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Ionic transient species in irradiated poly(vinyl chloride) film

J. Mayer, M. Szadkowska-Nicze*

Institute of Applied Radiation Chemistry, Technical University, Wróblewskiego 15, 93-590 Łódź, Poland

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Abstract

The studies of transient species in irradiated poly(vinyl chloride) (PVC) film have been carried out with the main aim of investigating the charge trapping in a pure system. In PVC, pulse radiolysis gives electron-positive hole pairs. The electron can generate a matrix anion due to the presence of chlorine atom in the PVC macromolecules followed by Cl^- detachment. The positive hole may be stabilized as a short-lived matrix cation characterized by visible absorption band with wide maximum in the 350–650 nm range. The positive holes can be scavenged by additives like pyrene, Py and respective radical-ions of Py can be detected. The rate of Py radical cations decay at ∼450 nm was found to be temperature dependent. Two linear parts of the Arrhenius plot were observed which intersected in the 200–240 K range, which is close to the mechanical loss peak connected with the β relaxation in PVC matrix. The activation energies calculated for two parts of Arrhenius plot were equal to 0.40 kJ mol^{-1} for $T < 200$ K and 52.6 kJ mol^{-1} for $T > 240$ K. The novel mechanism of the ionic and radical reactions in PVC is proposed and discussed.

Keywords: Poly(vinyl chloride); Pulse radiolysis; Ion recombination; Pyrene; Radical ions; Matrix relaxation

1. Introduction

Poly(vinyl chloride), PVC, after modification due to different type of additives is one of the most used polymer system in the world. Among many applications plasticized PVC is used in the production of disposable medical devices which have to be sterile. The "killing" of microorganisms can be done by exposure to ionizing radiation (e.g. gamma rays, electron beams) although the irradiation can also stimulate the degradation processes in PVC.

The sensitivity of the PVC towards heat, light, aging and radiation can be illustrated by the formation of hydrogen chloride, discoloration, changes in the mechanical properties and molecular weight.

It is generally assumed that the degradation of PVC proceeds through the radical mechanism.

The general characteristics of radiation chemistry of PVC have been described in few, rather old, monographs [1–3]. A number of research studies have been made on the radiation-induced degradation of PVC [4–14].

The radiation effects on PVC are very complex since many reactions take place simultaneously resulting mainly in hydrogen chloride evolution and polyene chains formation as the end products. It was proved by ESR technique that polyenyl radicals as well as allyl ones are the main intermediates formed as a result of irradiation.

However, the primary processes taking place in irradiated PVC have not yet been fully elucidated. Torikai et al. [15–17] found some evidences and suggested that the precursors of the free radicals can be the ionic species. They observed the formation of additive radical cations during the gamma irradiation of PVC film at liquid nitrogen temperature and they proposed the mechanism involved.

In this paper, we decided for the first time, to investigate the primary ionic reactions taking place in irradiated PVC pure and in the presence of scavengers in the temperature range down to 77 K. Due to their transparency, the PVC film – samples can be examined using pulse radiolysis technique and hence we hope to generate the original data

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* Corresponding author. Tel.: +48 42 631 3173; fax: +48 42 636 0246.
E-mail address: magdanis@mitr.p.lodz.pl (M. Szadkowska-Nicze).

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concerning the short-lived species produced there by ionizing radiation.

In addition, the PVC results we intend to compare with other polymeric systems, e.g. polyethylene [18,19], polypropylene [20,25], poly(methyl methacrylate) [21], poly(dimethylsiloxane) [22], nafion [23] and poly(ethylene terephthalate) [24] investigated so far in our laboratory.

2. Experimental details

2.1. Materials

Three types of poly(vinyl chloride), PVC as a powder have been used in our experiments. PVC for medical application, S-70 SM product of Anwil SA (Poland) was used as received. The PVC, secondary standard, (Aldrich, product no. 28,262-1, molecular weights as determined by Aldrich using light scattering and gel permeation chromatography methods equaled 77,300 and 87,000, respectively) was used as received and for comparison some experiments were done using PVC (Aldrich, product no. 189588, $M_w = 62{,}000$) for R&D only.

Tetrahydrofuran, THF, HPLC grade, inhibitor free (Aldrich, product no. 27038-5) was used as a solvent. In some experiments THF containing inhibitor, butylated hydroxytoluene (BHT) was also used.

