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Pulse radiolysis study of charge transfer processes in polyethylene film containing two solutes

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Abstract

Intermolecular charge transfer reactions were studied by the pulse radiolysis of polyethylene containing two solutes, i.e. dimethyldiphenyl (DMD) and pyrene (Py). Positive and negative charges can be transferred from DMD ions to Py. Kinetic measurements of Py ion growth and DMD ion decay allowed us to calculate the activation energies (E_a) for these charge transfer processes. E_a was found to be temperature dependent and equalled 83.1–88.9 and 1.8–4.4 kJ mol^{-1} for $T > T_g$ and $T < T_g$ respectively.

Keywords: Polyethylene; Pulse radiolysis; Charge transfer; Pyrene; Dimethyldiphenyl

1. Introduction

Pulse radiolysis studies of polymers are generally aimed at elucidating the mechanism of radiation-induced reactions in relation to radiation processing as well as radiation modification and degradation of polymer materials.

The pulse radiolysis method offers the advantages that the system can be studied over a wide temperature range, aromatic ions and excited states can be detected and the kinetics of charge transfer reactions may be analysed.

There are only a few data on the pulse radiolysis investigation of solid polyethylene doped with aromatic scavengers [1–4].

The aim of this work is to investigate the kinetics of charge transfer reactions in a polyethylene film containing two aromatic solutes. These processes are of special importance in the case of polymers containing additives such as antioxidants, photostabilizers, etc.

Positive charge transfer between solute molecules was examined in poly(methyl methacrylate) matrices [5].

Electron transfer reactions between poly(4-vinyldiphenyl) anions and poly(1-vinylpyrene) were investigated in 2-methyltetrahydrofuran–tetrahydrofuran (1:1 by volume) solution at low temperatures [6]. Electron migration along the polymer chain was observed in poly(4-vinyldiphenyl-co-1-vinylpyrene) dissolved in 2-methyltetrahydrofuran [7]. Intermolecular charge transfer processes in solid hydrocarbon-related polymers doped with two additives have not been reported so far.

2. Experimental details

2.1. Materials

Additive-free low density polyethylene (PE) supplied by Pavia University was soaked for several weeks in the alkane solvent (*n*-hexane, *c*-hexane) with repeated changing of the solution in order to remove impurities. Pyrene (Py) of analytical grade (UEB, Belgium) was recrystallized twice from ethanol. 3,3′-Dimethyldiphenyl (DMD) of purest available grade (Aldrich) was used as received.

2.2. Preparation of PE samples

Acceptors were introduced into PE by immersing the previously purified PE film (1.5×1.5 cm^2, 250 μm thick) in a hydrocarbon solution containing the two solutes for at least 1 week in order to establish an equilibrium concentration of the additives in PE. Afterwards the PE film was rinsed with methanol to remove any surface acceptor molecules. The film strips were dried in vacuum (10^{-4} Torr for few hours) in order to remove any vestiges of the solvent used. The concentration of DMD in the PE film was not higher than about 2×10^{-2} mol dm^{-3}, while the Py concentration was in the range 10^{-4}–10^{-3} mol dm^{-3}.

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2.3. Methods

The average acceptor concentration in PE was determined spectrophotometrically (Hewlett–Packard 8452 A diode array spectrophotometer).

Pulse radiolysis measurements were carried out using a linear accelerator ELU-6 (USSR made) which delivered 1 μs pulses (dose about 200 Gy per pulse). The signals from a Hammamatsu R-928 photomultiplier were recorded on a digitizing oscilloscope (HP 64610 A) and transferred via an interface to an IBM-AT computer for storage and analysis. Certain measurements were done in the presence of appropriate interference filters IF450 and IF500 (VEB Carl Zeiss Jena) in order to decrease the photobleaching effects. More details on the detection system, the cryostat and the accelerator can be found elsewhere [3,4,8].

