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High hole mobilities in the mixtures of oligo(methylphenylsilylene) and phenylenediamine derivatives

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Abstract

Oligo(methylphenylsilylene)s of the number average molecular mass ranging from 1240 to 13410 have been synthesised and characterised by gel permeation chromatography and differential scanning calorimetry. The ionisation potentials of the materials were measured by the electron photoemission in air method. Hole drift mobilities have been measured by time of flight technique in neat oligo(methylphenylsilylene)s and in their molecular mixtures with the different derivatives of phenylenediamine. It was found that hole drift mobilities in the mixtures of oligo(methylphenylsilylene) with some phenylenediamine derivatives at high electric fields approach 10^{-2} cm^2 V^{-1} s^{-1} and markedly exceed those in neat oligo(methylphenylsilylene)s and in phenylenediamines. The materials exhibit high electrophotographic photosensitivities and low residual potentials. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Oligo(methylphenylsilylene); Phenylenediamine; Hole drift mobility

1. Introduction

A number of technical processes in the rapidly growing field of information processing are based on photoconductive materials [1]. Silicon-based polymers, especially polysilylenes used as photoconductive materials have been the subject of an increasing numbers of studies [2]. Organo-substituted linear polysilylenes are the polymers containing only silicon atoms in the backbone. Their electronic properties are associated with σ-electron conjugation in the Si backbone, which allows significant delocalization of electrons along the chain. Therefore, polysilylenes constitute an interesting class of polymeric materials that continue to attract attention in a number of areas. Due to the electronic and charge transport properties, applications in microlithography, electrophotography, display fabrication, data storage, photorefractivity have been investigated [3]. Several methods of the synthesis of polysilylenes are known [4,5]. The first polysilylene derivatives were probably prepared by Kipping in the early 1920s by condensation of diphenyldichlorosilane with sodium metal [6]. It is interesting to note that in spite of considerable efforts invested in a search for alternatives, the modified Wurtz coupling of dichlorosilanes remains currently the most viable general procedure for preparation of high-molar-mass, linear polysilylene derivatives. The most widely studied polysilane poly(methylphenylsilylene) (PMPS) is usually also prepared by Wurtz coupling of the corresponding dichlorosilane [7]. In order to recreate the surface of the sodium metal permanently ultrasound is often used in this reaction. The relative weight average molecular weight of the polymer obtained by such procedure usually exceeds 200 000. The hole drift mobility of high-molar-mass PMPS is rather high. Most of the authors report room temperature mobility of ca. 10^{-4} cm^2 V^{-1} s^{-1} at an electric field of 10^5 V cm^{-1} [7,8]. Heavy doping with molecules, which themselves are transport-active can markedly increase hole mobility in PMPS [9]. For example, heavy doping of PMPS with phenylenediamine (PDA) derivative 1,3-bis(3,3′-dimethyldiphenylamino)benzene results in hole mobility which is not only greater than in neat undoped PMPS, but greater than PDA derivative would show if it was molecularly dispersed in polycarbonate at the same concentrations. High hole mobilities exceeding 10^{-3} cm^2 V^{-1} s^{-1} at room temperature have been recently observed in self-organised individual oligomerhomologues of poly(dimethylsilylene) [10]. In this presentation we report on the synthesis

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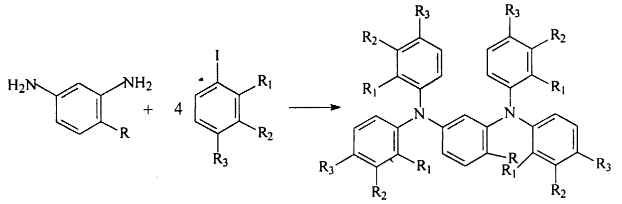


(a) R = H, $R_1 = CH_3$, R_2 = H, R_3 = H;
(b) R = H, R_1 = H, $R_2 = CH_3$, $R_3 = CH_3$;
(c) R = CH_3, R_1 = H, R_2 = H, $R_3 = CH_3$;
(d) R = H, R_1 = H, $R_2 = CH_3$, R_3 = H.

Scheme 1.

