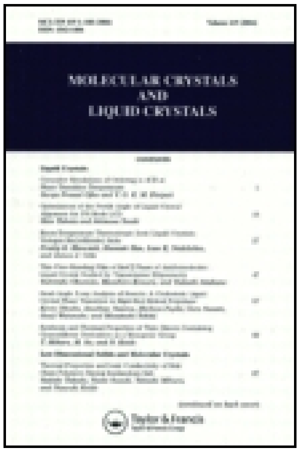

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UV Photoelectron Spectroscopy of Photoconducting Polymers and 1:1 Alternating Copolymers Containing Pendant π-Electron Systems

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UV PHOTOELECTRON SPECTROSCOPY OF PHOTOCONDUCTING POLYMERS AND 1:1 ALTERNATING COPOLYMERS CONTAINING PENDANT π-ELECTRON SYSTEMS

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Abstract Threshold ionization potentials of photoconducting polymers, an electrochemically-doped polymer, and 1:1 alternating copolymers containing pendant π-electron systems in thin films have been determined by UV photoelectron spectroscopy; the results are discussed in relation to their properties and molecular structures.

INTRODUCTION

Organic photoconductors have been practically used as photoreceptors in electrophotography and have potential applications as photoactive materials for solar cells or photosensors. Recently developed photoreceptors using organic photoconductors usually have a layered structure which consists of a charge carrier generation layer (CGL) and a charge carrier transport layer (CTL).[1-3] An important requirement for attaining high sensitivity in layered photoreceptors is highly efficient injection of a charge carrier from CGL to CTL. A principal factor for affecting the injection efficiency of a charge carrier, e.g., hole, is the ionization potentials of the materials of both CTL and CGL. Knowledge of the ionization potentials of materials in the solid state is of crucial importance not only for evaluating performance characteristics of layered photoreceptors or photovoltaic devices but also for understanding the photogeneration process of charge carriers or rectification and photoelectrical properties of molecular materials.

UV photoelectron spectroscopy (UPS) is a useful method for

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determining ionization potentials of molecules in the solid state. There have been extensive studies of UPS of low-molecular organic solids, and threshold ionization potentials of a number of molecules in the solid state along with polarization energies have been determined.[4,5] There have also been UPS studies of organic polymers such as polyethylene, polystyrene, and various π-conjugated polymers;[6-12] however, there have been few systematic UPS studies of photoconducting polymers and 1:1 alternating copolymers. Alternating copolymers containing aromatic pendants may serve as suitable model compounds for gaining a deeper insight into photophysical and photoconductive properties of vinyl aromatic polymers.

In the present study we have determined the threshold ionization potentials of several photoconducting and related polymers, an electrochemically-doped polymer, which functions as a photoactive material in photovoltaic devices, and 1:1 alternating copolymers containing pendant π-electron systems in thin films by UPS. The results are discussed in relation to their properties and molecular structures.

EXPERIMENTAL

Materials

Three different samples of poly(N-vinylcarbazole) (PVCz) were used for the measurement. They include commercially available PVCz (Luvican M170, BASF Co. Ltd.), and PVCz samples prepared by free radical and cationic polymerizations of N-vinylcarbazole (VCz) using initiators of 2,2'-azobis(isobutyronitrile) (AIBN) and boron trifluoride etherate, respectively. The number-average molecular weights ($\overline{Mn}$) of the PVCz samples prepared by radical and cationic polymerizations of VCz are ca. 210,000 and 44,000, respectively. Poly(3-bromo-N-vinylcarbazole) (PBrVCz), poly(3,6-dibromo-N-vinylcarbazole) (PDBrVCz), poly(N-carbazolyl vinyl ketone) (PCzVK), poly(2-methyl-N-vinylindole) (PMVI), and poly[4-(N,N-diphenylamino)phenylmethyl methacrylate] (PDAPM) were prepared by AIBN-initiated polymerizations of the corresponding monomers, which were synthesized by the methods described in the literature.[13-15] $\overline{Mn}$=45,000 for PBrVCz; $\overline{Mn}$=50,000 for PCzVK; $\overline{Mn}$=55,000 for PDAPM. Poly[1,3-diphenyl-5-(p-vinylphenyl)-2-

