

*Der Liaw¹, Ying Huang¹, Cheng Chang¹, Boris Rumyantsev², Tat'yana Lozinova²,
Vitaly Zubov³, Anatoly Olkhov⁴, Victor Bagratashvili⁵,
Gennady Zaikov² and Anatoly Ischenko³*

PHOTOELECTRON PROPERTIES AND PARAMAGNETISM OF POLYIMIDES BASED ON *N,N,N',N'*-SUBSTITUTED *p*-PHENYLENEDIAMINE AND DIANHYDRIDES

¹*Department of Chemical Engineering, National Taiwan University of Science and Technology,
Taipei 10607, Taiwan*

²*Emanuel Institute of Biochemical Physics, RAS, Moscow 119991, Russia*

³*Moscow Lomonosov State University of Fine Chemical Technologies, Moscow 119571, Russia*

⁴*Plekhanov Russian University of Economics, Moscow 117997, Russia*

aolkhov72@yandex.ru aischenko@yasenevo.ru

⁵*Institute on Laser and Information Technologies, RAS, Troitsk, Moscow 142190, Russia*

Received: March 11, 2015 / Revised: May 21, 2015 / Accepted: September 02, 2015

© Liaw D., Huang Y., Chang C., Rumyantsev B., Lozinova T., Zubov V., Olkhov A., Bagratashvili V.,
Zaikov G., Ischenko A., 2015

Abstract. The photoelectric characteristics and paramagnetic properties of newly synthesized polyimides (PI) have been investigated using the electrophotographic method and an ESR signal study. The polyimides based on *N,N,N',N'*-substituted *p*-phenylenediamine and dianhydrides, were prepared *via* polycondensation. The polymers exhibit excellent solubility in common organic solvents, and have high thermal stability. The PI films exhibit photoelectric sensitivity in the UV, and visible spectral regions. The mechanism of photogeneration has been investigated. Paramagnetism of the air stored PI samples has been determined by the air oxidized PI donor fragments (stable radicals). PI ESR spectra in a solid state and solution have been investigated as well as the effect of light excitation on those spectra.

Keywords: polyimide, electrophotographic method, ESR signal, polycondensation, photoelectric characteristics, photogeneration, cation-radical.

1. Introduction

In the last two decades, *p*-conjugated polymers have attracted considerable interests because of their potential applications in electrochromics [1-4], light emitting diodes [5-9], organic thin film transistors [10-14], photovoltaic [15-18], and polymer memory [19, 20]. Fluorine and its

analogous derivatives have drawn much attention in optoelectronics because they generally have good solubility, high luminescent efficiency, and very good charge carrier mobility [21-24]. However, they are also known to have drawbacks such as unsatisfied thermal stability and the formation of excimers in the solid state [25, 26]. Essentially higher thermal, photochemical and radiation stability are inherent to polyimides (PIs) and their photoelectrical, optical and other properties are determined to a great extent by the electron charge transfer between donor and acceptor units of the polymer chain.

The exceptional photoelectric characteristics of organosoluble PIs based on triphenylamine and its derivatives [27], as well as their composites with the organic and inorganic semiconductors [28, 29] (the photoelectric sensitivity (PES) S , quantum yield of the charge carrier photogeneration β , drift length l_D , and collection coefficient $C(Z)$) are the basis of their applications in a series of optoelectronic devices: photovoltaic and electroluminescent cells [30, 31], photodetectors [32] and organic phototransistors [33]. In the present work, the photoelectric characteristics, paramagnetism and their correlation for the newly synthesized PI [34, 35] are investigated *via* the electrophotographic (EPG) method [36] and an electron spin resonance (ESR).

The effect of radical product (Poole-Frenkel pairs, PFP) on the photoelectric sensitivity (photostimulated

currents) in PI films based on diphenylbenzidine is observed for the first time in [37, 38]. As shown in these works PFP is a triphenylamine cation radical (TPA⁺) that is stabilized in the field of Cl⁻ (Br⁻) anion, generated by a free-radical photochemical reaction with participation of C₂H₂Cl₄ or CBr₄. Furthermore under photostimulation of long-lived PFP in TPA (red and near IR spectral range) or charge transfer complex absorption bands, a transformation into short-lived Onsager type ion-radical pair occurs, which undergoes field-assisted thermal dissociation, resulting in a charge carrier photogeneration. Similar processes with PFP formation and accumulation and their subsequent photostimulation are observed on the interface of organic polymer heterostructures [32].

In the present work photoelectric properties, paramagnetism and their correlation for newly synthesized organosoluble PI based on *N,N,N',N'*-substituted *p*-phenylenediamine with propeller-shaped triarylamine fragments are investigated. Their synthesis is described in [39]. All polymers with high molecular weight form flexible and strong films. The electrochromic properties of PI films are found to be characterized by their color alternation from a pale-yellow in a neutral form to green (for the single-oxidized state, cation radical) and finally blue for the second oxidized state under potential variation from 0 to 1.5 V in an electrochemical cells with a liquid electrolyte. Cyclovoltammetry of the polymer films shows two reversible redox couples at potentials of 0.91–0.99 V and 1.30–1.38 V. Investigation of the oxidation mechanism suggests that oxidation involves not only electron removal from the nitrogen atom but from alkyl-phenyl groups as well. The results of the work prove that electron rich triarylamine fragments are oxidized easily, forming stable cation-radicals. In the present work it is found that cation-radicals can be also generated in other processes: under dark hole injection from the corona charged polymer film surface (labile radicals) and in the solid state samples stored in the air (ESR registered stable radicals as a result of interaction with O₂). The increase of ESR signal intensity is observed under short wavelength UV excitation of PI solutions indicating radical generation. On the basis of the revealed dependence of photoelectric sensitivity on labile radical accumulation the conclusion can be drawn regarding the charge carrier photogeneration as a result of labile radical photostimulation in the absorption band (photostimulated currents).