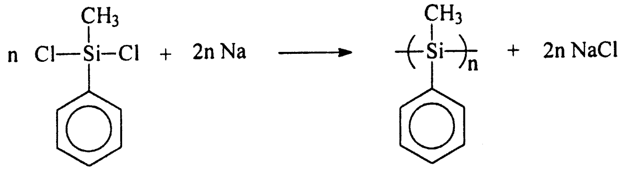
of semi-crystalline oligomers of PMPS and investigation of the charge transport properties of the neat oligomers and their molecular mixtures (solid solutions) with PDA derivatives 1,3-bis(2,2′-dimethyldiphenylamino)benzene (**a** in the Scheme 1, (a) $R = H, R_1 = CH_3, R_2 = H, R_3 = H$; (b) $R = H, R_1 = H, R_2 = CH_3, R_3 = CH_3$; (c) $R = CH_3, R_1 = H, R_2 = H, R_3 = CH_3$; (d) $R = H, R_1 = H, R_2 = CH_3, R_3 = H$), 1,3-bis(3,3′,4,4′-tetramethyldiphenylamino)benzene (**b**), 1,3-bis(4,4′-dimethyldiphenylamino)-4-methylbenzene (**c**), and 1,3-bis(3,3′-dimethyldiphenylamino)benzene (**d**).

2. Experimental

2.1. Preparation of phenylendiamine derivatives (Scheme 1)

Synthesis of *N*,*N*,*N*′,*N*′-tetraarylphenylene diamines **a**–**d** was carried out according to the following procedure [11].

A 0.5 l flask equipped with a reflux condenser (0.25 m length), attached to a Liebig condenser was charged with diamine (0.02 mol), corresponding iodoarene (0.2 mol), anhydrous potassium carbonate (0.12 mol), and electrolytic copper powder (4 g) in 100 ml of nitrobenzene. The mixture was stirred vigorously under nitrogen at the boiling temperature of nitrobenzene. The reaction mixture was heated at such a rate that water, liberating in the course of the reaction together with a little amount of nitrobenzene and iodoarene was slowly distilled. The distillate was dried over anhydrous magnesium sulphate and returned back into reaction flask. After termination of the reaction (8 h) the copper and inorganic salts were removed by filtration of the hot reaction mixture. Nitrobenzene and unreacted iodoarene is distilled off, and the residue was dissolved in chloroform and then was adsorbed by 100 g of powdered Al_2O_3. The later was dried and subjected to extraction with *n*-hexane in a 0.5 l Soxhlet extractor. (The procedure is carried out until hexane turns colourless). The extraction solution was worked up with activated charcoal and the solvent evaporated. The residue was dissolved in acetone (1:1) and cooled to 0°C. The separated crystalline products were filtered off. Products were purified by column chromatography (Al_2O_3, *n*-hexane:1,2-dichloroethane, 5:1) and subsequent recrystallisation from glacial acetic acid or *n*-octane.



Scheme 2.

For **a** the yield was 32.5%, mp 142–143.5°C (acetic acid).
For **b** the yield was 28%, mp 129.5–130.5°C (*n*-octane).
For **c** the yield was 45%, mp 160.5–161.5°C (*n*-octane).
For **d** the yield was 37.1%, mp 61–63°C (*n*-octane).

Spectral and elemental analysis data of *N*,*N*,*N*′*N*′-tetraarylphenylenediamine derivatives **a**–**d** have been reported [11].

2.2. Preparation of poly(methylphenylsilylene) (Scheme 2)

The synthesis of PMPS was carried out in a three-neck flask, equipped with a mechanical stirrer, a nitrogen inlet and a condenser. Sodium was dispersed in refluxed toluene, afterwards dichloromethylphenylsilane was slowly dropped into the suspension. The reaction mixture was stirred for 5–6 h then inorganic precipitates were removed by filtration of the hot reaction mixture. Polymers were precipitated in hexane or methanol and dried until the constant mass.

2.3. Measurements

Gel permeation chromatography (GPC) analysis was performed on a Waters Styragel, Pumpe Waters 590 equipped with a UV (Waters 486) detector and refractomer (Waters 410) detector using THF as an eluent and polystyrene standards at a rate of 0.5 ml min^{-1}. Differential scanning calorimetry (DSC) curves were recorded by a differential scanning calorimeter Perkin–Elmer DSC 7 at a heating rate 10 K min^{-1}.