Pyrene, Py, (Sigma, product no. P-2146) after the crystallization from ethanol was additionally purified by sublimation. Triethylamine (TEA) 99% (Lancaster Synthesis) and methanol, pure pro analysis (POCh, Poland) were used as received.

PVC films were cast from the THF solution. Solvent was removed from the film by evaporation at room temperature and finally in vacuum (ca. 10^{-4} mmHg for at least 10 h). Py was dissolved in THF solution of PVC and polymeric film containing an additive was obtained by the described method. TEA were added by soaking the deareated PVC film in this chemical then the sample was washed using methanol. Ten pieces of PVC film (ca. 0.1 mm thickness each) can be conveniently introduced into pulse radiolysis sample holder.

2.2. Methods

The pulse radiolysis measurements were carried out using a linear electron accelerator ELU-6 (USSR made) which delivered 17 ns (dose ca. 50 Gy), 1 μs (dose ca. 200 Gy) and 4 μs (dose ca. 500 Gy) pulses. The accelerator was also used in certain experiments as a stationary irradiation source. The home-made styrofoam-copper cryostate through which cold nitrogen was passed enabled experiments at temperatures down to 100 K. The Hamamatsu R-928 photomultiplier was used as a light detector. The signals were recorded on digitizing scopes either Philips PH 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 [26].

The low temperature steady-state radiolysis products were examined at 77 K and at higher temperatures using Carry 5 spectrophotometer (Varian) and CF 1204 (Oxford Instr. Ltd.) continuous flow cryostate.

3. Results and discussion

Fig. 1 shows UV–vis absorption spectra of pulse irradiated, deareated PVC film (S-70 SM, Anwil SA) measured at ca. 100 K, taken 10 μs and 1.75 ms after the 4 μs electron pulse. In general, the absorbance increased towards shorter wavelengths but no characteristic maxima were observed in UV–vis spectral range (down to 300 nm). It is clearly seen in the next picture (Fig. 2), where the absorbances which disappeared during the first 100 μs (A_0–A_{100}) and 1.5 ms (A_0–$A_{1.5}$) were shown for pulse irradiated PVC film (Aldrich, secondary standard). These absorption bands start to be negligible for wavelengths higher than 750 nm. The faster decay of red wing of the spectrum is shown (inset, Fig. 2). The absorption band under consideration was influenced by TEA (Fig. 1, insert) suggesting that intermediates responsible for such absorption have been generated via positive charge transfer.

So far nothing is known about the ionic species produced during the irradiation of pure PVC. The mechanism of radiation-induced reaction in PVC has been explained by radical mechanism. The radicals, probably alkyl ones may be responsible for the UV absorption (<350 nm).

Following the steady-state irradiation of PVC film at room temperature, UV–vis absorption spectra of polymeric sample are characterized by a distinctive shape (Fig. 3) which is connected with polyenyl radicals [8]. The post-irradiation storage at 353 K resulted in a series of weak absorption peaks corresponding to a polyene formation which are superimposed

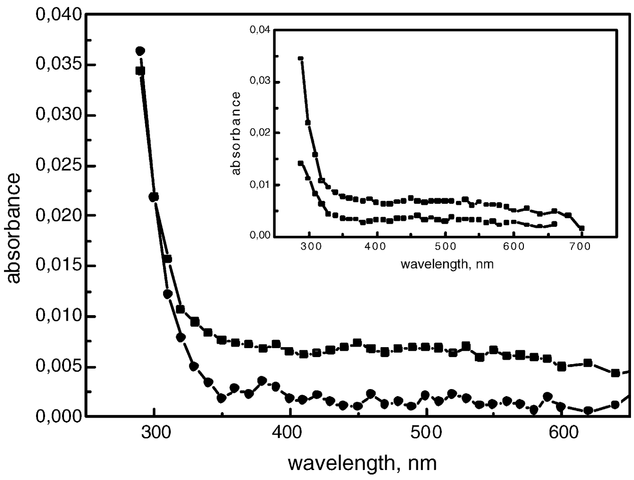

Fig. 1. Transient absorption spectra of pulse irradiated, deareated PVC film (Anwil S-70 SM) measured at ca. 100 K, taken 10 μs (■) and 1.75 ms (●) after the 4 μs electron pulse. Inset: 10 μs spectra of pulse irradiated PVC film pure (□) and in the presence of TEA (■).