3. Results and discussion

In our experiments the following pair of aromatic solutes was used: DMD and Py. The ionization potential (IP) in the gas phase of DMD is higher than for Py [9] ($IP_{DMD}=8.27$ eV, $IP_{Py}=7.55$ eV), while Py has a higher electron affinity (EA) than DMD [10] ($EA_{Py}=0.42$ eV, $EA_{DMD}=-0.29$ eV).

Taking these data into account, one may expect the following charge transfer reactions to be possible:

$$\mathrm{DMD}^{\bullet -}+\mathrm{Py}\longrightarrow \mathrm{Py}^{\bullet -}+\mathrm{DMD} \qquad (1)$$

$$\mathrm{DMD}^{\bullet +}+\mathrm{Py}\longrightarrow \mathrm{Py}^{\bullet +}+\mathrm{DMD} \qquad (2)$$

Since the DMD concentration was kept higher than that of Py, DMD ions can be produced by primary charge transfer from the pulse-irradiated matrix:

$$\mathrm{PE}\longrightarrow e_t^{-}+\mathrm{PE}^{\oplus} \qquad (3)$$

$$e_t^{-}+\mathrm{DMD}\longrightarrow \mathrm{DMD}^{\bullet -} \qquad (4)$$

$$\mathrm{PE}^{\oplus}+\mathrm{DMD}\longrightarrow \mathrm{DMD}^{\bullet +}+\mathrm{PE} \qquad (5)$$

Fig. 1 shows optical absorption spectra of pulse-irradiated PE containing DMD and Py as solutes at 290 K. The absorption peak at 410 nm and the broad band centred at 650–700 nm observed 5 μs after pulse irradiation correspond to DMD radical ions [11,12], while the maximum at 380 nm represents DMD triplets [11]. The assignment of the bands centred at 460 and 500 nm to the Py radical cation ($\mathrm{Py}^{\bullet +}$) and radical anion ($\mathrm{Py}^{\bullet -}$) respectively is consistent with the spectra reported for these species in the PE system previously [1,3].

An increase in Py concentration in the range 10^{-4}–10^{-3} mol dm^{-3} caused an increase in the absorptions at 460 and 500 nm, while the broad band with the maximum at about 650–700 nm decreased (inset in Fig. 1). For the highest concentration of Py one may expect on a 5 μs time scale the direct scavenging of charges by Py in competition with DMD.

Fig. 2 shows in a qualitative way that the absorptions of $\mathrm{Py}^{\bullet -}$ (500 nm) and $\mathrm{Py}^{\bullet +}$ (460 nm) grow after the pulse,

