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Pulse radiolysis study on transient species produced in polydimethylsiloxane

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Abstract

The primary and secondary ionic reactions were investigated in pulse irradiated, crosslinked polydimethylsiloxane, PDMS, matrix. The UV-VIS, structureless spectra of pulse irradiated PDMS, in the temperature range 100–295 K can be attributed to the transient radical species. Some evidences were presented that PDMS itself was able to scavenge the primary charges i.e. electrons and positive holes but the absorption spectra of products of these reactions were not found. The electronic spectra of PDMS doped with pyrene, Py, represented Py radical ions bands (450 nm and 490 nm maxima), Py triplets (410 nm) and Py radical (400 nm) absorptions. The lowering of temperature down to 100 K led to substantial increase of Py radical ions yield detected after the pulse. The decay of Py radical ions was found to be temperature and matrix dynamics dependent. Activation energies for Py radical anion decay were calculated to be equal 19.5 kJ mol^{-1} for T>215 K; 61.5 kJ mol^{-1} in the temperature range 215–165 K and only 0.6 kJ mol^{-1} for T<165 K. The pulse irradiated Py–PDMS system generated at room temperature solute monomer and excimer fluorescence. The lowering of temperature caused the excimer emission to disappear and the Py monomer emission intensity and lifetime to increase. These temperature-dependent phenomena can be explained by photochemical mechanisms. The detection of the delayed Py fluorescence observed after the pulse can be treated as an evidence for the ionic origin of Py emission. The Py radical ions formation in irradiated PDMS and their secondary reactions strongly support the conclusion that ionic mechanism contributes to the radiation induced processes in PDMS. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Polydimethylsiloxane; Pyrene; Pyrene radical ions; Pyrene ion recombination; Pyrene excited states; Pulse radiolysis; Low temperature measurements

1. Introduction

Organosilicon polymers are gaining an increasing role in various fields of material science and technology. Rubbers based on polydimethylsiloxane, $(\text{–Si(CH}_3)_2\text{O–})_n$ have some excellent properties such as high structural resistance towards heat, ozone and chemicals [1].

The chemical inertness is mainly due to the high bond energy of the Si–O linkage (424–495 kJ mol^{-1}) [2].

Silicon fluids are generally held to have good resistance to ionizing radiation although signs of degradation or crosslinking are apparent under certain conditions. Recently both high radiation resistant and sensitive polymers have been worthy of remark in the areas of advanced technology such as fusion and nuclear reactor engineering, space science, high resolution fabrication of semiconductor devices as well as in the field of different applications of silicon based biomaterials.

The radiation chemistry of polysiloxane polymers, mainly polydimethylsiloxane type, had been studied in some detail a long time ago [3–7]. It has been shown that organopolysiloxanes are crosslinked on exposure to high energy radiations via radical mechanism.

No detailed work has been published on the pulse radiolysis of such polymers. Pulse radiolysis studies on similar type of silicon containing resists such as partly chloromethylated polydiphenylsiloxane have been done [8,9]. Revina et al. [10] have investigated the formation of radical species during the pulse radiolysis of cyclohexane solution of polysiloxanes.

The aim of this work is to investigate the primary and secondary ionic events in a crosslinked polydimethylsiloxane 'pure' and doped with aromatic compound i.e. pyrene.

For the first time the influence of temperature down to 90 K on additive ion recombination and excited state formation is estimated using pulse radiolysis technique.

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2. Experimental details

2.1. Materials

The polydimethylsiloxanediol, Polastosil M-2000 (2000 cP viscosity) supplied by Institute of Industrial Chemistry, Silicon Experimental Branch, Nowa Sarzyna (Poland) was used. The solid polymer samples, PDMS, for pulse irradiation were prepared from crosslinked Polastosil M-2000. As a crosslinking agent, catalyst 0L-1 (dibutyl tindilaurate/tetraethoxysilane) was applied.

The decamethyltetrasiloxane, DMTS, was synthesized according to the method described by Patnode and Wilcock [11]. All solvents i.e. 2-propanol, methanol (both for spectroscopy, Uvasol, Merck) and sec-butyl chloride (GC, 99+%, Aldrich) were used as received. Pyrene, Py, analytical grade (Sigma) was recrystallized twice from ethanol. Py was introduced into PDMS samples via sublimation/adsorption under vacuum. Afterwards the samples were rinsed with methanol to remove any surface acceptor molecules. Py concentration in polymer film was determined using array spectrophotometer Hewlett-Packard, HP 8452 A. The PDMS samples were deoxygenated using typical vacuum line (10^{-4} torr for at least 10 h).

2.2. Methods

The pulse radiolysis measurements were carried out using a linear accelerator ELU-6 (USSR made) which delivered 17 ns (dose ca. 55 Gy) and 1 μs (dose ca. 250 Gy) pulses. The ELU-6 accelerator was used in certain stationary radiolysis experiments too.

The Hamamatsu R-928 photomultiplier was used as the light detector. The signals were recorded on a digitizing scope (HP 64610 A), transferred via interface to IBM-AT computer for storage and analysis. More details concerning detection system and the accelerator can be found elsewhere [12]. Low temperature experiments were done either at 77 K (liquid nitrogen) or in the temperatures down to 90 K using home-made styrofoam-copper cryostat, through which cold, gaseous nitrogen was passed.

The low temperature steady-state radiolysis products were examined at 77 K using Cary 5E spectrophotometer (Varian). The room temperature fluorescence spectra of the