2. Experimental

2.1. Synthesis of Polyimides

The polyimides were prepared by a procedure similar to the one described in [39]. An example is described as

follows (Scheme 1). To a stirred solution of 0.6 g (0.883 mmol) of diamine in 5 ml DMAc, 0.382 g (0.883 mmol) of 4,4'-(hexafluoroisopropylidene) diphthalic anhydride (6FDA) was gradually added. The mixture was stirred at room temperature for 4 h in the nitrogen atmosphere to form poly(amic acid). Chemical cyclodehydration was carried out by adding equal molar mixtures of acetic anhydride and pyridine into the poly(amic acid) solution under stirring at room temperature for 1 h, and the solution was then treated at 373 K for 4 h. The polymer solution was poured into methanol. The precipitate was collected by filtration, washed thoroughly with methanol, and then dried at 373 K under vacuum.

2.2. Electrophotographic Study

The electrophotographic method involves the study of the kinetics of dark and photoinduced decay of the surface potential in polymer films that are charged in the field of positive or negative corona discharge [36]. The maximum potential of charging V and the rate of the potential dark decay $(dV/dt)_D$ are determined by the dark conductivity of the films: higher dark conductivity results in a lower value of V and higher $(dV/dt)_D$. The photoinduced decay potential $(1/I)(dV/dt)$ (where I is the intensity of excitation) is determined by the rate of the capacitor photodischarging due to ionic contact (aero ions on the film surface) of one electrode with a glass conducting support (indium tin oxide, ITO) as the second electrode on which the induced charge has the opposite sign. The potential photodischarging rate depends on the effective charge carrier photogeneration quantum yield in the film volume (xerographic output, β_{eff}), carrier collection efficiency of the electrodes $C(Z)$ and the portion of absorbed exciting light, P :

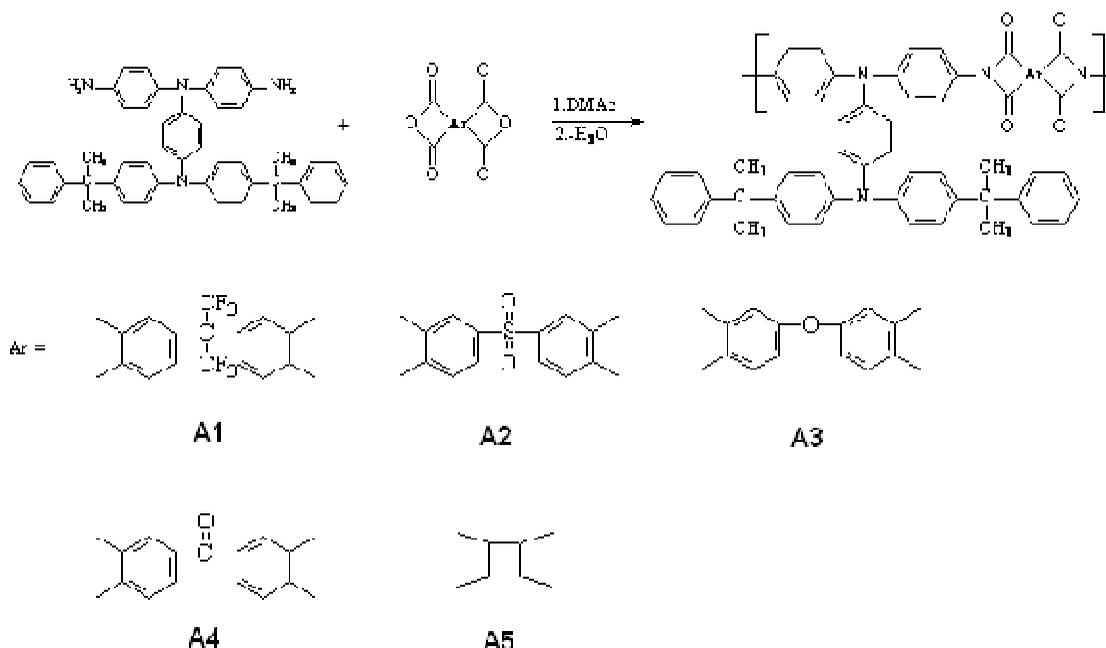
$$(1/I) \cdot [dV/dt - (dV/dt)_D] = (ed/\epsilon\epsilon_0) \cdot \beta_{eff} P \quad (1)$$

where $\beta_{eff} = \beta C(Z)$; $C(Z)$ – charge carrier collection efficiency; $Z = \mu V \tau / d^2$ – ratio of the carrier drift length ($l_D = \mu V \tau / d$) to the film thickness d ; μ – carrier drift mobility; τ – carrier lifetime; e – electron charge.