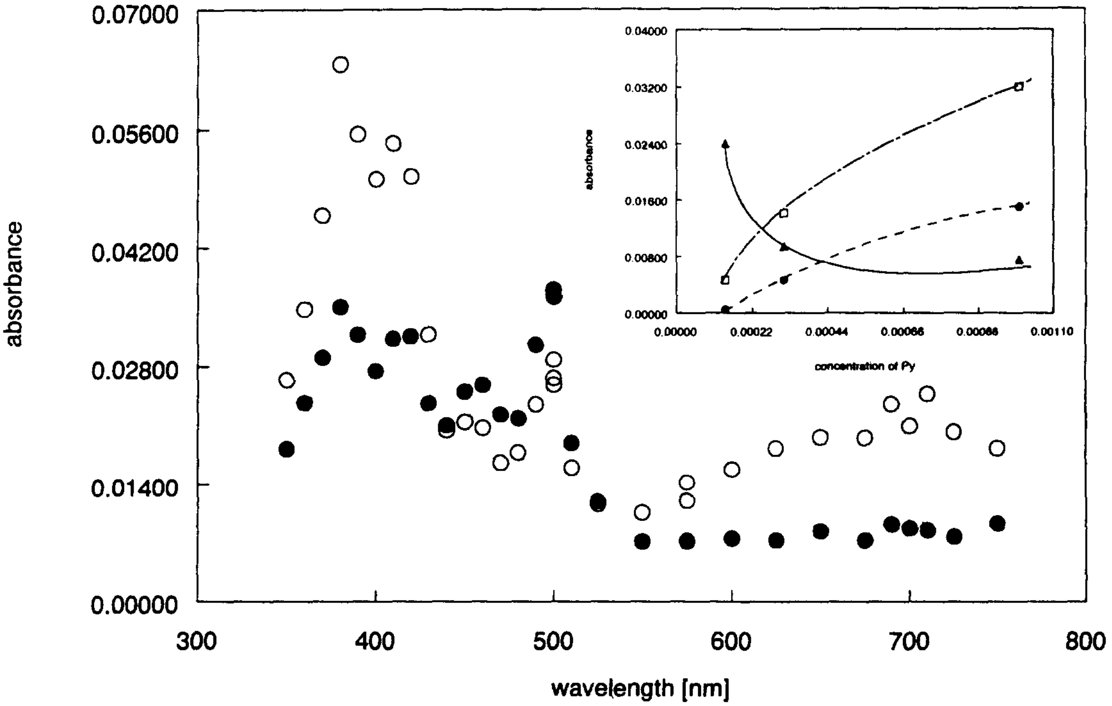

Fig. 1. Optical spectra of PE film (2×250 μm thick) containing 1.5×10^{-2} mol dm^{-3} DMD+3.13×10^{-4} mol dm^{-3} Py pulse irradiated at 290 K: ○, 5 μs after pulse; ●, 100 μs after pulse. Inset shows 5 μs absorbance (background absorption substracted) vs. Py concentration: ●, 460 nm; □, 500 nm; ▲, 650 nm.

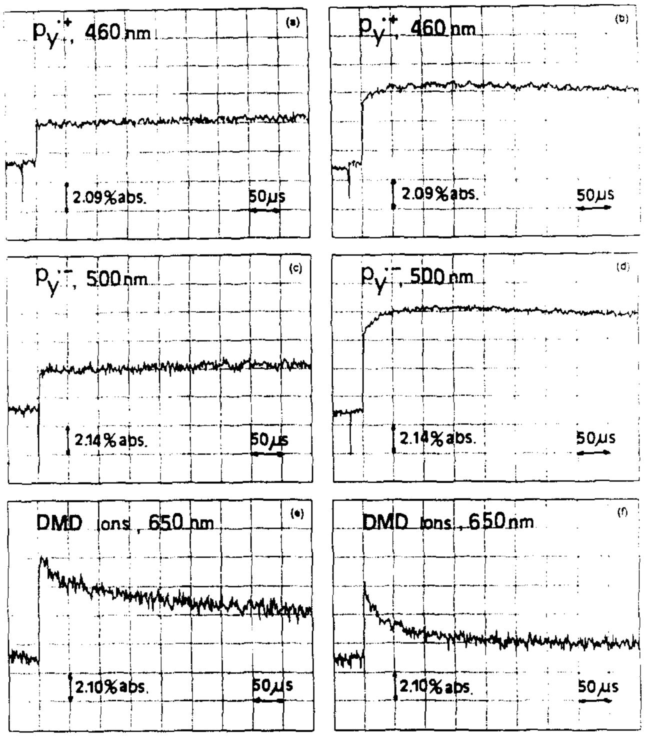

Fig. 2. Influence of Py concentration on time profiles of radical ion absorption for PE–DMD–Py systems at 290 K: (a, c, e) [DMD] = 2.16×10^{-2} mol dm^{-3}, [Py] = 1.4×10^{-4} mol dm^{-3}; (b, d, f) [DMD] = 1.5×10^{-2} mol dm^{-3}, [Py] = 3.13×10^{-4} mol dm^{-3}.

while the decay of DMD ions at 650 nm is accelerated in the presence of Py. For [Py]/[DMD] = 2×10^{-2} (Figs. 2(b), 2(d) and 2(f)) the rate of DMD ion decay is faster than in the [Py]/[DMD] = 6.5×10^{-3} system (Figs. 2(a), 2(c) and 2(e)). A similar trend is observed for the Py ion growth. In PE containing Py alone the decay of Py ion absorption was observed at room temperature [3,4].