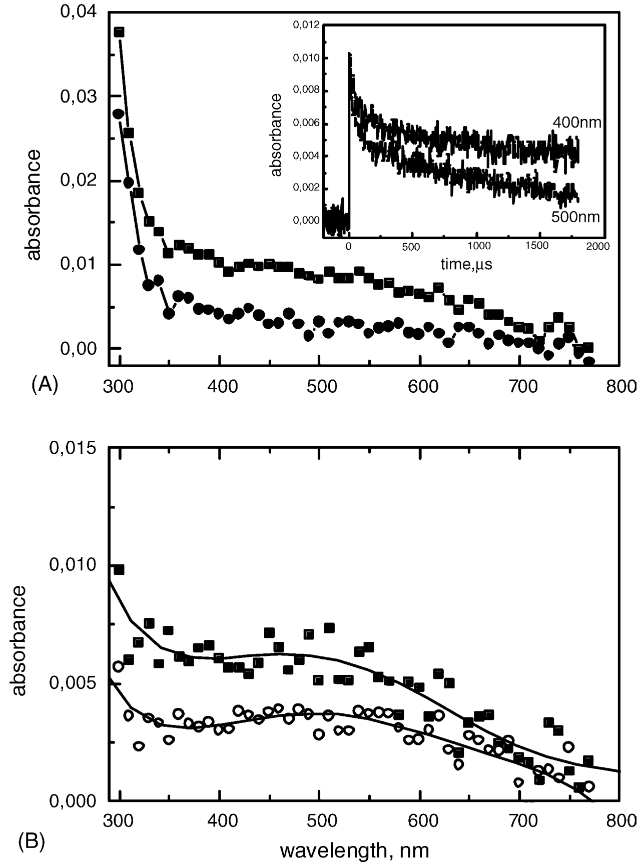

Fig. 2. Part A: transient absorption spectra of pulse irradiated, deareated PVC film (Aldrich, secondary standard) measured at ca. 100 K, taken 10 µs (■) and 1.5 ms (●) after the 4 µs electron pulse. Inset: oscilloscope traces of absorbance time profiles measured at 400 and 500 nm. Part B: the spectral distribution of the absorbance which disappeared during the first 100 µs (○) and 1.5 ms (■) for deareated PVC film. Data taken from Part A.

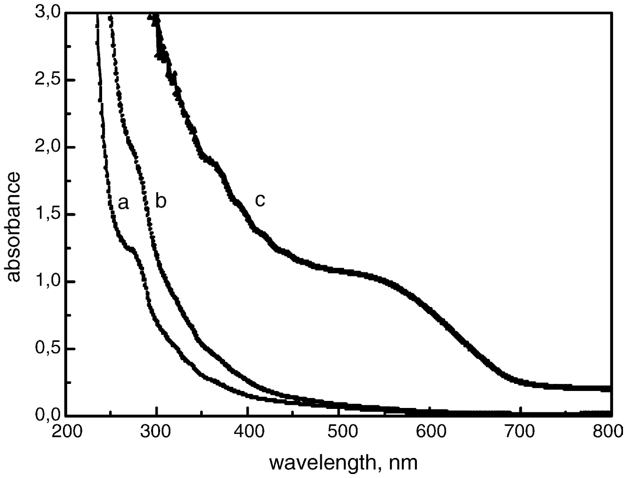

Fig. 3. The absorption spectra of PVC irradiated with dose ca. 4 kGy (a) and 29 kGy (b,c) at room temperature. The curve c represents absorption spectrum of PVC after storage of the irradiated sample during 2 h at temperature 353 K.