Hole drift mobilities and the electrophotographic parameters were measured using laminar samples, which consist of casein layer, charge transporting layer and photogeneration layer of the dispersion of Y form of titanyl phthalocyanine particles in polyvinylbutyral coated on a conductive substrate. The hole drift mobility was measured by time of flight method [12]. Electric field was created by positive corona charging. The charge carriers were generated at the layer surface by illumination with pulses of nitrogen laser (pulse duration was 2 ns, wavelength 337 nm). The capacitance probe that was connected to the wide frequency band electrometer measured the rate of the surface potential decrease dU/dt. The transit time t_t was determined by the kink on the curve of the dU/dt kinetics. The drift mobility was calculated by the formula $\mu = d^2/U_0 t_t$, where d is the

Table 1
Conditions of the synthesis and characteristics of poly(methylphenylsilylenes)

Sample	Na:monomer molar ratio	Reaction time (min)	Yield (%)	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
PMPS-1	2.017:1	60	17.3	4410	11920	2.7
PMPS-2	1.765:1	180	24	2710	8400	3.1
PMPS-3	1.765:1	180	43.3	13410	16 830	1.26
PMPS-4	2.444:1	180	33	1240	3070	2.48
PMFS-5	2.444:1	180	13.3	9440	13 430	1.42
PMPS-6	2.105:1	360	27	9280	15 220	1.64
PMPS-7	2.318:1	180	26	1410	1810	1.28
PMPS-8	1.801:1	360	19	3940	13 180	3.34

layer thickness, U_0 is the surface potential at the moment of illumination.

The samples for the ionisation potential measurement were prepared as follows. The transporting materials were dissolved in THF and were coated on Al plates precoated with ~0.5 μm thick methylmethacrylate and methacrylic acid copolymer adhesive layer. The role of this layer was also to eliminate the electron photoemission from Al layer. The thickness of the charge transporting material layer was 0.5–1 μm.

The ionisation potential (Ip) of the polymer layer was measured by the electron photoemission method in air. Usually the photoemission experiments with metal or inorganic semiconductor samples are carried out in vacuum and high vacuum is one of the main requirements for these measurements [13,14]. If vacuum is not high enough the sample surface oxidation and gas adsorption are influencing the measurement results. In our case, however, the organic materials investigated are stabile enough with respect oxygen. The samples are prepared from solutions in organic solvents in air, so oxygen and other air gases may not only be adsorbed on the surface, but they also may saturate the volume of the samples. Such organic layers are also used in practice in air, for example in electrophotography, so we believe this justifies measurement of the characteristics of these materials in air.

The measurement method is, in principle, similar to the described in Ref. [15]. The samples were illuminated with monochromatic light from the quartz monochromator with deuterium lamp. The power of the incident light beam was $2–5 \times 10^{-8}$ W. The negative voltage of −300 V was supplied to the sample substrate. The counter-electrode with the 4.5×15 mm^2 slit for illumination was placed at 8 mm distance from the sample surface. The counter-electrode was connected to the input of the BK2-16 type electrometer, working in the open impute regime, for the photocurrent measurement. The $10^{-15}–10^{-12}$ A strong photocurrent was flowing in the circuit under illumination. The photocurrent I is strongly dependent on the incident light photon energy $h\nu$. The $I^{0.5} = f(h\nu)$ dependence was plotted. Usually the dependence of the photocurrent on incident light quanta energy is well described by linear relationship between $I^{0.5}$ and $h\nu$ near the threshold [16]. The linear part of this dependence was extrapolated to the $h\nu$ axis and Ip value was determined as the photon energy at the interception point.