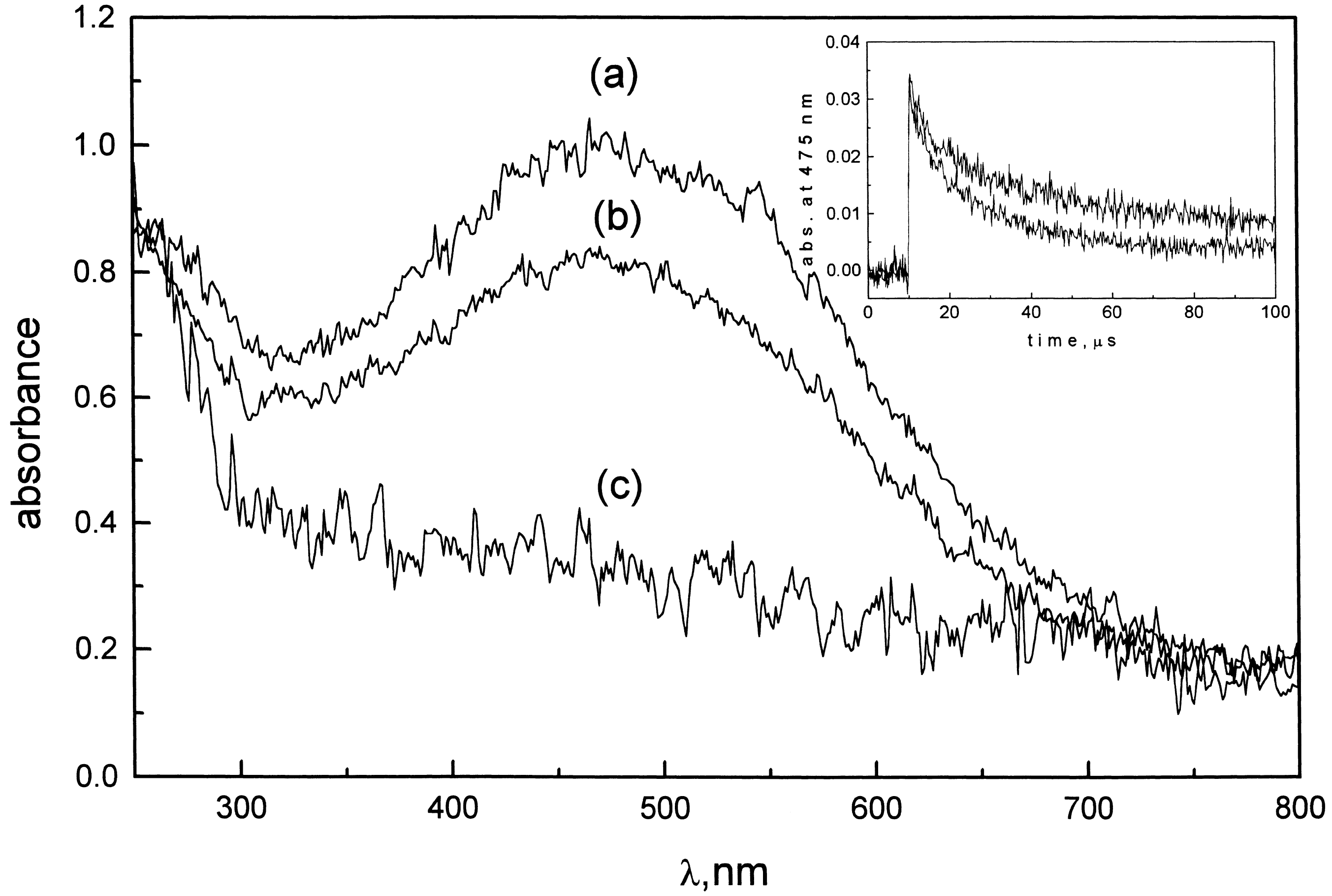

Fig. 1. The electronic absorption spectra at 77 K for the irradiated sec-butyl chloride matrix pure (a) and containing 0.05 mol dm^{-3} DMTS (b) and 0.5 mol dm^{-3} DMTS (c). Dose 3.5 kGy. Inset: the decay of 475 nm transient absorption at 138 K; pure sec-butyl chloride (upper curve) and in the presence of 0.1 mol dm^{-3} DMTS (lower curve); 1 μs pulse, dose ca. 250 Gy.

polymer samples were done using Aminco–Bowman spectrofluorometer.

3. Results and discussion

The reactions leading to the formation of polysiloxane ions have not yet been investigated carefully. One of the studies [8,9] demonstrated the formation of ionic transient species in pulse radiolysis of chloromethylated polydiphenylsiloxane solution in $CHCl_3$.

In the present paper the scavenging ability of DMTS (model compound for the PDMS polymer) against electron and cations were investigated.

Fig. 1 shows the absorption spectra of irradiated pure sec-butyl chloride (positive charge donor) and DMTS-sec-butyl chloride samples at liquid nitrogen temperature. The absorption spectrum detected for pure, glassy sec-butyl chloride (λ_{max} ~480 nm) can be attributed to matrix cations [13]. The intensity of this absorption band decreased at 77 K in the presence of DMTS. The decay of matrix cation absorption was accelerated for samples containing DMTS as it was observed in pulse radiolysis experiment at 138 K (Fig. 1, inset). The absorption spectrum of positive charge transfer reaction product in DMTS–sec-butylchloride system was not found in the spectral range under investigation.

Fig. 2 shows the absorption spectra of irradiated, pure 2-propanol (negative charge donor) and DMTS-2-propanol samples at liquid nitrogen temperature. The absorption spectrum detected for pure, glassy 2-propanol can be attributed to well known trapped electrons, e_t^- (λ_{max} ~700 nm). The e_t^- absorption decreased in the presence of DMTS. For 1 mol dm^{-3} solute content in the alcohol matrix e_t^- absorption was totally eliminated.

The decay of e_t^- absorption was accelerated in the presence of DMTS as it was observed in pulse radiolysis experiment at 200 K (Fig. 2, inset). No influence of the solute on the decay of e_t^- absorption was found at room temperature. Again, the absorption spectra of negative charge scavenging reaction products in DMTS-2-propanol were not observed in the spectral range under investigation.