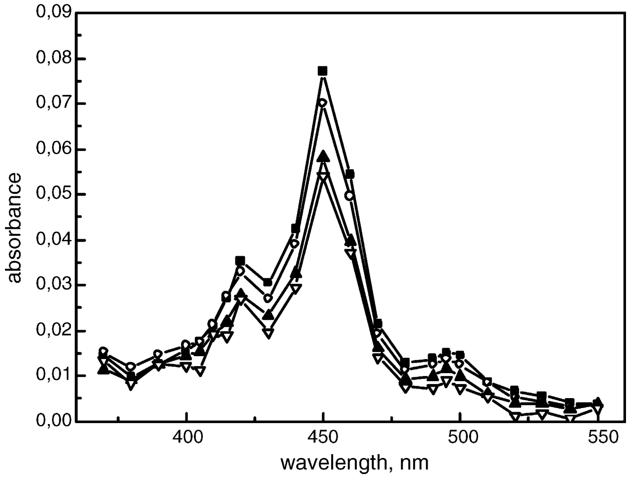

Fig. 4. The transient absorption spectra of PVC containing Py (10^{-1} mol dm^{-3}) pulse irradiated at 100 K taken 10 µs (■), 50 µs (○), 500 µs (▲) and 1.75 ms (▽) after the 4 µs pulse.

upon a band absorption maximum (Fig. 3) as it was observed previously [7].

In order to find more evidences concerning the formation of ionic species in PVC in the short time scale the pulse radiolysis of PVC in the presence of Py was performed. The use of Py as an intrinsic probe to investigate polymer systems behaviour has been an interesting subject of research for some time.

The concentration of Py added as a charge scavenger was in the range from 10^{-3} to 10^{-1} mol dm^{-3}. Solovey et al. [8] had found that free radical species were very sensitive even to the traces of reactive additives occluded in the PVC solid polymer.

The absorption spectra of pulse irradiated PVC doped with Py at 100 K are shown in Fig. 4. The assignment of the absorption band centered at 450 nm to the Py radical cation (Py$^{\bullet +}$) seems to be consistent with the spectra of these species in the other polymeric systems [19–23] and in PVC–Py system gamma-irradiated at 77 K and observed at higher temperatures up to 233 K in the steady-state conditions [16].

As would be expected only traces of Py radical anion (Py$^{\bullet -}$) absorption were detected in 490–500 nm range (Fig. 4). The weak maximum at 420 nm represents the same kinetic decay as it is found for Py$^{\bullet +}$ radical cation absorption. The absorption spectra of Py species in PVC matrix containing lower Py concentration (3.5×10^{-3} mol dm^{-3}) at 130 K are, in general, similar to the results shown in Fig. 4. At room temperature, the decay of Py radical ions (in particular Py$^{\bullet +}$) is faster comparing to low temperature results (Fig. 5). Again, the decay of 420 nm absorption band seems to be similar to the Py radical ions absorption behaviour. In the same time a new peak having λ_{max} at ∼410 nm grows (Fig. 5). The absorption peak at 409 nm was found in gamma-irradiated PVC–Py system and Torikai et al. [16] assigned this maximum to the cyclohexadienyl type Py radical. It was suggested that such radical might be produced from Py$^{\bullet +}$ as a

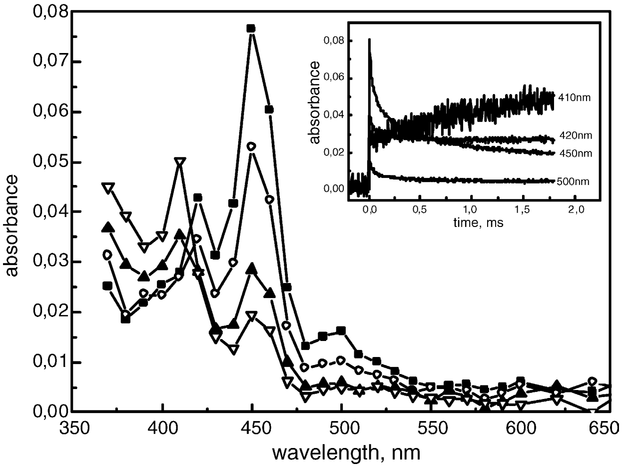

Fig. 5. The transient absorption spectra of PVC containing Py (10^{-1} mol dm^{-3}) pulse irradiated at room temperature taken 10 μs (■), 50 μs (○), 500 μs (▲) and 1.75 ms (▽) after the 4 μs pulse. Inset: oscilloscope traces of absorbance measured at 410, 420, 450 and 500 nm.

precursor [16]. As it was earlier mentioned some pulse radiolysis experiments had been done for PVC containing traces of 2,6-di-tert-butyl-4-methylphenol, BHT used as a common antioxidant preventing oxidation of THF. The absorption spectra of BHT–PVC system at 100 K are shown in Fig. 6. The absorption band at 410 nm may be tentatively attributed to the radical cation of BHT generated by positive charge transfer from PVC matrix primary cation.