The results demonstrate unambiguously that the charge transfer reactions occur from DMD ions to Py molecules (reactions (1) and (2)). The charge transfer processes slowed down with decreasing matrix temperature (Figs. 3A and 3B).

Since the concentration of Py was sufficiently high (about 10^{-3} mol dm^{-3}) compared with the concentration of DMD ions calculated from the experimental absorbance at 410 nm ([DMD$^{\cdot-}$] ≈ 3×10^{-5} mol dm^{-3} assuming $\epsilon_{410} = 3.7 \times 10^4$ mol^{-1} dm^3 cm^{-1} found for diphenyl [12]), the charge transfer processes under consideration can be regarded as a pseudo-first-order reaction. Our experimental results can be approximated by the first-order kinetic equation

$$-\frac{dc}{dt} = k(t)c \qquad (6)$$

with a time-dependent rate constant of the form [13]

$$k(t) = \beta t^{\alpha - 1} \qquad (7)$$

where β and $0 < \alpha \leqslant 1$ are constants. The lower the numerical value of α, the wider is the distribution function $f(k)$; for $\alpha = 1$ one gets mono-exponential decay and β corresponds to the time-independent constant known in classical kinetics. The first-order kinetic equation (6) yields upon integration

$$\frac{c}{c_0} = \exp\left(\frac{-\beta t^{\alpha}}{\alpha}\right) = \exp\left[-\left(\frac{t}{\tau_0}\right)^{\alpha}\right] \qquad (8)$$

which for an effective lifetime $\tau_0 = (\alpha/\beta)^{1/\alpha}$ can be interpreted as a superposition of many simple exponential decays, i.e.

$$\exp\left[-\left(\frac{t}{\tau_0}\right)^{\alpha}\right] = \int_0^{\infty} f(\tau) \exp\left(\frac{-t}{\tau}\right) d\tau \qquad (9)$$

The parameter α measures the dispersivity of reaction [13]. In the solid state the statistical disorder of the system is temperature and time dependent. The higher the temperature or the longer the time scale, the less dispersive are the processes in a given system.

The experimental decay–growth curves were always approximated by Eq. (8) using α as a fitting parameter (Figs. 3A and 3B). The growth of Py ions is very complex, because the experimental curves represent the superposition of the Py ion decay (time dependent [3,4]) and Py ion generation due to charge transfer (probably time dependent too). The rate parameters k applied in the Arrhenius equation were calculated as $1/\tau_0$.

The Arrhenius relations shown in Fig. 3 can be characterized by two linear regions which intersect at 218–232 K, which is very close to the glass transition temperature (T_g) estimated for PE [14]. Activation energies calculated from the two linear parts of the Arrhenius plot were equal to 83.1–88.9 kJ mol^{-1} for temperatures higher than T_g and 1.8–4.4 kJ mol^{-1} below T_g respectively. These results are very similar to those obtained for PE–Py [3] and PE–DMD [4] systems (Table 1). The decay curves of Py$^{\cdot-}$ and DMD ion absorptions were detected for these systems respectively and treated kinetically [3,4].

At temperatures higher than T_g one may expect that a diffusion mechanism contributes to the charge transfer reac-

Table 1
Activation energies (E_a) and glass transition temperatures (T_g) found from kinetic measurements

Reaction investigated	T_g (K)	E_a (kJ mol^{-1}) $T > T_g$	E_a (kJ mol^{-1}) $T < T_g$	Ref.
Py$^{\cdot-}$ + Py$^{\cdot+}$	~240	84.1	1.77	[3]
DMD$^{\cdot-}$ + DMD$^{\cdot+}$	~222	73.3	2.3	[4]
DMD ions + Py calculated for:				
Py ion growth (460, 500 nm)	~232	88.9	4.4	This paper
DMD ion decay (650 nm)	~218	83.1	1.8	This paper