Fig. 3 shows the transient absorption spectra of pure PDMS solid polymer measured at 295 K and 105 K. The absorbance detected at room temperature increased towards

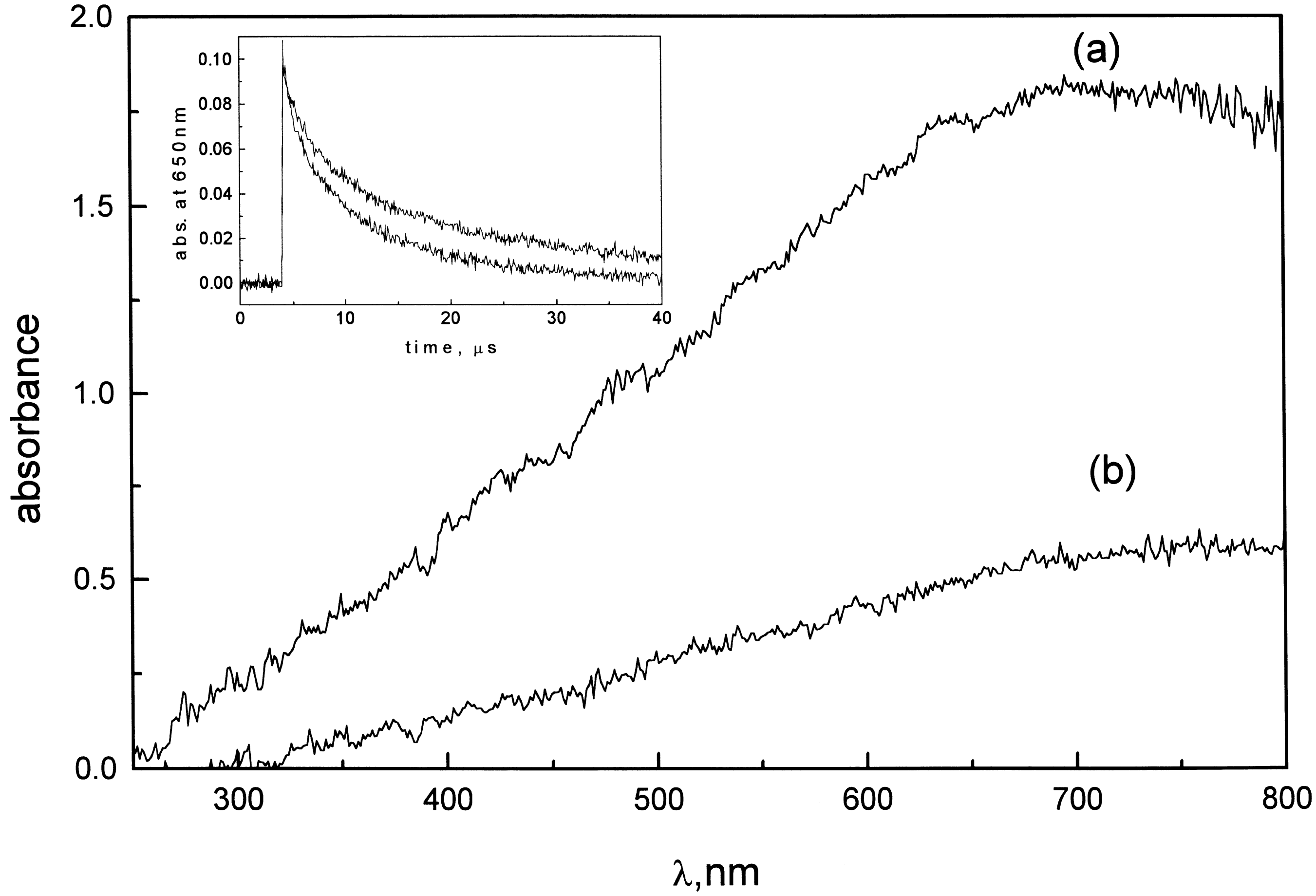

Fig. 2. The electronic absorption spectra at 77 K for the irradiated 2-propanol matrix pure (a) and containing 0.5 mol dm^{-3} DMTS (b). Dose 3.5 kGy. Inset: the decay of 650 nm transient absorption at 200 K; pure 2-propanol (upper curve) and in the presence of 0.1 mol dm^{-3} DMTS (lower curve); 1 μs pulse, dose ca. 250 Gy.

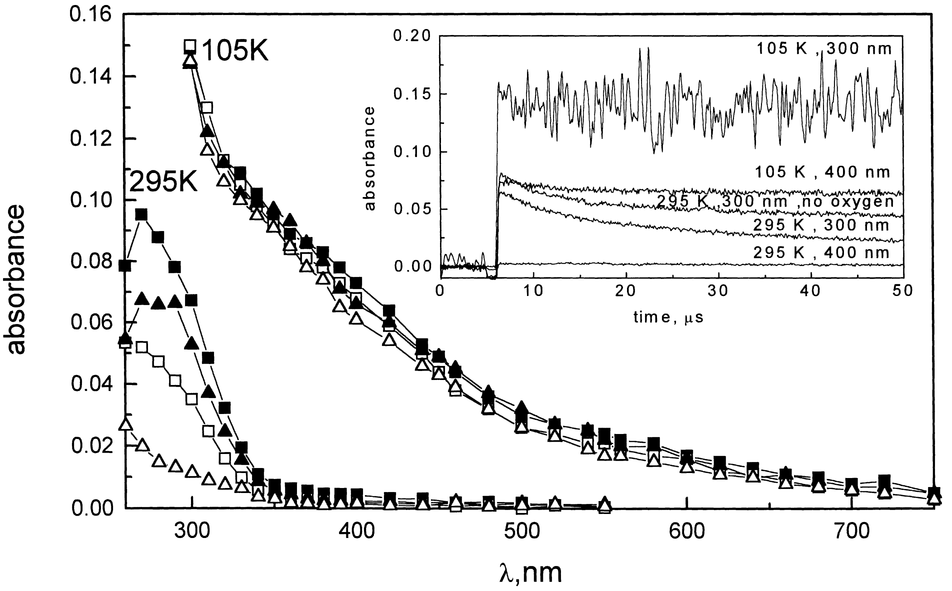

Fig. 3. The influence of temperature and oxygen content on transient absorption spectra of pulse irradiated (1 μs pulse, dose ca. 250 Gy) PDMS samples (light path length ~0.45 cm). ■, □ – no oxygen; ▲, △ – in the presence of air. ■, ▲ – measured 5 μs after the pulse at 295 K or 10 μs after the pulse at 105 K; □, △ – measured 200 μs after the pulse at both temperatures. Insert: the influence of temperature on time profiles of transient absorption decay for PDMS samples in the presence of air; 300 nm absorption decay at 295 K for deaerated sample was shown for comparison.

UV wavelengths starting from ca. 350 nm. In the presence of oxygen from air the UV absorption decreased and its decay was accelerated comparing with deaerated polymer samples.

At 105 K the spectra of pulse irradiated PDMS deaerated and in the presence of oxygen represented a broad, structureless absorption in the UV and visible ranges, which increased continuously toward the shorter wavelength side but no maximum could be observed in the range up to 300 nm. No influence of oxygen was found on the decay of absorption at low temperature.