The function $C(Z)$ for strong and weak absorption is given in [36], from which it follows that for $Z < 1$, $C(Z) = Z$, and for $Z > 1$, $C(Z) = 1$ (strong absorption) and $C(Z) = 1/2$ for weak absorption. It is observed [39], that the β and $C(Z)$ values of the polymers are usually strongly dependent on the field strength $E = V/d$. The accuracy of the β measurement is determined by the accuracy of the I , P and film thickness d measurements and is estimated as ~20%. The photoelectric sensitivity (PES) S , [m²/J], is defined as the reciprocal value of the half decay exposure time $t_{1/2}$ of the initial charging potential V :

$$S = (It_{1/2})^{-1} = (\beta_{eff} P d e) / [E(h\nu) V \epsilon \epsilon_0] \quad (2)$$

where $E(h\nu)$ – photon excitation energy.



Scheme 1. An example of polyamides synthesis

The accuracy of the S value measurement is estimated to be $\sim 10\%$ and this value was determined by the accuracy of the excitation intensity (I) measurements. Thus, the electrophotographic method makes it possible to obtain the following photoelectric characteristics of polymer samples: photoelectric sensitivity, the carrier photogeneration quantum yield (1), and from the field dependence of $\beta_{\text{eff}}(E)$ it is possible to estimate carrier drift length: at a field strength of E_0 , for which the change of the $C(Z)$ dependence from $C(Z) = Z$ to $C(Z) = \text{const}$ is observed, the drift length is equal to the film thickness, $l_D = \mu E_0 \tau = d$.

The experimental setup makes it possible to determine both the optical density of the sample D_λ under monochromatic or integral excitation, and to measure the influence of the ionic contact field on the sample. Knowing the optical density, it is possible to estimate the portion of the absorbed excitation light energy:

$$P = 1 - \exp[-(D - D_0)] \quad (3)$$

where D is the film optical density and D_0 – is the equivalent optical density as a result of light reflection from the front and rear sample surfaces as well as light scattering.

The sign of the majority carriers can be determined via the comparison of PES values for the positive (S^+) and negative (S^-) corona charging of the free surface under the heterogeneous excitation by absorbed UV light: for $S^+ > S^-$,

the majority carriers are holes, while for $S^- > S^+$ the majority carriers are electrons. PI films of $3 \mu\text{m}$ thickness are prepared by casting of polymer solutions in chlorinated solvents onto conducting ITO glass supports followed by drying under ambient conditions at 323–373 K. The PIs under study possess good solubility and excellent film-forming properties.

3. Results and Discussion

3.1. Study of the Photoelectric Sensitivity of the Films Prepared with PI Samples and its Connection with the Charge Transfer Complex Formation

Photoelectric sensitivity for films prepared with PI samples is observed and the charge carrier photogeneration quantum yield is determined for the films of the new class of PI based on *N,N,N',N'*-substituted paraphenylene-diamine (electron-donor fragment D) and dianhydrides (electron-acceptor fragment A). The PI series are denoted as PI A1 to PI A5 (see Scheme 1). A study of the PES spectral dependence $S(\lambda)$ shows that the highest sensitivity (up to $30 \text{ m}^2/\text{J}$) is observed within the UV region (200–400 nm). In the visible region (400–700 nm) there is a PES band that collapses to a long-wave edge (Fig. 1).

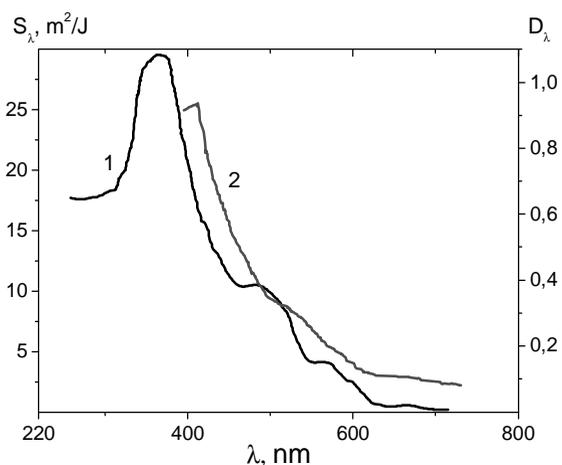


Fig. 1. Spectra of the photoelectric sensitivity S_λ (1) (+ charging, $V = 30\text{--}36$ V; the number of cycles $N > 10$) and optical density D_λ (2) for film PI A2 (thickness $d = 3$ μm)

Comparison of the PES spectral dependence with the absorption spectra of the films indicates that the PES in the visible region is due to the formation of weak donor-acceptor (D-A) charge-transfer complexes (CTC) with absorption maxima in the region of 400–600 nm [37]. The maxima and band absorption edge of the CTC are determined. The most clearly expressed CTC bands are observed for the PI A2 and PI A3 films with flat absorption maxima in 500–560 nm region. For the PI A1, PI A4 and PI A5 films the CTC bands are essentially weaker with flat maxima shifted to short wavelengths of 420–480 nm. The energy position of the long-wavelength absorption band edge of the CTC and PES is determined, which is an analogue of the band gap for semiconductors, E_g , that allows the relative affinity energy values for the acceptor fragments E_A to be estimated (at the same values of ionization potential of the donor fragments, $I_D = 7.0 - P_h = 5.5$ eV; P_h – polarization energy of holes) from the following expression:

$$E_g = I_D - E_A - (P_h + P_e) \quad (4)$$

where P_e is the polarization energy for electrons.