Since the decay of Py$^{•+}$ radical ions has been very sensitive to the temperature changes it was possible to investigate the structural transitions of PVC matrix in the temperature range 100–290 K. The Arrhenius dependence for Py$^{•+}$ radical cation decay in PVC measured at 450 nm is shown in Fig. 7. Two linear parts of the Arrhenius plots were found which intersected in the temperature range 200–240 K, which is close to the mechanical loss peak (210–230 K, at 1–10 Hz) [27]. The exact nature of the β relaxation in PVC is not clear [27]. The activation energies calculated from two linear regions of the Arrhenius plot (Fig. 7) were equal to 0.40 kJ mol^{-1} for temperatures below 200 K and 52.6 kJ mol^{-1} for temperatures higher than 240 K. In the latter case one may expect that diffusion contributes to the charge recombination, whereas at temperatures below 200 K, tunneling is probably involved.

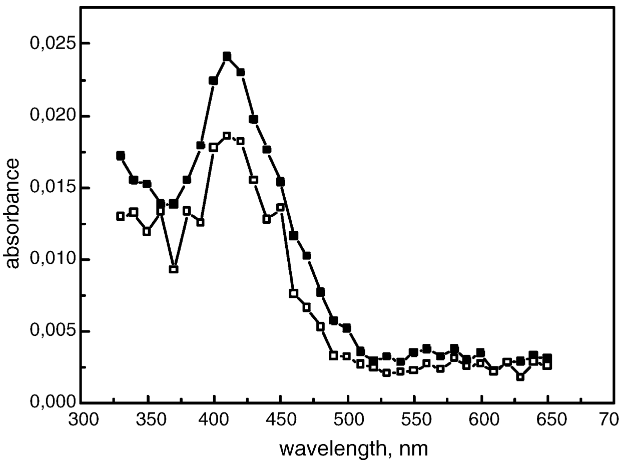

Fig. 6. The transient absorption spectra of PVC containing BHT pulse irradiated at 100 K taken 10 μs (■) and 1 ms (□) after the 4 μs pulse.

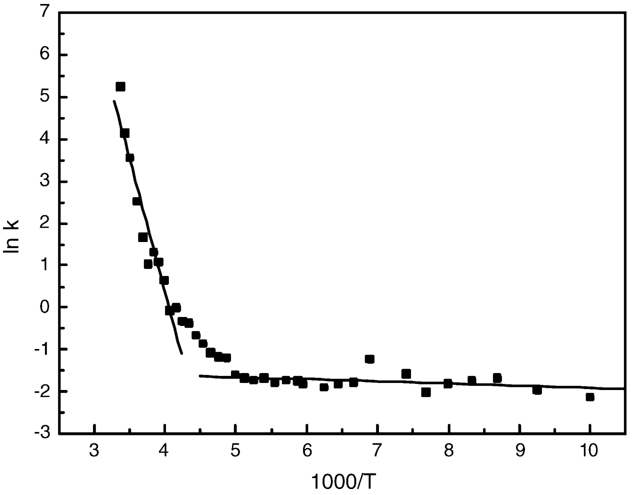

Fig. 7. The Arrhenius dependence for Py$^{•+}$ radical cation decay in PVC containing 10^{-1} mol dm^{-3} Py measured at 450 nm after 1 μs pulse. The k values were calculated as a reciprocal of the first half-life of Py$^{•+}$ decay.

The pulse irradiated pure PVC did not generate short time scale emission. The 17 ns pulse irradiated PVC–Py system (Py concentration: 10^{-1} mol dm^{-3}) generated solute luminescence. Fig. 8 shows the emission spectra of Py doped PVC measured at room temperature and 100 K. Both spectra represent the well known Py monomer fluorescence peaking at 390 nm. No excimer emission band at ca. 475 nm was detected. The change of temperature from room one to 100 K has no appreciable influence on the intensities of fluorescence bands taken at 50 ns time scale. Distinct temperature effect can be seen in the 300 ns time scale. The lifetimes of