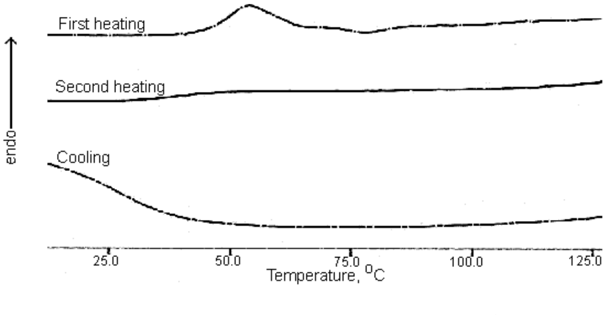


Fig. 1. DSC curves of PMPS-4. Heating rate 10 K min^{-1}, cooling rate 40 K min^{-1}.

3. Results and discussion

Phenylenediamines were synthesised by the Ullmann reaction (Scheme 1) [11].

All PDA derivatives synthesised can exist in amorphous phase and form glasses. PMPS was synthesised by the Wurtz-type coupling of dichloro-methylphenylsilane (Scheme 2).

Conditions of the synthesis, yields and relative molecular masses of the selected samples of PMPS are presented in Table 1. It is evident that the molecular mass and polydispersity index of the polymers obtained do not depend on the molar ratio of sodium and dichloromethylphenylsilane in the initial reaction mixture as well as on the reaction time. This observation can be explained by the heterogeneity of the reaction mixture. The number average molecular weight of the synthesised PMPS ranges from 1240 to 13 410. It is evident that most of the PMPS samples reported in this presentation are oligomers.

The synthesised samples of PMPS have been characterised by DSC. The typical DSC curve is shown in Fig. 1. The first heating run has revealed melting at 54°C while the second heating after recooling at 40 K min^{-1} showed no any signal of crystallisation or melting and revealed only glass transition at 41°C. These observations allow to presume that oligo(methylphenylsilylene)s synthesised in this work and isolated by precipitation in hexane or methanol are semi-

Table 2
Characteristics of the morphological transitions of PMPS

Sample	First heating		Second heating	
	Enthalpy change ΔH (J g^{-1})	T_m (°C)	Heat capacity change ΔC_p (J g^{-1} °C^{-1})	T_g (°C)
PMPS-4	5.228	54	0.136	41
PMPS-6	1.762	66	0.128	76

crystalline oligomers. Fast cooling from the melt enables to obtain fully amorphous oligo(methylphenylsilylene)s.

Table 2 shows characteristics of the morphological transitions of selected samples of oligomeric PMPS. The value of enthalpy change of melting decreases with the increase of the relative molecular mass of the oligomers. This observation shows that the degree of crystallinity of the oligomers of low relative molecular mass is higher than that of high-molar-mass samples of PMPS. The value of heat capacity change at glass transition also decreases with the increase of relative molecular mass.

Fig. 2 shows the room temperature dependencies of hole drift mobility on electric field in oligo(methylphenylsilylene)s of different relative molecular mass. It is evident that the charge mobility in the sample of higher relative molecular mass (PMPS-6) is slightly lower than that in low-molar-mass oligomers PMPS-4 and PMPS-7. This observation is consistent with the data of Nakayama et al. [17] indicating that room temperature hole drift mobility decrease slightly in PMPS with the increase of the relative molecular mass. At high electric fields hole mobility in the samples of oligo(methylphenylsilylene) studied exceeds 10^{-3} cm^2 V^{-1} s^{-1}. The mobility values at low electric fields are about the same, as in Ref. [18], but the field dependence is stronger in our case.

We have measured hole drift mobilities in molecular glasses of neat PDA derivatives using no polymer binders. The results are presented in Table 3 and in Figs. 3 and 4. The hole mobility values are dependant on the on the number of methyl substituents and their position in a PDA molecule. The highest mobility was observed in the compound **c** containing methyl groups at the *para* positions of the side benzene rings and at the central ring. The lowest mobility was observed in the compound **a** containing methyl groups in the *ortho* positions at the side rings and no substituent at the central ring.

