scale [Fig. 5(b,c)]. In both cases, the rising absorption towards UV (300–330 nm range) with well defined shoulder up to 400 nm can be observed. At longer time scale (1 ms), the weak bands with maxima at 370 nm were still observed. Irganox 1076 (Scheme 2) can be characterized as having two centers active towards electrons i.e., the aromatic ring of substituted phenol structure as well as the ester group in  $-\text{CH}_2\text{CH}_2\text{COOC}_{18}\text{H}_{37}$  side chain. While, Irgastab PVC 11 (Scheme 3) can be characterized by electron accepting center based on aromatic ring of substituted phenol only. The similar spectra of anionic-product detected for both admixtures in 2-propanol may strongly suggest that the active sites



**Figure 5** The room temperature transient absorption spectra of 2-propanol solutions containing: (a) Tinuvin P,  $2.6 \times 10^{-3} \text{ mol dm}^{-3}$ ; (b) Irgastab PVC 11,  $2 \times 10^{-3} \text{ mol dm}^{-3}$ ; (c) Irganox 1076,  $2 \times 10^{-3} \text{ mol dm}^{-3}$  taken at 5  $\mu\text{s}$  (□), 10  $\mu\text{s}$  (■), 100  $\mu\text{s}$  (●), and 1 ms (△), after the 1  $\mu\text{s}$  electron pulse.



**Figure 6** The room temperature transient absorption spectra of *sec*-butyl chloride containing: (a) Tinuvin P; (b) Irgastab PVC 11; (c) Irganox 1076; solute concentration  $2 \times 10^{-3} \text{ mol dm}^{-3}$ , taken  $5 \mu\text{s}$  ( $\square$ ),  $10 \mu\text{s}$  ( $\blacksquare$ ),  $100 \mu\text{s}$  ( $\bullet$ ), and  $1 \text{ ms}$  ( $\triangle$ ) after the  $1 \mu\text{s}$  pulse.

towards electrons in these compounds are similar i.e., aromatic ring of substituted phenol molecule.

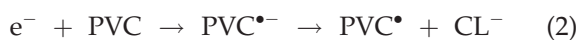
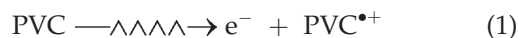
In the irradiated PVC-stabilizer system the most probable mechanism should involve the scavenging of positive holes.<sup>1</sup> Figure 6 shows the absorption spectra of pulse irradiated *sec*-butyl chloride (positive charge donor)-stabilizer samples at room temperature.

For *sec*-butyl chloride-Irgastab PVC 11 and *sec*-butyl chloride-Irganox 1076 systems the very similar absorption spectra of the cationic products were detected. In both cases the well defined maxima at 380 and 400 nm and the rising absorption towards UV (with maxima at  $\sim 310 \text{ nm}$ ) can be observed. Using the same arguments as were used for anion structure one may suggest that the positive charge is localized on aromatic ring of substituted phenol molecules. Low temperature spectra of Irgastab PVC 11 and Irganox 1076 products observed in PVC film at low temperature (Fig. 1) may be treated as primary cations where positive charge is localized on whole

molecule. The Irgastab PVC 11 and Irganox 1076 cations absorption spectra obtained in irradiated *sec*-butyl chloride solutions at room temperature resemble absorption spectra of these additives in irradiated PVC film at the same temperature (Figs. 2 and 6). It is worth to mention that Irganox 1076 as a positive charge scavenger was suggested to be active in pulse irradiated polypropylene films.<sup>12</sup>

Tinuvin P can react with positive holes generated in pulse irradiated *sec*-butyl chloride and the solute cation UV absorption band can be observed in 390–500 nm spectral range. The weak maxima were detected at 410 nm in the time range of 5–100  $\mu\text{s}$  (Fig. 6).

Taking into account the results described earlier, the following main reactions may be taken into consideration:



where, Stab. denotes stabilizers—Tinuvin P, Irgastab PVC 11, and Irganox 1076 (antioxidant);  $\text{PVC}^{\bullet-}$  and  $\text{PVC}^{\bullet+}$ —matrix radical ions; and  $\text{PVC}^{\bullet}$ —matrix macroradicals. Having in mind the kinetic data found in 2-propanol solutions and ionic product absorption spectra (Figs. 2 and 6) one can suggest that Irgastab PVC 11 and Irganox 1076 are mainly involved in reaction (4) and consequently may interfere into macroradical formation mechanisms.<sup>1</sup> The concentration of stabilizers in PVC matrix is not so high (few % by weight), hence the effect should not be so distinct. Tinuvin P due to high reactivity towards the negative charges (electrons) may decrease in addition the hydrogen chloride generation too.<sup>1</sup> The involvement of additives in reaction (3) and (4) is strongly dependent on local concentration of stabilizers in solid PVC film which may be different from the average one because of the heterogeneity of solid phase. One has to remember that stabilizers can decompose during the radiolysis (see Tinuvin P results) influencing the concentration dependent mechanisms.

## CONCLUSIONS

- The stabilizers under consideration can interfere into ionic mechanisms of PVC degradation during radiolysis.
- These ionic reactions ought mainly contribute to the macroradical formation processes although

one may expect the decrease of HCl formation in the case of good  $e^-$  scavengers (i.e., Tinuvin P).

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## References

1. Mayer, J.; Szadkowska-Nicze, M. J Photochem Photobiol A 2006, 177, 185; and literature cited there.
2. Mayer, J.; Szadkowska-Nicze, M. J Photochem Photobiol A 2006, 183, 106.
3. Lerke, I.; Szymanski, W. J Appl Polym Sci 1977, 21, 2067.
4. Świerz-Motysia, M. B. Polimery (Warsaw) 2003, 48, 434.
5. Vinhas, G. M.; Souto-Maior, R. M.; de Almeida, Y. M. B. Polym Degrad Stab 2004, 83, 429.
6. Vinhas, G. M.; Souto-Maior, R. M.; de Almeida, Y. M. B.; Neto, B. B. Polym Degrad Stab 2004, 86, 431.
7. Karolczak, S. In Properties and Reactions of Radiation Induced Transients. Selected Topics.; Mayer, J., Ed.; Polish Scient. Publ. PWN: Warszawa 1999; Chapter 1, pp 11-37.
8. Koester, R.; Asmus, A.-D. Z Naturforsch Teil B 1971, 26, 1108.
9. Nakagawa, S. Radiat Phys Chem 2005, 74, 86.
10. Shida, T. Phys Sci Data 1984, 34, 205.
11. Feitelson, J.; Hayon, E. J Phys Chem 1973, 77, 10.
12. Mayer, J.; Szreder, T. Radiat Phys Chem 2002, 63, 161.