The absorption spectra of pulse irradiated at 295 K deaerated PDMS doped with Py are shown in Fig. 4. The assignment of the bands centred at 450 nm and 490 nm to the Py radical cation ($Py^{\cdot +}$) and anion ($Py^{\cdot -}$) respectively, is consistent with the spectra reported for these species in other polymer systems [14–16]. The decay of Py radical ions was partly accompanied by growth of Py triplets absorption band detected at 410 nm [17]. The Py triplets absorption overlapped the Py radical band centred at 400 nm [18]. The Py radicals can be produced via H atom addition [18].

The intensity of absorption and the decay of Py radical ions were temperature-dependent (Figs. 5 and 6). At 100 K the 3 μs absorptions of Py radical ions were much higher than at room temperature (Fig. 4). Slight decay of $Py^{\cdot -}$ absorption was observed in the time scale up to 0.2 ms whereas the $Py^{\cdot +}$ absorption band seemed to grow in this time range. We were unable to detect transient absorption in the range below 420 nm but the fluorescence from Py excited states made measurements in this spectral range and time scale ($\leq$3 μs) very uncertain.

The decay of Py radical ions can be satisfactorily described by the second-order equal concentration kinetic equation with the time-dependent rate constant [19]. Assuming that Arrhenius relation holds for time-dependent rate constant the activation energy for Py radical ions decay can be calculated.

The Arrhenius plot shown in Fig. 6 can be characterised by three approximately linear regions which change directions at $T_1 \approx 215$ K and $T_2 \approx 165$ K. Activation energies, E_a calculated from linear parts of Arrhenius plot were equal to 19.5 kJ mol^{-1} for temperatures higher than T_1; 61.5 kJ mol^{-1} in the intermediate temperature range from 215 K to 165 K and only 0.6 kJ mol^{-1} for temperatures lower than T_2.

The T_1 temperature, most probably can be attributed to the melting point (T_M) of silicon chain [2] whereas T_2 temperature can be related to the glass transition temperature, T_g of PDMS which according to published data should be equal to ~153 K [2].

The 17 ns pulse irradiated PDMS–Py system generated solute luminescence. Fig. 7 shows the emission spectra of Py doped PDMS measured at 295 K and 100 K. The room temperature emission spectrum represented the well known Py monomer (λ_{max}=380 nm) and excimer fluorescence (λ_{max} ~475 nm). The comparison of the latter band measured 50 ns after the pulse with the similar one but detected using stationary excitation technique (Fig. 7, inset) clearly showed that transient excimer emission band was perturbated in the range 450–480 nm. This effect can be attributed to the self-absorption of the emission in this spectral range by short lived transient absorption due to excited singlet state of Py [17]. Richards et al. [17] observed three singlet–

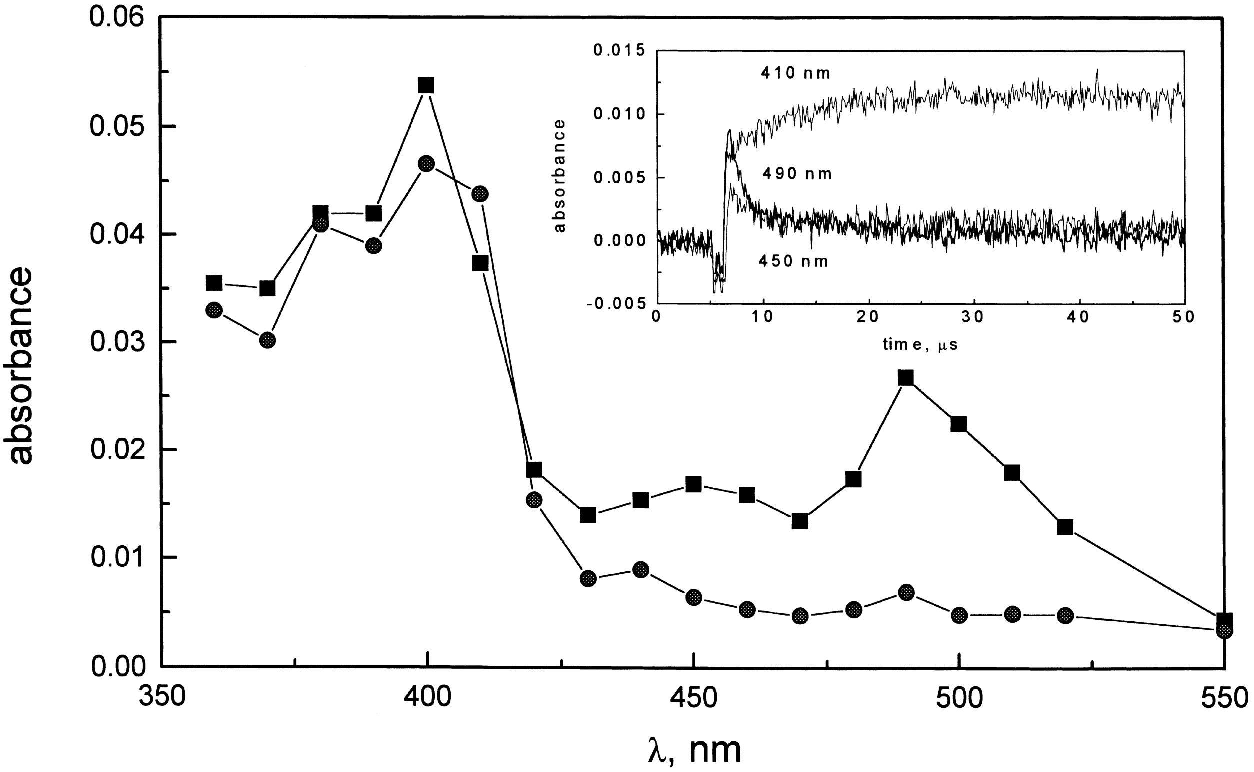

Fig. 4. Optical spectra of pulse irradiated at 293 K PDMS containing Py (3×10^{-3} mol dm^{-3}). The light path ~0.43 cm. The spectra were taken 3 μs (■) and 10 μs (●) after the 1 μs pulse. Insert: absorption time profiles measured at 410 nm (Py triplets); 450 nm (Py^{+}) and 490 nm (Py^{-}) for PDMS sample thickness ~0.15 cm. For such samples the absorption measurements at 410 nm were less disturbed by Py emission.