pyrazoline] (PVTPP) and poly[1,3-diphenyl-5-(p-methacryloyloxyphenyl)-2-pyrazoline] (PMTPP) were prepared according to the previous paper.[16] $\overline{M}n$=18,000 for PVTPP; $\overline{M}n$=25,000 for PMTPP. Poly[2-phenyl-5-(p-methacryloylaminophenyl)-1,3-oxazole] (5-PMPPO) and poly[5-phenyl-2-(p-methacryloylaminophenyl)-1,3-oxazole] (2-PMPPO) were prepared by radical polymerizations of the corresponding monomers. $\overline{M}n$=11,000 for 5-PMPPO; $\overline{M}n$=19,000 for 2-PMPPO. 1:1 Alternating copolymers of VCz with diethyl fumarate (DEF), fumaronitrile (FN), and maleic anhydride (MAn), formulated as poly(VCz-alt-DEF), poly(VCz-alt-FN), and poly(VCz-alt-MAn), were prepared as described in the previous papers.[17,18] $\overline{M}n$=25,000 for poly(VCz-alt-DEF); $\overline{M}n$=16,000 for poly(VCz-alt-FN); $\overline{M}n$=5,800 for poly(VCz-alt-MAn). The copolymers of 2-vinylnaphthalene (2-VN) with FN and with MAn and the copolymers of vinylferrocene (VFe) with FN and with MAn were likewise prepared by radical copolymerizations in the presence of AIBN,[19,20] and copolymer samples with compositions close to 1:1 were used for the measurements. All the samples were purified by repeated reprecipitation and dried in vacuo. 1,3-Bis(N-carbazolyl)propane was prepared according to the literature.[21] 2,4-Bis(N-carbazolyl)pentane was prepared starting from acetyl acetone; 2,4-pentanediol prepared from acetyl acetone was reacted with p-toluenesulfonyl chloride to give the 2,4-pentanediol tosyl ester, which was reacted with the potassium salt of carbazole. The resulting 2,4-bis(N-carbazolyl)pentane was isolated by silicagel column chromatography, followed by repeated recrystallization from methanol, m.p. 204°C. It was identical with the meso-isomer reported by De Schryver et al.[22]

Measurements

Photoelectron spectra were measured for thin films of these polymers deposited on a copper disk of 12 mm in diameter. The thin films were made from two drops of 0.4 and 0.2 wt% THF solutions of these polymers by the method of spin coating (2,200 rpm). The measurement was carried out by using the apparatus described previously.[23] The light from a hydrogen discharge lamp was monochromatized by a 0.5 m Seya-Namioka-type vacuum-ultraviolet monochromator and irradiated onto the sample. The electron energy analysis was performed by a spherical retarding-field-type analyzer, the inside of which was coated with graphite. The photoelectron spectra were obtained by differentiating current-voltage curves electrically with an ac-modulation method.[23]

RESULTS AND DISCUSSION

Determination of Threshold Ionization Potential in the Solid State

The UV photoelectron spectra of polymers were measured at incident photon energies of 6.89, 7.75, and 9.18 eV. When the incident photon energy is greater than the threshold ionization potential, electrons are emitted from the sample, and the excess energy is transformed into kinetic energy of the photoelectron. The maximum kinetic energy of the photoelectron emitted from the sample (E_{kin}^{max}) is expressed by Eq. (1), and is correlated with the stopping voltage (V_0) and saturation voltage (V_s), respectively, of the retarding potential, as expressed by Eq. (2), where $h\nu$ is the incident photon energy and I_s^{th} is the threshold ionization potential of the molecule in the solid state. Thus I_s^{th} is determined from Eq. (3).