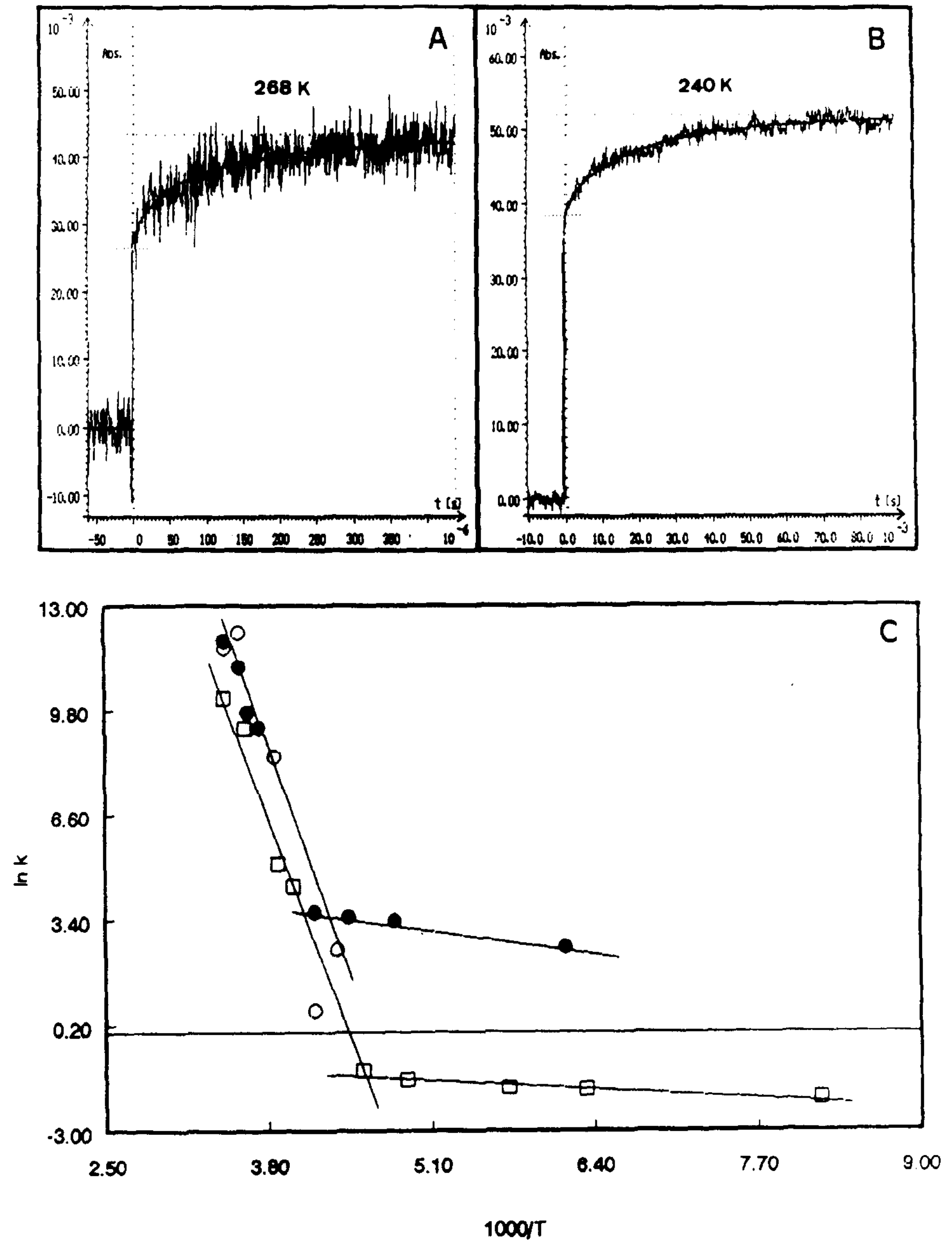

Fig. 3. (A,B) Influence of temperature on $Py^{\cdot-}$ absorption growth at 500 nm (experimental curves). The full curves represent the best fit using Eq. (8). Calculations were done for (A) $\alpha = 0.599$, $\tau_0 = 8.82 \times 10^{-5}$ s and (B) $\alpha = 0.745$, $\tau_0 = 1.87 \times 10^{-2}$ s. (C) Arrhenius dependences of rate parameters $k = 1/\tau_0$ for Py ion growth and DMD ion decay ([DMD] $= 2.16 \times 10^{-2}$ mol dm^{-3}, [Py] $\approx 10^{-3}$ mol dm^{-3}): ○, $Py^{\cdot+}$, 460 nm; ●, $Py^{\cdot-}$, 500 nm; □, DMD ions, 650 nm.

tion. The α values found in this temperature region were in the range 0.60–0.75 required for a diffusion-assisted process [13].

According to Kitamaru and Hori [15], for $T > T_g$ one may expect a liquid-like molecular mobility in the amorphous regions of PE. Tay et al. [16], using ^{13}C high resolution solid state nuclear magnetic resonance (NMR) measurements, estimated the rotational correlation time of the Py molecule dissolved in PE to be shorter than 50 ns at room temperature. There is no doubt that in the amorphous regions of PE, diffusion-assisted motion seems to be possible, at least at room temperature.

In order to find any correlation with rate data found by another method (i.e. diffusion coefficient), the second-order rate constant k_{II} for the charge transfer reaction from DMD ions to Py was estimated on the basis of the reaction half-life to be about 1.5×10^8 mol^{-1} dm^3 s^{-1} at 290 K for the PE+DMD (2.16×10^{-2} mol dm^{-3}) + Py (10^{-3} mol dm^{-3}) system. This value should be treated with some caution because of the non-homogeneous distribution of scavenger molecules in PE, at least for the highest scavenger concentration [17].

The rate constant k_{II} for a bimolecular diffusion-controlled reaction of spherical particles is represented by the Stokes–Einstein–Smoluchowski relation

$$k_{II}=4\pi RD \tag{10}$$