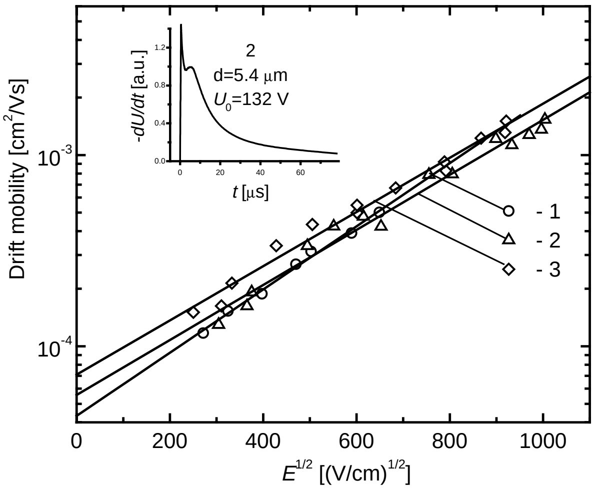


Fig. 2. The electric field dependencies of the hole drift mobility in charge transport layers of selected samples of PMPS at 20°C. PMPS-4 (1), PMPS-6 (2), PMPS-7 (3). The typical small charge transient shape is shown on the insert.

Figs. 3 and 4 compare the electric field dependencies of the hole mobilities in the molecular mixtures of PMPS and the PDA derivatives with those in pure PMPS and in neat PDA derivatives. All the mixtures show higher hole mobilities than pure PMPS. The presence of methyl group at the central aromatic ring of the PDA derivatives as well as increase of number of methyl groups at the side rings apparently leads to the increase of the hole mobility in the mixtures of PMPS and PDA derivatives. The values of hole drift mobility μ and μ_0 found by extrapolation of the experimental dependencies to the values of electric field $E = 10^6$ V cm^{-1} and to $E = 0$ V cm^{-1} are given in

Table 3
Hole drift mobilities, ionisation potentials and electrophotographic parameters of the hole-transporting compounds and their molecular mixtures

Components of the charge transport layer	μ (cm^2 V^{-1} s^{-1}), $E = 10^6$ V cm^{-1}	μ_0 (cm^2 V^{-1} s^{-1}), $E = 0$ V cm^{-1}	Ip (eV)	d (μm)	U_0 (V)	U_R/U_0	$S_{1/2}$ (m^2 J^{-1}), 780 nm
PMPS-6	1.5×10^{-3}	5.6×10^{-5}	5.59	5.4	920	0.16	99
a	1.4×10^{-3}	$\sim 8\times10^{-6}$	5.63	6.6	710	0.067	1.9[a]
PMPS-6 + **a**	3.5×10^{-3}	5×10^{-5}		9.7	1200	0.14	148
b	5×10^{-3}	$\sim 1.5\times10^{-4}$	5.36	2.7	384	0.23	9.1[a]
PMPS-6 + **b**	8.3×10^{-3}	3.2×10^{-4}		9.0	840	0.095	148
c	8×10^{-3}	5×10^{-4}	5.53	5.6	630	0.032	6.2[a]
PMPS-6 + **c**	9.5×10^{-3}	3.1×10^{-4}		7.6	800	0.10	154
d	4.6×10^{-3}	1.2×10^{-4}	5.59	7.2	640	0.13	123
PMPS-6 + **d**	1×10^{-2}	4×10^{-4}		11.5	1100	0.13	142

[a] 280 nm.

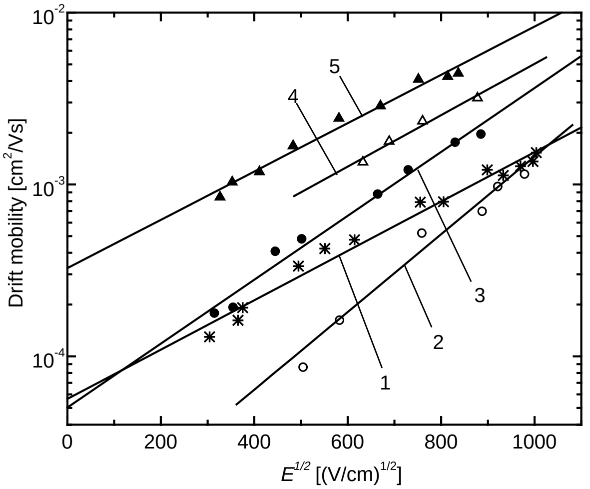


Fig. 3. The electric field dependencies of the hole drift mobility in charge transport layers of poly(methylphenylsilylene) and of its molecular mixtures with phenylene diamines (1:1 by mass) at 20°C: PMPS-6 (1), **a** (2), PMPS-6 + **a** (3), **b** (4), PMPS-6 + **b** (5).