$$E_{kin}^{max} = h\nu - I_s^{th} \tag{1}$$

$$E_{kin}^{max} = e(V_0 - V_s) \tag{2}$$

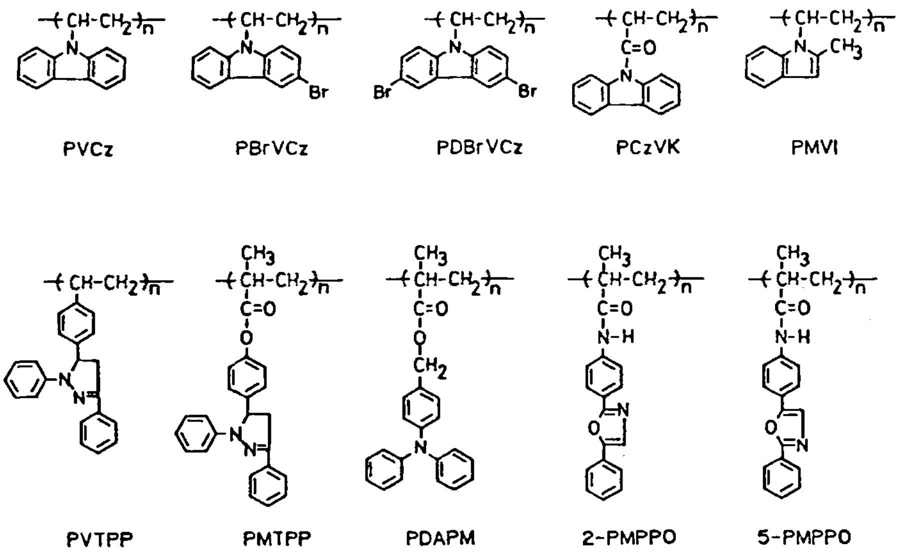
$$I_s^{th} = h\nu - e(V_0 - V_s) \tag{3}$$

The values of V_0 and V_s were obtained from linear extrapolations of the right- and left-hand side edges, respectively, of the photoelectron spectra. The spectra of the polymers were reproducibly obtained when the measurement was carried out at a pressure below 2×10^{-5} Torr. Although the accuracy of the absolute values of I_s^{th} is estimated to be ±0.1 eV due to common systematic uncertainties such as the resolutions of the monochromator and the energy analyzer, the values of I_s^{th} were reproduced with a precision of ±0.05 eV at each photon energy. This enabled us to make a detailed comparison of the I_s^{th} values among the compounds studied.

Photoconducting and Related Polymers

The polymers studied include poly(N-vinylcarbazole) (PVCz), poly(3-bromo-N-vinylcarbazole) (PBrVCz), poly(3,6-dibromo-N-vinylcarbazole)

(PDBrVCz), poly(N-carbazolyl vinyl ketone) (PCzVK), poly(2-methyl-N-vinylindole) (PMVI), poly[4-(N,N-diphenylamino)phenylmethyl methacrylate] (PDAPM), poly[1,3-diphenyl-5-(p-vinylphenyl)-2-pyrazoline] (PVTPP), poly[1,3-diphenyl-5-(p-methacryloyloxyphenyl)-2-pyrazoline] (PMTPP), poly[2-phenyl-5-(p-methacryloylaminophenyl)-1,3-oxazole] (5-PMPPO), and poly[5-phenyl-2-(p-methacryloylaminophenyl)-1,3-oxazole] (2-PMPPO) (Scheme 1). Many of these polymers may function as materials for CTL in layered photoreceptors. Among these polymers, PVCz, which is a well-known photoconducting polymer, and bromo-substituted PVCz were put into practical use as photoreceptor materials in electrophotography.[24] Certain derivatives of 1,3,5-triphenyl-2-pyrazoline dispersed in polycarbonate were also practically used as charge-transport materials in a layered photoreceptor.[1] Poly(N-vinylindole) has been patented as a candidate for photoreceptor materials.[25] Since poly(N-vinylindole) produced by polymerization of the corresponding monomer contains an indoline moiety,[26,27] PMVI is selected in the present study. Poly[4-(N,N-diphenylamino)phenylmethyl methacrylate] has been reported to show hole mobility of 6×10^{-6} cm^2 V^{-1} s^{-1} at an electric field of 5×10^5 V cm^{-1}.[15]



Scheme 1

Figure 1 shows an example of the photoelectron spectra of PVTPP measured at 9.18, 7.75, and 6.89 eV. Table I summarizes the values of I_s^{th} determined for these polymers in solid thin films. The results show that the polymers containing a pendant 1,3,5-triphenyl-2-pyrazoline group have the lowest I_s^{th} values among the polymers studied and that the polymer containing a pendant triphenylamine chromophore has the second lowest I_s^{th} value. The polymers, PBrVCz, PMVI, 5-PMPPO, and 2-PMPPO, have similar I_s^{th} values. The I_s^{th} value of 5.85 eV for PVCz is in good agreement with the one (5.85 eV) reported by Vilesov et al.[7] The present results show that the I_s^{th} value of PVCz does not differ among the three different samples, i.e., Luvican M170, and those prepared by radical and cationic polymerizations of VCz, despite the fact that they differ from each other in their tacticities and molecular weights. Higher I_s^{th} values of PBrVCz and PDBrVCz compared to PVCz are ascribed to the electron-withdrawing inductive effect of the bromine atom. In contrast to PVCz, PCzVK has been reported to show much lower photoconductivity.[28] It has been reported that UV