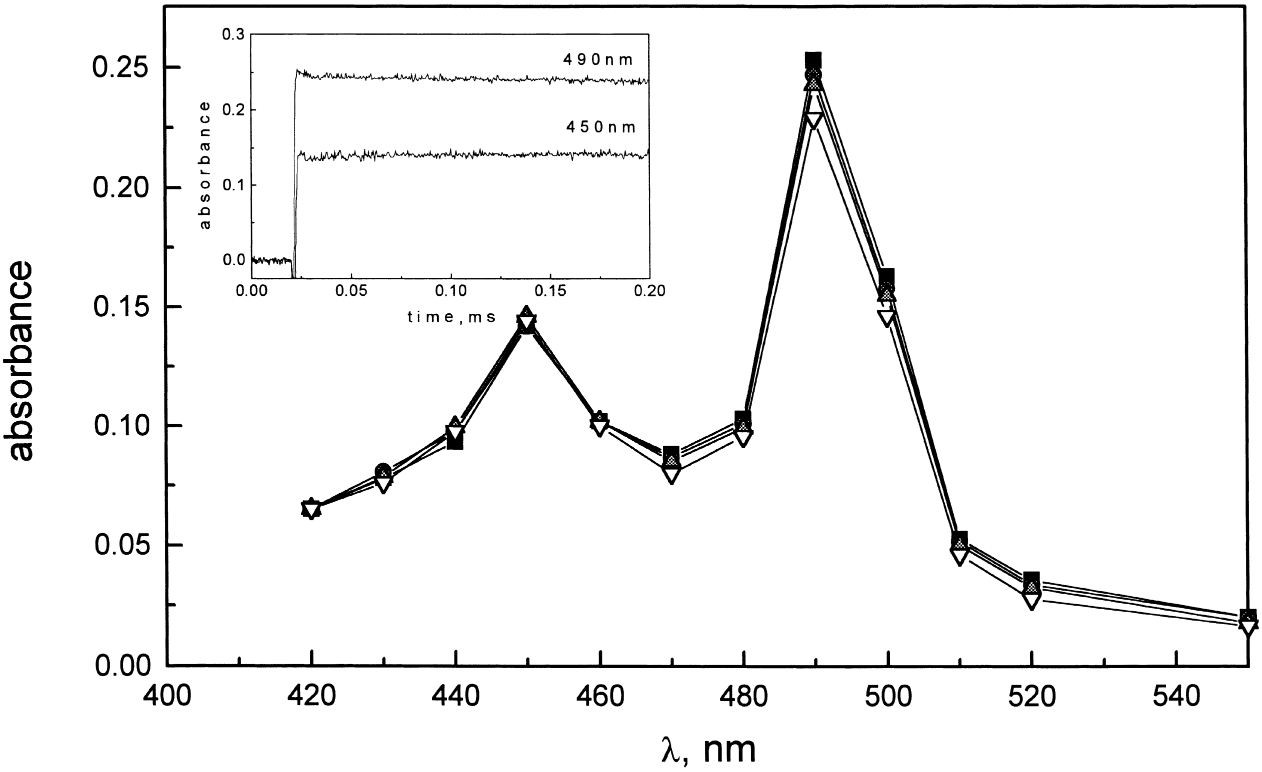

Fig. 5. Optical spectra of pulse irradiated at 100 K PDMS containing Py (3×10^{-3} mol dm^{-3}). The light path ~0.43 cm. The spectra were taken 3 μs (■), 10 μs (●), 100 μs (▲) 1 ms (▽) after the 1 μs pulse. Insert: absorption time profiles measured at 450 nm (Py^{+}) and 490 nm (Py^{-}).