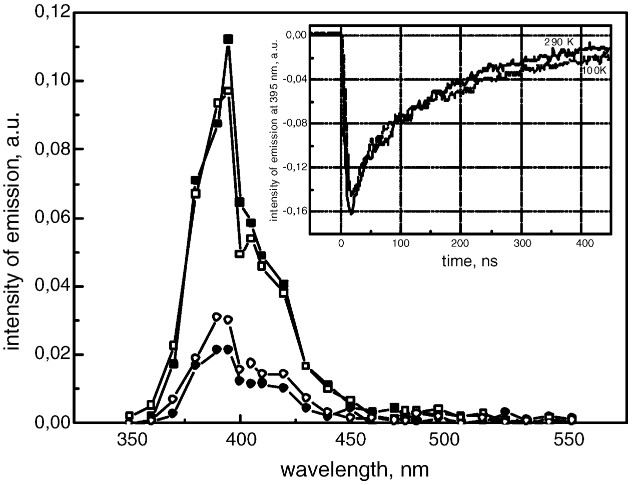

Fig. 8. The emission spectra of PVC containing Py (10^{-1} mol dm^{-3}) pulse irradiated at room temperature (■, ●) and at 100 K (□, ○) taken 50 ns (■,□) and 300 ns (●,○) after the 17 ns pulse. Inset: oscilloscope traces of emission measured at 395 nm in room temperature and 100 K.

Py fluorescence detected after the 17 ns pulse were found to be equal to 165 and 232 ns at room and 100 K temperatures, respectively. Similar effect of temperature on Py fluorescence lifetime was observed in other polymeric matrices [20–23]. The lifetime of Py fluorescence was calculated as $\tau = 1/k$, where k represents the first-order rate constant estimated from typical decay curve approximated by exponential function. The increase of fluorescence lifetime at low temperature is attributed to temperature sensitive internal conversion and intersystem crossing [28,29].

Py fluorescence in μs time scale was not detected but may be the very low intensity of this emission in long time range would be the reason.

The experimental results presented in this paper can be explained by assuming that the first primary step of the PVC matrix radiolysis has to be the ionic one:

$$\sim CH_2\text{-}CHCl\sim \quad —\wedge\wedge\wedge\wedge\rightarrow \quad e^- + \oplus \tag{1}$$

where e^- and $\oplus$ denote mobile electrons and positive holes. The positive hole can be stabilized as a cation structures $\sim^{\oplus}CH_2\text{–}CHCl\sim$ and $\sim CH_2\text{–}^{\oplus}CHCl\sim$. The positive holes can be mobile along the polymer chain. The absorption band of matrix cation generated in irradiated sec-butyl chloride at 77 K was found in the visible range ($\lambda_{max} \sim 470$ nm) [22,30]. Sumiyoshi et al. [31] have reported the observation of radical cations generated in liquid 1,2 dichloroethane ($CH_2ClCH_2Cl^{\bullet+}$, $CH_2ClCH_2{}^+$) by means of ps and ns pulse radiolysis methods. These short-lived species were characterized by absorption bands in the range 400–550 nm. Hasegawa et al. [32] proved the formation of $CH_2ClCH_2Cl^{\bullet+}$ radical cation using the low temperature ESR analysis. The spectra of cationic species shown in Figs. 1 and 2 and attributed to PVC cations were also observed in visible absorption range.

Electrons after termalization can be attached to the matrix giving respective anion (reaction (2)):

$$e^- + \sim CH_2\text{–}CHCl \sim \rightarrow \sim CH_2\text{–}CHCl^{\ominus}\sim \tag{2}$$

whereas positive holes can generated free radicals via intramolecular or intermolecular proton transfer to PVC macromolecules (for example reaction (3)):

$$\oplus + \sim CH_2\text{–}CHCl \sim$$
$$\rightarrow \sim C^{\bullet}H\text{–}CHCl \sim + \sim CH_2H^{\oplus}\text{–}CHCl \sim \tag{3}$$

The additional source of free radicals can be connected with dissociative decomposition of matrix anions formed in reaction (2):

$$\sim CH_2\text{–}CHCl^{\ominus}\sim \rightarrow \sim CH_2\text{–}C^{\bullet}H \sim + Cl^- \tag{4}$$

The neutralization of Cl^- in reactions with matrix cations may produce reactive chlorine atoms, $^{\bullet}Cl$.