Table 3. The most effective dopants for PMPS among the PDA derivatives studied have appeared to be the compounds **b** and **d**. The hole mobility in the molecular mixtures of PMPS with these PDA derivatives approaches 10^{-2} cm^2 V^{-1} s^{-1} at high electric fields. This is a very high value for organic disordered solids. PMPS-6 heavily doped with **d**, exhibits higher hole drift mobility than neat PMPS-6 and the amorphous film of neat PDA **d**. The enhancement of mobility in PMPS blends with the PDA derivative of the **d** structure was also reported in Ref. [9]. The mobility value of 10^{-3} cm^2 V^{-1} s^{-1} was recorded in the 1:1 mixture. In our case, however, the mobility value is by one order of magnitude higher.

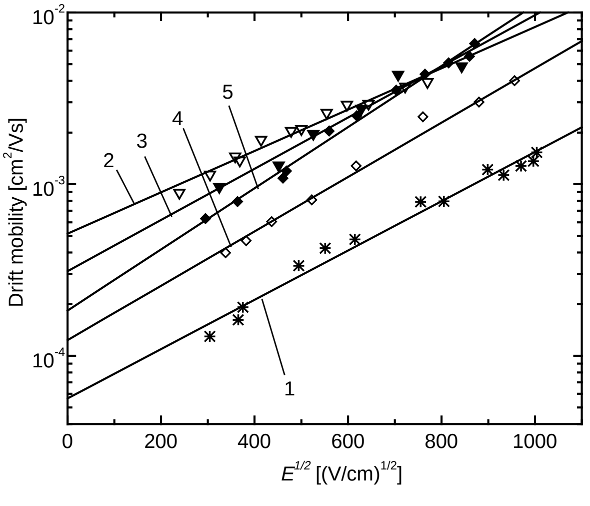


Fig. 4. The electric field dependencies of the hole drift mobility in a charge transport layers of poly(methylphenylsilylene) and of its molecular mixtures with phenylene diamines (1:1 by mass) at 20°C: PMPS-6 (1), **c** (2), PMPS-6 + **c** (3), **d** (4), PMPS-6 + **d** (5).

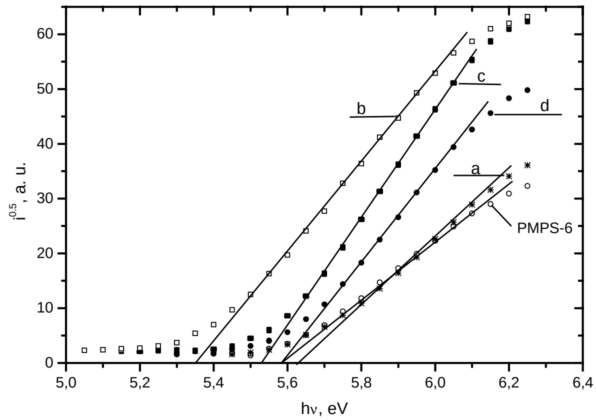


Fig. 5. The electron photoemission in air spectra of PMPS-6, and of PDA derivatives **a**, **b**, **c**, and **d**.