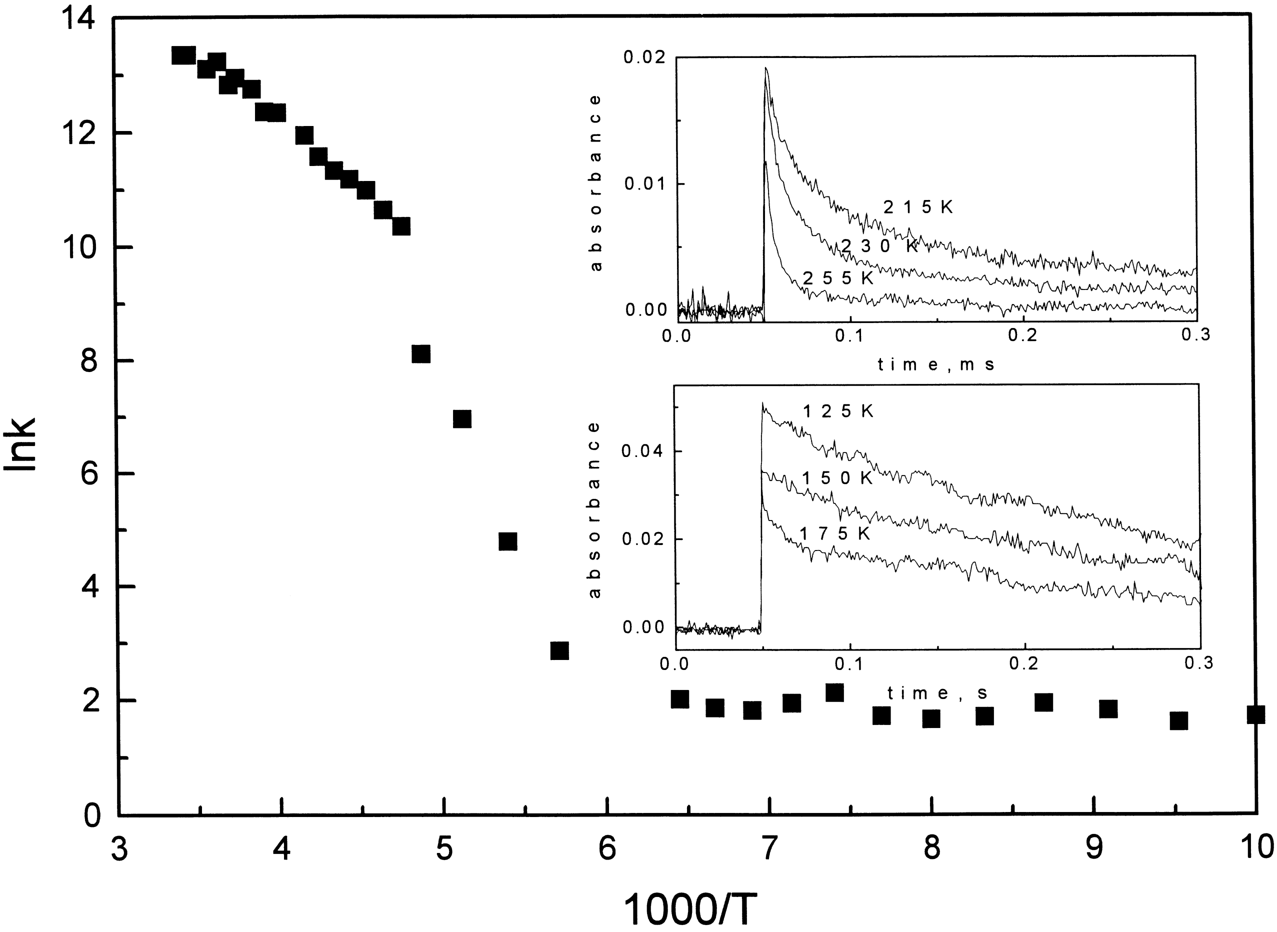

Fig. 6. The Arrhenius dependence for Py radical anion decay in PDMS measured at 490 nm. The light path ~0.15 cm. [Py]≅4×10^{-3} mol dm^{-3}, 1 μs pulse. Insert: 490 nm absorption time profiles measured at different temperatures.

singlet absorption maxima at 470 nm, 365 nm and 254 nm which lifetimes were always identical with that of the Py monomer fluorescence.

The generation of the Py excimer emission on a ns time scale at room temperature (see Fig. 8, insert) may indicate that solute molecules in PDMS polymer are in close proximity allowing considerable overlap. During the first 50 ns after the pulse the Py*–Py pair can reach the excimer equilibrium configuration. Similar observations concerning the 'delayed' Py excimer formation in polymer systems were found previously for polyethylene–Py [20,21] and poly(methyl methacrylate)–Py [22,23] systems. The decrease of temperature down to ca. 100 K caused a substantial increase of Py monomer fluorescence intensity whereas Py excimer emission was stopped at all (Figs. 7 and 8).

In addition, the decrease of Py excimer band intensity with lowering of temperature was accompanied by the increase of Py monomer fluorescence lifetime (Fig. 8). The lifetimes of Py fluorescence detected after the 17 ns pulse were found to be equal ~520 ns in the temperature range 100–150 K comparing with the room temperature value ~80 ns, all data for Py concentration ~3×10^{-3} mol dm^{-3}.

The similar spectral distribution of Py–PDMS system was found for 1 μs pulse irradiated samples (Fig. 9). The change of temperature from 295 K down to 100 K influenced the experimental data in two-fold way: (i) the intensity of Py monomer fluorescence at 100 K was twice higher comparing with 295 K (see ns measurements for comparison), (ii) the time profiles of fluorescence at 390 nm at low temperatures were broadened and distinct, after the pulse, tail emission was observed, in particular at 100 K.

Taking into account all experimental results described above the following reaction mechanism can be proposed in order to explain pulse irradiation induced transient events in PDMS pure and in the presence of Py.

$$\text{PDMS} \rightsquigarrow e^- + \oplus \qquad (1)$$

where e^- and $\oplus$ denote mobile electrons and positive holes. Both primary charges seem to be reactive towards the matrix itself as well as added solute molecule. DMTS, the model compound for PDMS polymer was found to be moderate acceptor for electron and positive charges in 2-propanol and

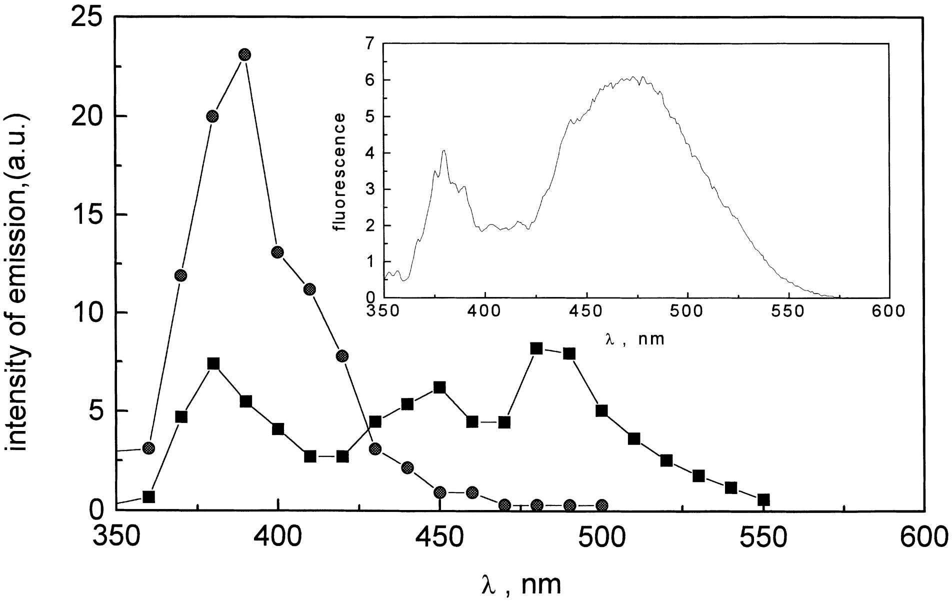

Fig. 7. The influence of temperature on emission spectra of pulse irradiated (17 ns) PDMS containing Py (3×10^{-3} mol dm^{-3}) ■ – 295 K; ● – 100 K. Sample thickness ~0.1 cm. Experimental points were measured 50 ns after the pulse. Insert: stationary fluorescence spectrum of PDMS–Py system taken at room temperature; [Py]=3×10^{-3} mol dm^{-3}.

sec-butyl chloride systems, respectively. Unfortunately the absorption spectra attributed to charge transfer reaction products were not identified hence the transient spectra of pulse irradiated PDMS must be tentatively assigned to radical species only (Fig. 3). Ormerod and Charlesby [7] as well as Tsvetkov et al. [3] using epr technique found few kind of radicals at 77 K i.e.