Table 1

E_g and $(E_A + P_e)$ values (in eV) for the PI A1 – PI A5 film samples; $P_e = 1.5$ eV

PI A1	$E_g = 2.2^*$	$(E_A + P_e) = 3.3^*$
PI A2	1.9	3.6
PI A3	2.0	3.5
PI A4	2.6	2.9
PI A5	2.4	3.1

Note: *estimated average uncertainty for the E_g and $(E_A + P_e)$ values is 0.1 eV.

As shown in Table 1, the highest $(E_A + P_e)$ values are observed for the PI A2 and PI A3 acceptor fragments

(3.6 and 3.5 eV, respectively) which are characterized by the lowest E_g (1.9 and 2.0 eV) and the most pronounced CTC band as well as high PES in the visible region (up to 5–20 m^2/J). The PI A1, PI A4 and PI A5 films possess lower E_A values, weaker CTC bands and lower PES (of approximately 1–4 m^2/J).

The distinct spectral peaks (in the region of 440–480 nm, 540–560 nm and 640–660 nm) are registered for PI A1, PI A3, PI A5 (absorption spectrum) and PI A2 (PES spectrum, Fig. 1). In this work they are ascribed to the formation and accumulation of the cation-radicals (D^+) (and perhaps anion-radicals (A^-)) of polymer fragments that arise in the PI as a result of the dark- and photo-processes [38]. Some evidence of this assumption is the PES found in the red spectral region ($\lambda > 600$ nm, outside the CTC band) with a weak maximum in the triphenylamine cation-radical absorption band (640–660 nm) due to its photostimulation [38].

The photogeneration quantum yield for UV (PI A1–PI A5) and visible spectral region (PI A1) is determined. By varying the charging potential V , a non-linear field dependence of the photogeneration quantum yield $\beta(E) \sim E^n$ (Fig. 2) is revealed. The exponent n increases with increasing excitation wavelength λ from $n \sim 1.2$ to $n \sim 1.8$ as λ varies from 257 to 547 nm, indicating that photogeneration occurs *via* the field assisted thermo-dissociation (FATD) of ion pairs (IP), kinetically coupled with the excited states of the CTC:

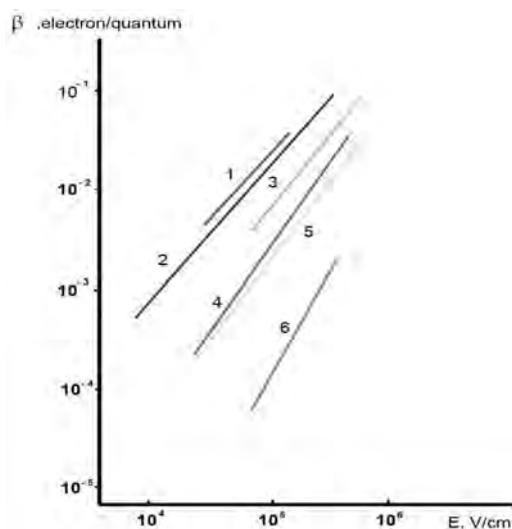
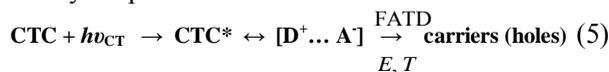


Fig. 2. Field dependence of the charge carrier photogeneration quantum yield $\beta(E)$ for the PI A2 (1), PI A1 (2, 4-6) and PI A3 (3) films, under excitation by monochromatic light: 257 nm (2) and 365 nm (1, 3 and 4); 436 nm (5) and 547 nm (6). Positive charging ($N > 10$), the field changed by the time variation of corona charging. β in electrons/quanta, E in V/cm

The highest β values in the UV region (up to 0.1 in a field $E = 5.7 \cdot 10^5$ V/cm) are obtained for films PI A3 and PI A2 ($\beta = 0.02$, $E = 10^5$ V/cm). Using the geminate recombination Onsager model to interpret the field dependence of $\beta(E)$, it is possible to determine the ion-pair parameters: the initial yield F_0 and initial separation r_0 . For PI A1 with increasing excitation wavelength (from 257 to 547 nm) the value of r_0 decreases from 3.6–4.5 to 2.0 nm, and the value of F_0 increases from 0.2 to 0.7. However, under excitation in the red spectral region (640–680 nm, outside the CTC band), the value of r_0 increases to 3.0 nm, which suggests that under photostimulation of the labile cation-radical IP_1 is formed that differs from the IP in Eq. (3). Comparison of the field dependences of S and β leads to the conclusion that for the PI films drift length of the generated carriers (holes) $l_D > d$ (3 μm) for $E > 10^5$ V/cm and hence it requires to estimate $\mu\tau > 3 \cdot 10^{-9}$ cm²/V. The majority carriers in the studied PI are – holes that are under free surface excitation by strongly absorbed UV light, $S^+ > S^-$.