In order to explain enhanced hole mobilities in the mixtures studied we have measured the Ip values of PMPS-6 and of the PDA derivatives. The results of the electron photoemission investigations are shown on Fig. 5. The ionisation potential values are given in Table 3. The extrapolation of the linear parts of the $I^{0.5}$ dependencies on $h\nu$ for the PMPS-6 and **d** materials intercept with the abscissa at the same point indicating the equal ionisation potential values for these two materials 5.59 eV. The equal, but somewhat higher ionisation potential values of 5.62 eV for these two materials were reported in Ref. [14], while the values for PMPS of varying molecular mass are in the range 5.47 to 5.66 eV in Ref. [18]. The equality of the Ip values for PMPS-6 and **d** may be an important factor, leading to high hole mobility in the mixture of these two materials. The hole transport should proceed freely by hopping between PMPS and **d** molecules. However, in other blends, especially in the blend of PMPS-6 and **b**, such a hopping should be hindered by the considerable ionisation potential difference. It is likely, that the hole transport proceeds by hoping mainly between the **b** molecules, while the PMPS-6 molecules are acting as inert binder material. Despite this, the hole mobility in the PMPS-6 and **b** mixture is only slightly lower, than in the mixture with **d**, and well exceeds the mobility values in the neat PMPS-6 or **b**. This allows for the suggestion that there is a strong factor leading to an increase of charge carrier mobility. Such an enhancement can be explained by the structural constrains on the charge carrying molecules imposed by the polymer matrix. According to Baessler [19] such constrains favour charge exchange and minimise disorder effects. The effect of the disorder is also seen in the small charge transient shapes (Fig. 6). In pure PMPS-6 and in its mixtures with PDA derivatives, except the compound **a**, the characteristic kink is well seen on the double linear plot, while in the neat **b** it may be found only on log–log plot. This means, that there is higher disorder level in the pure **b** than in its mixtures with PMPS. On the other hand, the kink is well seen in case of the layers of neat **c** on double linear plot and addition of PMPS has little effect on mobility despite the fact, that

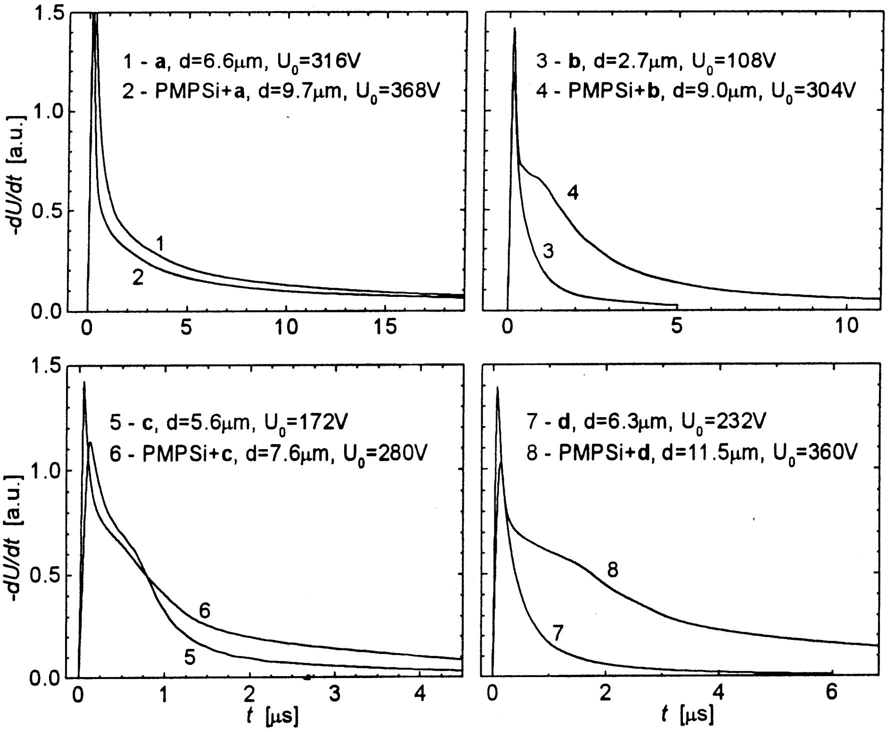


Fig. 6. The small charge transient shapes of PDA derivatives **a**, **b**, **c**, **d**, and their mixtures with PMPS-6.

the ionisation potential values of the two materials differ by only about 0.05 eV.

Table 3 also shows some electrophotographic parameters of the electrophotographic layers containing oligomeric PMPS and its molecular mixture with the derivatives of PDA as hole transport layers. The photosensitivity was measured at the wavelength of 780 nm for the samples with the charge generation layer and at 280 nm for the samples without it. It is evident that the layers containing the mixtures of PMPS and PDA derivatives exhibit the highest photosensitivity and the lowest ratios of the residual and initial potentials. High hole mobility in the molecular mixtures of oligomeric PMPS and the derivatives of PDA may enable to use them in preparation of photoreceptors for high-speed printers or copying machines.

Acknowledgements

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