$-O-(CH_3)\dot{S}i-O-$, $-O-(CH_3)Si(\dot{C}H_2)-O-$, $\cdot CH_3$,
$-O-(CH_3)Si(CH_3)-\dot{O}$

On warming to 195 K the radicals started to disappear. These radicals might be observed as a UV-VIS absorption band in ms time scale using pulse radiolysis technique.

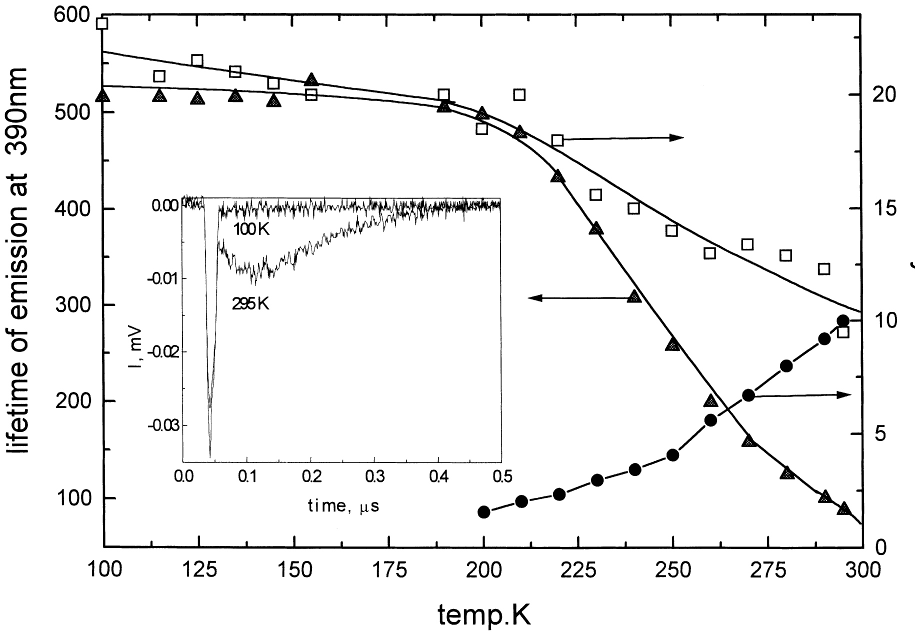

Fig. 8. The influence of temperature on intensities of Py emission and lifetimes of Py monomer fluorescence. □ – intensity of Py monomer fluorescence (λ=390 nm) just after the 17 ns pulse; ● – intensity of Py excimer fluorescence (λ=480 nm) taken 50 ns after the pulse; ▲ – lifetime of Py monomer fluorescence. Insert: influence of temperature on emission time profiles measured at 480 nm. Sample thickness ~0.1 cm [Py]=3.5×10^{-3} mol dm^{-3}.