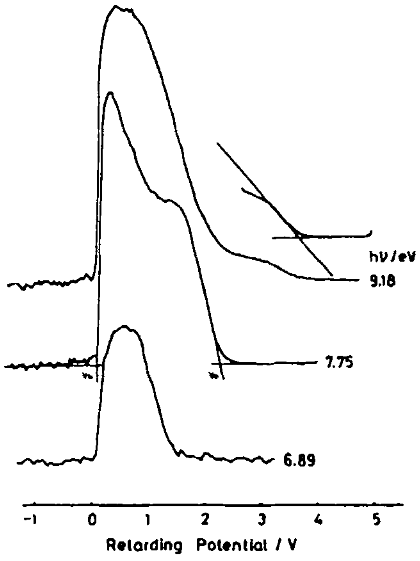


FIGURE 1 Photoelectron spectra of PVTPP.

TABLE I I_s^{th} Values of polymers.[a)]

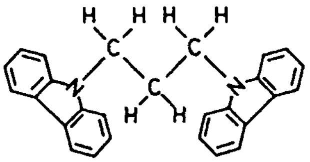
Polymer	I_s^{th} (in eV)
PVCz	5.8_5
PBrVCz	6.0_3
PDBrVCz	6.1_3
PCzVK	6.3_5
PMVI	6.0_2
PVTPP	5.5_3
PMTPP	5.5_6
PDAPM	5.6_5
5-PMPPO	6.0_3
2-PMPPO	5.9_6

a) The I_s^{th} values were obtained from the spectra taken at incident photon energies of 6.89, 7.75, and 9.18 eV.

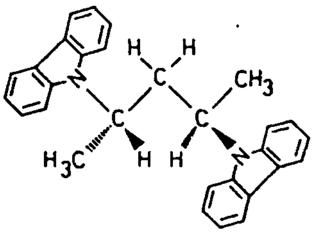
photogeneration of charge carriers in dopant-free PVCz takes place by the extrinsic process involving the electron transfer from PVCz in the electronically excited state to an electron-accepting impurity in the ground state giving an ion pair, followed by dissociation of the ion pair into charge carriers under an external electric field.[29,30] Oxygen or photooxidation products of PVCz have been suggested to be candidates for the electron-accepting impurities.[30] The present result of an I_s^{th} value for PCzVK 0.5 eV higher than that of PVCz suggests that the efficiency of photogeneration of charge carriers in PCzVK is much lower relative to PVCz.

Comparison of I_s^{th} between Vinyl Polymers with Aromatic Pendants and Corresponding Low-Molecular Compounds

It is of interest to compare the ionization energies of vinyl polymers containing aromatic pendants with those of the mother compounds. The I_s^{th} values for 1,3-bis(N-carbazolyl)propane and meso-2,4-bis(N-carbazolyl)pentane were measured by UPS and compared with that for PVCz. It was found that the vacuum-deposited thin films of the former two compounds have almost the same I_s^{th} value of 5.90 eV, which is essentially the same as the value for PVCz. The present result is in accord with the result of Duke et al.[11] for polystyrene and poly(2-vinylpyridine). It is indicated that no specific pendant-pendant interaction exists in the vinyl polymer.