3.2. Effect of Labile Cation-Radical Accumulation during Repeated Charge – Discharge Cycles on the Photoelectric Characteristics of the PI Films; the Observation of the Photostimulated Currents (PSC)

A strong dependence of the photoelectric characteristics of the samples (the potential of charging, PES in the red region, S_{red}) on the number of charge-discharge cycles N is found: as N varies from 1 to 10, V and S_{red} values significantly increase (by approximately several multiples), Fig. 3. In the UV region only V is increased; the growth of PES is very small or negligible.

Usually the absence of surface charging is associated with the dark injection of carriers from the electrodes into the bulk of the film (holes in the case of a positively charged free surface), leading to a sharp increase in dark conductivity. The increase in the V value at the positive charge indicates blocking of the dark hole injection from the free surface when $N > 3-4$. The most probable reason for this effect is the appearance of a positively charged layer of labile cation-radicals in the bulk film near the electrode (electrode polarization). The latter are holes (h^+) trapped by deep centers:



The accumulation and stabilization of the cation-radicals near the electrode leads not only to stoppage of the dark hole injection, but also to a reduction of the dark

conductivity, an increase of V and the observation of photostimulated currents (PSC), which manifest themselves as a growth of PES in the red spectral range S_{red} , outside the absorption band of CTC (absorption of cation-radicals), Fig. 3:

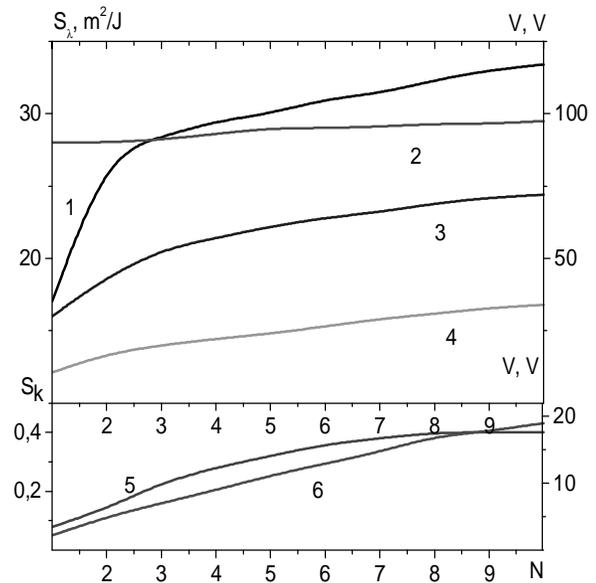
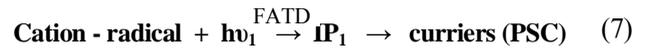


Fig. 3. Photoelectric sensitivity in the UV ($\lambda = 365$ nm) S_λ (1, 2) and red region ($\lambda > 600$ nm) S_{red} (5), as well as the maximal charge potential V (3, 4, 6) vs. the number of charge-discharge cycles N for films PI A5 (2, 3) and PI A2 (1, 4-6); + charging

The growth of S_{red} with increasing N (Fig. 3) is partly due to its field dependence caused by the growth of the field strength according to $E = V/d$. Therefore, it was specifically confirmed that, in the red region the pure field dependence due to the ion pair IP_1 FATD (7) has the following form: $\beta \sim E^n$ ($n = 1.35-1.60$) and, by (2), $S \sim E^{n-1}$, i.e. it is weakly dependent on E , so that the growth of $S_{red}(N)$ is partly due to the accumulation of the cation-radicals. Under conditions when V does not depend on N (for $N > 10$), the V value changes with variation of the corona discharge time. In some cases (Fig. 3) the growth of S_{red} was observed at constant V which indicates the effect of the cation-radical accumulation.

It should be noted that photostimulated currents are observed not only in a long wavelength spectral region but also in a shorter wavelength region where radicals absorb. This is evidenced by the appearance of the corresponding maxima in both PES and absorption spectra (Fig. 1) in blue and yellow-green spectral ranges which are ascribed above to cation-radicals. For these maxima the positive electric field effect on optical density (electrochromic effect [40]) is observed due to cation-radical formation in

a photoprocess (5) but not to Stark effect on CTC absorption.

The observation of PSC indicates a long cation-radical lifetime, $t > (sI)^{-1}$ (s – absorption cross section). If $s = 10^{-17} - 10^{-16} \text{ cm}^2$ [40], $I = 10^{15} \text{ cm}^{-2} \text{ s}^{-1}$, an estimate of $t > 10 \text{ s}$ is obtained. It should be noted that the results of this study indicate that there is a range of cation-radical states from labile ($t = 1 - 10 \text{ s}$) to a fully stable ones ($t > 10^3 \text{ s}$) which participation in the process of photostimulated generation differ significantly. Similar cation-radicals and related photo-stimulated currents for the PI based on substituted triphenylamines resulting from irreversible photochemical transformation of free-radical type with the halogen hydrocarbons are observed in [38].