The protons may move along polymeric chains and may be attached to matrix anion structure:

$$\sim CH_2H^{\oplus}\text{–}CHCl \sim + \sim CH_2\text{–}CHCl^{\ominus}\sim$$
$$\rightarrow \sim CH_2\text{–}CHCl\sim + \sim CH_2\text{–}CHH^{\oplus}Cl^{\ominus} \sim \text{(I)} \tag{5}$$

and the neutral complex (I) may decompose with direct hydrogen chloride, HCl, formation. The quasi-ionic mechanism of one step dehydrochlorination of PVC was discussed and suggested as a explanation of this polymer thermal degradation [33].

Macroradicals formed in the reaction (3) and (4) as well as chlorine atoms (reaction (4) followed by neutralization) and process (5) can be responsible for polyenyl radicals production [2,3,6,13]. The sequential loss of hydrogen chloride molecules can lead to the formation of conjugated polyene sequences (Fig. 3) [3]. The strong support of our mechanism of PVC radiolysis including initial ionic species formation steps can be drawn from Py probing of the irradiated PVC system.

In the presence of Py molecules, in particular for high Py concentration ($\sim 10^{-1}$ mol dm^{-3}), the probe molecules can directly scavenge primary charges creating Py radical ions $Py^{\bullet+}$ and $Py^{\bullet-}$. Since PVC itself has been a very good scavenger of electrons (see reaction (2)) mainly $Py^{\bullet+}$ radical ions are generated due to positive charge transfer reaction (6):

$$\oplus + Py \rightarrow Py^{\bullet+} \tag{6}$$

The absorption band responsible for $Py^{\bullet+}$ was found as a peak at ∼450 nm [34] (Figs. 4 and 5). Only traces of $Py^{\bullet-}$ absorption in the range 490–500 nm was found because the yield of the reaction (7):

$$e^- + Py \rightarrow Py^{\bullet-} \tag{7}$$

due to PVC reactivity towards e^- seems to be not so high. The formation of monomer radical cations of Py has been reported during the pulse radiolysis of liquid CCl_4, $CHCl_3$ and CH_2Cl_2 containing this probe [35]. The decay of $Py^{\bullet+}$ band was found to be strongly temperature dependent in the temperature range 100 K to room temperature (Fig. 7).

The ∼420 nm absorption band found in Py–PVC system (Figs. 4 and 5) can be assigned to the Py triplet states [34] although the maximum is red shifted. The probable source of these triplets is connected with intersystem crossing from Py singlet excited states. The Py singlet excited states fluorescence was observed at both temperatures. It is interesting to note that having quite high Py concentration ($\sim 10^{-1}$ mol dm^{-3}) in PVC matrix no excimer fluorescence at 475 nm was detected even at room temperature. PVC polymer matrix prevents the aggregation of the probe molecules.

The Py excited states are generated in PVC matrix by photophysical excitation as a result of Čerenkov radiation absorption [29]. Py radical ions recombination as a possible source of excited states has to be reject because of Cl^- as a negative partner in recombination. No Py emission was observed in μs time scale. The Py fluorescence was detected in the hundreds ns time scale whereas the decay of $Py^{\bullet+}$ radical ions in such short time scale was not found. Comparing with another polymeric systems [18–24] PVC matrix seems to behave untypically.

The assignment of 410 nm absorption peak to Py cyclohexadienyl type radicals in PVC matrix needs some comment. It was proved by Zhang and Thomas [36], that in pulse irradiated methanol, H atom adduct of pyrene (1-hydropyrenyl radical) was detected. Following the interpretation of Torikai et al. [16] in our case the precursor of the 410 nm absorption peak seems to be $Py^{\bullet +}$. Assuming that such conclusion is right, in order to generate neutral radical adduct the negative partner is necessary. In the system under consideration the Cl^- ions seem to be available and Py radical adduct should the chlorine atom adduct.

4. Conclusions

- The pulse radiolysis experiments proved the formation of PVC matrix cations during the primary step of radiolysis. The electrons generated at that time are immediately scavenged by matrix itself by dissociative mechanism.
- The PVC solid matrix can be used as a good system for solute (Py, BHT) radical cation generation.
- The β relaxation transition for PVC in 200–240 K range has been confirmed using Arrhenius plots for Py radical cation decay.

Acknowledgements

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