1,3-Bis(N-carbazolyl) propane



meso-2,4-Bis(N-carbazolyl) pentane

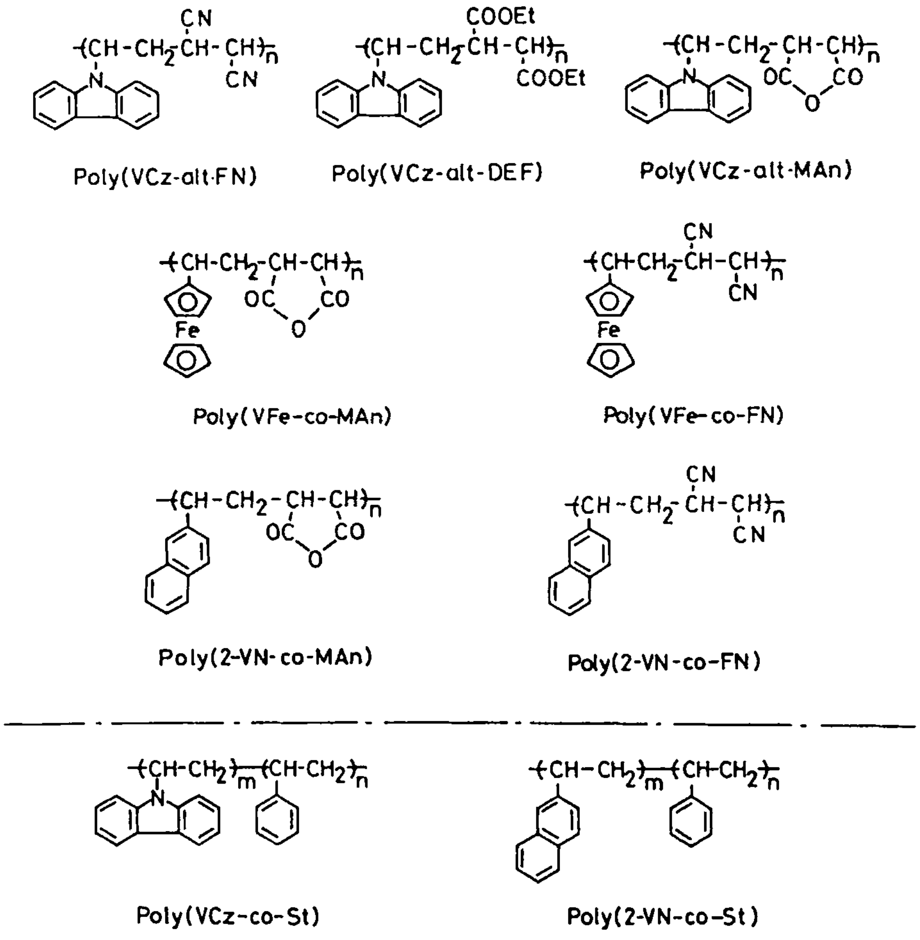
Generally the solid-state threshold ionization potential is lower by 1 ∿ 2 eV than that of the ionization potential in the gas phase. This is because the molecule cation is more stabilized by the surrounding molecules in the solid state. This stabilization energy is termed polarization energy. The ionization potential of carbazole in the gas phase has been reported to be 7.53 eV[31] and 7.60 eV[32]. The alkyl substitution lowers the ionization energy of the aromatic molecule, but at the same time, it reduces the polarization energy because in the present case the carbazole groups with mobile π-electrons are diluted by the alkyl chain. Nonetheless, the difference of ca. 1.7 eV between the gas-phase ionization potential of carbazole and the threshold ionization potentials of 1,3-bis(N-carbazolyl)propane, meso-2,4-bis(N-carbazolyl)pentane and PVCz in the solid state may be ascribed mainly to the polarization energy due to the carbazole groups.

Electrochemically-doped Polymer

Poly(N-vinylcarbazole) (PVCz) is a photoconducting polymer, but it is an insulating polymer in the dark. It is transformed into a semiconducting polymer by electrochemical doping.[33] By the controlled-potential anodic oxidation of PVCz in the presence of tetra-n-butylammonium perchlorate as a supporting electrolyte, a green-colored, partially oxidized radical cation salt of PVCz containing ClO_4^- as a dopant is formed. The pendant carbazole rings are partially cross-linked at the 3-position as indicated from the infrared absorption spectrum and the cyclic voltammograms. The electrochemically-doped PVCz has been shown to act as a photoactive material for a Schottky-type photovoltaic device.[34] The I_s^{th} value for the electrochemically-doped PVCz was determined to be 5.35 eV, which is ca. 0.5 eV lower than that of the PVCz. This may be attributed to the photoionization of the bicarbazole moiety formed during the electrochemical doping of PVCz. The formation of the depletion layer at the interface between aluminum and the electrochemically-doped PVCz, which is responsible for the rectification behavior in the Al/electrochemically-doped PVCz/Au cell, is due to the electron transfer from Al to the electrochemically-doped PVCz which acts as a p-type semiconductor. The I_s^{th} value obtained for electrochemically-doped PVCz is in accord with this.