3.3. Paramagnetism of Polyimides in Solid State and Solution

For PI samples with varying the PI acceptor unit while retaining the same donor, stored at the air for a long time interval (several months) the paramagnetism at room temperature is observed. A signal of electron paramagnetic resonance (ESR) with the apparent g -factor value $g = 2.0022$ is observed both in the solid state (powder sample) and in the solution (solvent: tetrachloroethane (TCE) and chloroform mixture), Fig. 4. The identity of the ESR signal for the solid state PIs with various acceptor units suggests unpaired electron localization on the donor polymer chain unit, *i.e.* cation-radical formation. The relative integral ESR signal intensities (Int), registered for various solid state PI samples are given in Table 2.

Table 2

ESR signal integral intensities at $T = 293 \text{ K}$ for PI solid state samples

Polyimides	PI A1	PI A2	PI A3	PI A4	PI A5
Int	19	338	49	59	341
S_{red} , a.u.	0.03	0.40	0.01	≤ 0.015	0.30
S , a.u.	0.15	10.0	1.4	1.5	4.0

Note: Int values are standardized with sample weights; correlation of PES in red spectral region S_{red} for fresh prepared PI films with ESR signal of air stored PI samples (concentration of stable radicals), $V = 10 \text{ V}$, $N = 1$; correlation of PES in near UV region S for fresh prepared PI films with ESR signal of air stored PI samples (concentration of stable radicals), $V = 10 \text{ V}$, $N = N_{max}$.

It should be noted that in spite of signal intensity depending on the acceptor unit structure its correlation

with electron affinity value E_A (Table 1) as well as PI charge transfer (CT) interaction is not observed. Indeed, the values for PIs A2 and A5 are the highest. CT interaction differs significantly: it is much stronger for A2 than for A5 with a very weak CT band. Therefore dark stable radical formation is not connected directly with CT interaction between PI units because of its insignificant intensity even for A2 so that the additional interaction (for example, with O_2) is required.

The Int of PI ESR signals registered in the solution are comparable with that of PI solid state (powder) samples if one takes into account the sample weight (Fig. 4). Computer simulation of the A2 and A5 signals observed in the solution using the SimFonia (Bruker) program shows that these signals are described well within the framework of the radical model with 4 equivalent protons (Fig. 4). In the case of A2 the simulation of experimental ESR spectra is also possible considering the interaction with two equivalent protons and a nitrogen atom ^{14}N but the difference between experimental and simulated spectra for A5 is appreciably higher in this case than in the first model.

The effect of light excitation on the ESR signal intensity in a diluted solution is found to depend on the excitation spectral composition. Under solution excitation by near UV light the ESR signal intensity increases (without deformation) after initial minutes of excitation (Fig. 5). Thus, it can be concluded that the generation of PI radicals occurs under near UV excitation. Under solvent excitation by long wavelength light ($\lambda > 580 - 640 \text{ nm}$, OS-14, KS-14 glass filters) the intensity of the dark signal does not change significantly.

The revealed photoelectric sensitivity (PES) of freshly prepared PI films in the red spectral region ($\lambda > 600 \text{ nm}$, out of CT band) S_{red} and near UV region S correlates well with the ESR signal intensity, Int (dark stable radical concentration in the sample volume), when the initial surface charge potential V under single corona charging is considered (Table 2).

However it is found that such correlation with stable radical concentration is absent both in red and near UV region for the films prepared from the air stored PI samples (oxidized samples) for which ESR signal is observed. The absence of such correlation indicates that stable radicals do not display photostimulated currents which are due mainly to labile radicals. The correlation of PES with stable radical concentration for freshly prepared PI films can be explained by the fact that the formation of both labile and stable radicals is determined mainly by the oxidation ability of PI donor fragments depending on PI acceptor fragment structure.

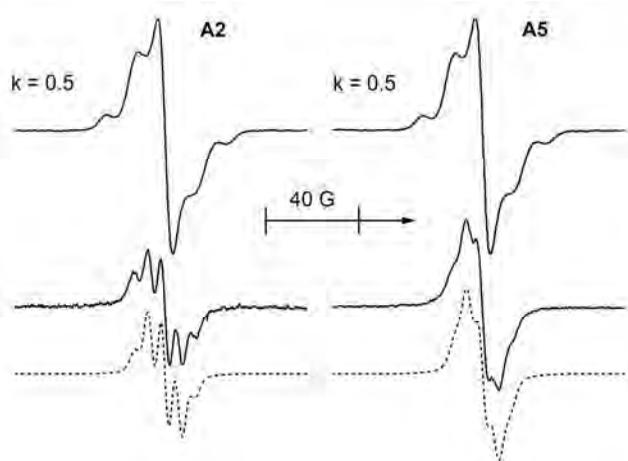


Fig. 4. Overhead – ESR signals observed for dry PI solid state samples (on account of 1 mg sample). In the center – ESR signals of PI solutions in tetrachloroethane-chloroform mixture with PI concentration of 0.1 wt %. Bottom – spectra simulated with the use of the SimFonia (Bruker) program. Simulation parameters: $a^H = 5.5$ G for A2 signal and $a^H = 5.0$ G for A5, with line widths of 4.6 G and 5.3 G, respectively