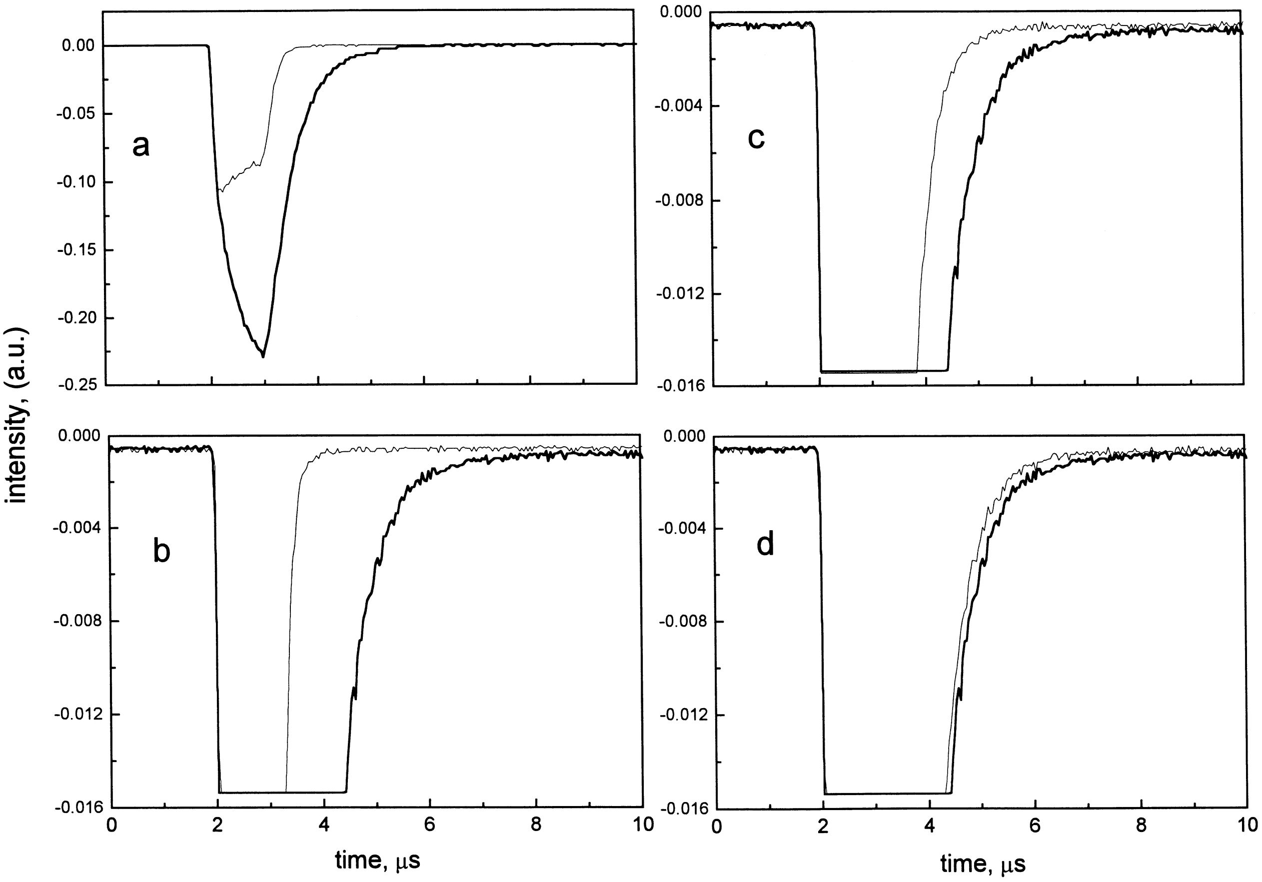

Fig. 9. The influence of temperature on time profiles of Py emission measured at 390 nm. 1 μs pulse (dose ∼250 Gy), sample thickness ∼0.13 cm, [Py]≅3×10^{-3} mol dm^{-3} ▬ emission time profiles at 100 K in all cases, (a) ——— room temperature, low sensitivity gain applied in order to detect full size emission signal, (b) ——— room temperature, high sensitivity gain applied in order to detect full size tail emission, (c) ——— 250 K, high sensitivity gain, (d) ——— 220 K, high sensitivity gain.

Room temperature UV band, oxygen sensitive, can be attributed to the residual$\equiv$Si$^{\cdot}$ radicals [7].

The all kinds of radical species are probably generated by decomposition of locally excited PDMS chain. The fast recombination of charges, free as well as stabilised on PDMS chain (like PDMS$^{\cdot -}$ and PDMS$^{\cdot +}$) seems to the source of PDMS excitation. The above discussion can be described by the following reactions:

$$e^- + \mathrm{PDMS} \rightarrow \mathrm{PDMS}^{\cdot -} \quad (2)$$

$$\oplus + \mathrm{PDMS} \rightarrow \mathrm{PDMS}^{\cdot +} \quad (3)$$

$$\mathrm{PDMS}^{\cdot -} + \mathrm{PDMS}^{\cdot +} \rightarrow \mathrm{PDMS}^{*} \rightarrow \mathrm{radicals} \quad (4)$$

Py radical-ion can be produced during the pulse due to reactions:

$$e^- + \mathrm{Py} \rightarrow \mathrm{Py}^{\cdot -} \quad (5)$$

$$\oplus + \mathrm{Py} \rightarrow \mathrm{Py}^{\cdot +} \quad (6)$$

The Py radical ions absorption spectra were identified unquestionably (Figs. 4 and 5). The decrease of temperature leads to higher yield of Py radical ions suggesting that the 'Py' reactions (5) and (6) are more efficient at low temperature than at room one.

The decrease of temperature slows down the Py radical ions recombination reaction

$$\mathrm{Py}^{\cdot -} + \mathrm{Py}^{\cdot +} \rightarrow \mathrm{Py}^{*} + \mathrm{Py} \text{ or } (\mathrm{Py})_2^{*} \quad (7)$$

hence the progress of this reaction during the 1 μs pulse at 100 K should be smaller than at 295 K. Certainly, such mechanism is mainly responsible for the high yield of Py radical ions detected after the pulse at low temperature in rigid matrix. The charge transfer process from matrix ions to Py seems to be possible too. The reaction

$$\mathrm{PDMS}^{\cdot +} + \mathrm{Py} \rightarrow \mathrm{Py}^{\cdot +} + \mathrm{PDMS} \quad (8)$$

was observed at ∼100 K. (Fig. 5, insert)

The Py radical ion recombination reaction (7) is strongly temperature/matrix dynamic dependent (Fig. 6). The activation energy of ion recombination found for temperature range higher than $T_1 \sim T_M$ is practically equal to the value of the E_a of viscous flow [24–26]. The mobility of the reactants is predominantly affected by the microviscosity of the matrix. According to this concept the translational motion of small molecules in PDMS at $T>T_M$ is determined by the mobility of free volume elements due to segmental motions [25,26]. The activation energy $E_a=61.5$ kJ mol^{-1} found for 'intermediate' temperature range $T_1>T>T_2$ is similar to the values of activation energies calculated for solute ion recombination at $T>T_g$ for polyethylene–Py [14]. In this temperature range one may guess that melt viscosity of the polymer governs the motion of solute molecules there. Certainly, in the temperature range $T>T_2$ diffusion-assisted mechanism is responsible for Py radical ions recombination. The very low E_a found at $T<T_2$ strongly suggests that the matrix rigidity at these temperatures prevents any significant mobility of solute ions and that tunnelling mechanism has to be involved in the electron exchange [14,16,23,27].

The solute emission observed during and in ns time scale after the pulse may originate from two sources i.e. photoexcitation by Čerenkov radiation [28] and very fast Py ionic recombination taking place during the 17 ns pulse.

Both temperature-dependent effects observed by us i.e. the increase of Py monomer fluorescence intensity and the lengthening of Py monomer emission observed at low temperatures (Figs. 7 and 8) can be explained by photophysical mechanism. The Py excimer formation [29] and temperature-dependence of Py fluorescence quantum yield caused by temperature-sensitive internal conversion and intersystem crossing [30,31] should be mention in this place.

Taking into account the observed temperature-dependence of ionic recombination rate (Fig. 6) one should expect the decrease of solute emission intensity during the pulse at low temperature comparing with room one. This type temperature-dependence of solute emission intensity was observed for hydrocarbon–solute systems [32,34] and polypropylene–solute matrix [16].

The experimental results shown in Fig. 8 demonstrate opposite effect suggesting the domination of photo-mechanism over ionic one at least in ns time scale. Hypothetically, solute fluorescence during the 17 ns pulse may be generated as a result of very fast electron–hole recombination along the polymer chain followed by energy transfer to the aromatic solute. Assuming the insignificant temperature effect on such chain assisted processes the time scale of solute emission in this case might be experimentally indistinguishable from the Čerenkov source.

Some evidences concerning the partly ionic origin of the Py emission can be derived from 1 μs pulse fluorescence experiments (Fig. 9). The Py fluorescence 'tail' observed in μs times after the pulse at 100 K can be only partly attributed to Py monomer emission lifetime lengthening at low temperature. Such delayed light generation can be explained by Py radical ion recombination shifted from in-pulse to after the pulse time scales. Some examples of such behaviour can be found in hydrocarbon–aromatic solute systems [32,33,35] where the contribution of ionic mechanism to the fast formation of solute excited states during the pulse seems to be evident.

Acknowledgements

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