where R is the radius of the reaction sphere and D is the sum of the diffusion coefficients of reacting species. In our case R can be regarded as the sum of the radii of DMD and Py molecules and is assumed to be about 0.7 nm. The values of D was estimated from the above experimental value of k_{II} to be 2.8×10^{-7} cm^2 s^{-1} at 290 K. The numerical value of our diffusion coefficient is almost equal to the D value obtained by the fluorescence method for *N,N′*-dimethylamine in a hydrocarbon-swollen PE film with covalently attached anthryl groups [18].

The diffusion coefficients of various antioxidants in PE obtained by direct methods were found to be two orders of magnitude lower than the D value estimated by us; however, the D values depend on the chemical structure and molecular weight of the diffusing molecule [19] as well as on the time scale of the measurements.

The very low activation energy for charge transfer in the temperature range below T_g strongly suggests that the matrix rigidity at these temperatures prevents any significant mobility of the solutes and that a tunnelling mechanism [20] must be involved in the electron exchange. In this temperature range the $k=1/\tau_0$ values for DMD ion decay were very different from the rate constants for Py ion growth (Fig. 3). Probably the Py–DMD ion tunnelling distance distribution is very different from that for DMD ions alone.

It is worth mentioning that the charge transfer kinetics observed in a PE + solutes system can be discussed in terms of the theoretical predictions based on the free-volume size distribution theory of Robertson [21]. In view of the packing differences and the resulting free-volume differences in PE above T_g and below T_g, one may expect different rates of charge transfer between molecular ions in these temperature ranges as observed.

It appears that the rate of charge transfer between DMD ions and Py is closely related to the dynamic properties of the polymer matrix. Since optical absorption measurements by the pulse method are quite sensitive, the charge transfer processes can be used as a probe of diffusional motion in polymer systems.

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