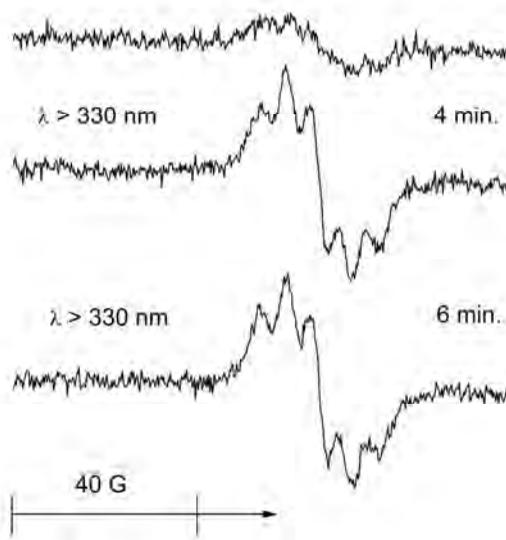


Fig. 5. Effect of near-UV excitation on the A2 ESR signal (PI solution in tetrachloroethane-chloroform mixture with concentration 0.6 wt %)

Such difference in functionalities of labile and stable radicals can be explained by the variable oxidation degree of donor fragments. Labile radicals, originating under corona charging or UV excitation which are assumed above to be trapped holes and so can be considered as incompletely oxidized donors (partially oxidized donors) $[D^{+}e^{-}]$, in which electrons and cations are incompletely separated, their energetic level being localized in a forbidden gap. These states are not assigned to the ion-radical pairs because their geminate

recombination is hindered if the electron being localized on some acceptor. So these states possess relatively high lifetime and radicals become labile. It is for these states possible photostimulation and charge carrier photo-generation occur under complete photooxidation of donor and geminate ion-radical pair formation. On the other hand stable radicals which appear in air stored PI samples are likely to be completely oxidized donor (with completely separated components) and stabilized by stable anion $[D^{+}A^{-}(O_2)]$. So they are not able to further oxidation and photostimulation.

4. Conclusions

Novel polyimides based on *N,N,N',N'*-substituted *p*-phenylenediamine and dianhydrides were prepared *via* polycondensation reaction. The polymers exhibited excellent solubility in common organic solvents, and had high thermal stability, for example, $T_{d10} = 726$ K in nitrogen atmosphere and $T_g = 413$ K.

Photoelectric sensitivity of the freshly prepared PI films (3 μm thickness) in the UV, and visible spectral regions was observed, due to charge transfer interactions between the donor and the acceptor fragments of the PI chains (formation of the CTC). Study of the field dependence of the photogeneration quantum yield provided evidence that the photo-generation mechanism is the field assisted thermo-dissociation of radical ion pairs kinetically associated with the excited CTC.

The second important mechanism of photo-generation is photostimulation of long-lived labile cation-radicals of the donor PI fragments, representing the hole (majority carriers) captured by deep centers (photostimulated currents). The accumulation of cation-radicals in the dark and photoprocesses leads to the dependence of photoelectric characteristics on the number of charge-discharge cycles of the sample.

The paramagnetism of PIs investigated under dark conditions in the air for the solid state samples and their solutions was found by the ESR method. The effect of UV excitation on the ESR signal intensity of PI solutions was observed. For the solid state samples the correlation of this result with the photoelectric sensitivity of the fresh prepared PI films was established.

Acknowledgements

This work is supported by RFBR: Grant No. 13-02-12409 OFI-m2, Grant No; RFBR and National Taiwan Science Foundation: 15-59-32401 RT-omi, and Grant of the Government of the Russian Federation for the Support of Scientific Investigations under the Supervision of Leading Scientists, Contract No. 14.B25.31.0019.

References

- [1] Beaujuge P., Vasilyeva S., Ellinger S. *et al.*: *Macromolecules*, 2009, **42**, 3694.
- [2] Han F., Higuchi M. and Kurth D.: *Adv. Mater.*, 2007, **19**, 3928.
- [3] Udum Y., Yildiz E., Gunbas G. and Toppare L.: *J. Polym. Sci. A*, 2008, **46**, 3723.
- [4] Thompson B., Kim Y., McCarley T. and Reynolds J.: *J. Am. Chem. Soc.*, 2006, **128**, 12714.
- [5] Michinobu T., Kumazawa H., Otsuki E. *et al.*: *J. Polym. Sci. A*, 2009, **47**, 3880.
- [6] Elschner A., Heuer H., Jonas F. *et al.*: *Adv. Mater.*, 2001, **13**, 1811.
- [7] Winter A., Friebe C., Chiper M. *et al.*: *J. Polym. Sci. A*, 2009, **47**, 4083.
- [8] Forrest S.: *Nature*, 2004, **428**, 911.
- [9] Liao L., Cirpan A., Chu Q. *et al.*: *J. Polym. Sci. A*, 2007, **45**, 2048.
- [10] Yu G., Gao J., Hummelen J., Wudl F. and Heeger A.: *Science*, 1995, **270**, 1789.
- [11] Kitamura M. and Arakawa Y.: *Appl. Phys. Lett.*, 2009, **95**, 023503.
- [12] Dimitrakopoulos C. and Malenfant P.: *Adv. Mater.*, 2002, **14**, 99.
- [13] Liu P., Wu Y., Pan H. *et al.*: *Chem. Mater.*, 2009, **21**, 2727.
- [14] Roberts M., LeMieux M., Sokolov A. and Bao Z.: *Nano Lett.*, 2009, **9**, 2526.
- [15] Durben S., Nickel D., Kruger R. *et al.*: *J. Polym. Sci. A*, 2008, **46**, 8179.
- [16] Segura J., Martin N. and Guldi D.: *Chem. Soc. Rev.*, 2005, **34**, 31.
- [17] Chang Y., Hsu S., Su M. and Wei K.: *Adv. Mater.*, 2009, **21**, 2093.
- [18] Zhou E., Tan Z., He Y. *et al.*: *J. Polym. Sci. A*, 2007, **45**, 629.
- [19] Ling Q., Liaw D., Zhu C. *et al.*: *Prog. Polym. Sci.*, 2008, **33**, 917.
- [20] Ling Q., Liaw D., Teo E., *et al.*: *Polymer*, 2007, **48**, 5182.
- [21] Scherf U. and List E.: *Adv. Mater.*, 2002, **14**, 477.
- [22] Naga N., Tagaya N., Noda H. *et al.*: *J. Polym. Sci. A*, 2008, **46**, 4513.
- [23] Wang B., Shen F., Lu P. *et al.*: *J. Polym. Sci. A*, 2008, **46**, 3120.
- [24] Xu Y., Guan R., Jiang J. *et al.*: *J. Polym. Sci. A*, 2008, **46**, 453.
- [25] Ranger M., Rondeau D. and Leclerc M.: *Macromolecules*, 1997, **30**, 7686.
- [26] Janietz S., Bradley D., Grell M. *et al.*: *Appl. Phys. Lett.*, 1998, **73**, 2453.
- [27] Kotov B., Berendyaev V., Rummyantsev B. *et al.*: *Doklady Ros.Acad.Nauk: Phys. Chem.*, 1999, **367**, 183.
- [28] Rummyantsev B., Berendyaev V., Tsegel'skaya A. and Kotov B.: *Mol. Cryst. Liq. Cryst.*, 2002, **384**, 61.
- [29] Rummyantsev B., Berendyaev V., Golub A. *et al.*: *J. High Energy Chem.*, 2008, **42**, 61.
- [30] Mal'tsev E., Berendyaev V., Brusentseva M. *et al.*: *Polymer Intern.*, 1997, **42**, 404.
- [31] Muhlbacher D., Brabec C., Sariciftsi N. *et al.*: *Synth. Metals*, 2001, **121**, 1550.
- [32] Rummyantsev B. and Berendyaev V.: *Russ. Chem. Phys.*, 2014, **33**, 1.
- [33] Marjanovich N., Singh T., Deunler G. *et al.*: *Organic Electronics*, 2006, **7**, 188.
- [34] Wu H., Wang K., Liaw D. *et al.*: *J. Polym. Sci. A*, 2010, **48**, 1469.
- [35] Chang C., Wang K., Jiang J. *et al.*: *Polymer*, 2010, **51**, 4493.
- [36] Grenishin S.: *Electrophotographicheskyyi Process*. Nauka, Moskva 1970.
- [37] Rummyantsev B., Berendyaev V., Vasilenko N. *et al.*: *Polym. Sci. A*, 1997, **39**, 506.
- [38] Rummyantsev B., Berendyaev V. and Kotov B.: *Russ. J. Phys. Chem.*, 1999, **73**, 538.
- [39] Chang C., Wang K., Jiang J. *et al.*: *Polymer*, 2010, **51**, 4493.
- [40] Rummyantsev B., Berendyaev V., Liaw D. *et al.*: *Russ. Polymers*, 2011, **12**, 9.

**ФОТОЕЛЕКТРОННІ ВЛАСТИВОСТІ І
ПАРАМАГНЕТИЗМ ПОЛІМІДІВ НА ОСНОВІ
N,N,N',N'-ЗАМІЩЕНИХ п-ФЕНІЛЕНДІАМІНУ
ТА ДІАНГІДРИДІВ**

Анотація. Досліджені фотоелектричні характеристики і парамагнітні властивості поліїмідів (ПІ) з використанням електрофотографічного методу та ЕПР. Поліїміди на основі N,N,N',N'-заміщених п-фенілендіаміну та діангідридів синтезовані за реакцією поліконденсації. Показано, що полімери добре розчиняються в звичайних органічних розчинниках, і мають високу термічну стабільність. Встановлено, що плівки синтезованих ПІ мають фотоелектричну чутливість в УФ і видимій областях спектру. Досліджено механізм фотогенерації носіїв заряду. Визначено парамагнетизм зразків ПІ, які зберігались на повітрі, за допомогою сигналу окиснених донорних фрагментів (стабільних радикалів). Досліджено ЕПР-спектри зразків у твердому стані і розчині; встановлено вплив світлового збудження на спектри.

Ключові слова: поліїмід, електрофотографічний метод, сигнал ЕПР, поліконденсація, фотоелектричні характеристики, фотогенерація, катіон-радикал.