1:1 Alternating Copolymers

The UV photoelectron spectra of 1:1 alternating copolymers of N-vinylcarbazole (VCz) with diethyl fumarate (DEF), fumaronitrile (FN), and maleic anhydride (MAn), formulated as poly(VCz-alt-DEF), poly(VCz-alt-FN), and poly(VCz-alt-MAn), were measured to determine their threshold ionization potentials in the solid state.[35] In addition, 1:1 alternating copolymers of vinylferrocene (VFe) with FN and with MAn, and copolymers of 2-vinylnaphthalene (2-VN) with FN and MAn, which have structures close to 1:1 alternation, were also studied. The structures of these copolymers are shown in Scheme 2.


Poly(VCz-alt-FN)
Poly(VCz-alt-DEF)
Poly(VCz-alt-MAn)
Poly(VFe-co-MAn)
Poly(VFe-co-FN)
Poly(2-VN-co-MAn)
Poly(2-VN-co-FN)
Poly(VCz-co-St)
Poly(2-VN-co-St)

Scheme 2

Small but distinct differences in the I_s^{th} values between PVCz and the 1:1 alternating copolymers of VCz were observed from repeated measurements using different incident photon energies and different film thicknesses (Table II). Namely, the I_s^{th} values of the 1:1 alternating copolymers, poly(VCz-alt-DEF), poly(VCz-alt-FN), and poly(VCz-alt-MAn), were found to be higher relative to that of PVCz by 0.1 to 0.3 eV and to increase in the following order:

poly(VCz-alt-DEF) < poly(VCz-alt-FN) ≃ poly(VCz-alt-MAn)

TABLE II I_s^{th} Values of 1:1 alternating copolymers.[a)]

Polymer	I_s^{th} (in eV)
Poly(VCz-co-St)[b)]	5.9_5
Poly(VCz-alt-DEF)	6.0_5
Poly(VCz-alt-FN)	6.1_5
Poly(VCz-alt-MAn)	6.1_5

a) The I_s^{th} values were obtained from the spectra taken at incident photon energies of 6.89, 7.75, and 9.18 eV.

b) The copolymer composition in molar ratio is 2:8 (VCz:St).

The I_s^{th} values tend to increase with an increase in the electron-accepting power of the comonomers. Although it is expected that the introduction of an electron-withdrawing group such as a CN or $CO_2C_2H_5$ group into an aromatic nucleus increases the I_s^{th} value of the aromatic nucleus, it is noteworthy that the I_s^{th} value is raised by up to 0.3 eV for the 1:1 alternating copolymers. The higher I_s^{th} values for the 1:1 alternating copolymers relative to that of PVCz are ascribed partly to the inductive effect by the electron-withdrawing groups in the comonomers through the two or three carbon atoms in the polymer chain and partly to a decrease in the polarization energies, i.e. decreased stabilization of the ionized carbazole chromophores by the surrounding pendant carbazole groups due to the intervention by the comonomer unit with smaller polarizability than that of the carbazole group. The higher I_s^{th} value for the copolymer of N-vinylcarbazole (VCz) with styrene (St) with molar composition of ca. 2:8 (VCz:St), poly(VCz-co-St), relative to PVCz is in support of this. In order to examine the generality of the decreased ionization potentials of 1:1 alternating copolymers relative to the corresponding homopolymers, threshold ionization potentials of other 1:1 alternating copolymers or copolymers with compositions close to 1:1 have been determined. They include copolymers of VFe with MAn and with FN, and copolymers of 2-VN with MAn and with FN (Table III). The decrease in I_s^{th} of the 1:1 alternating copolymers or copolymers with compositions close to 1:1 relative to the corresponding homopolymers seems to be a general phenomenon.

TABLE III I_s^{th} Values of polymers.$^{a)}$

Polymer	I_s^{th} (in eV)
PVFe	5.3_5
Poly(VFe-co-St)	5.3_5
Poly(VFe-co-FN)	5.5_0
Poly(VFe-co-MAn)	5.4_5
Poly(2-VN)	6.3_5
Poly(2-VN-co-St)	6.4_5
Poly(2-VN-co-FN)	6.5_5
Poly(2-VN-co-MAn)	6.5_5

a) The I_s^{th} values were obtained from the spectra taken at incident photon energies of 6.89, 7.75, and 9.18 eV.

Preliminary results show that poly(VCz-alt-FN) exhibits over one order of magnitude lower photoconductivity with comparable contributions of both hole and electron transport relative to PVCz, but that photoconductivity of the copolymer distinctly increases in the presence of a weak electron acceptor such as p-dicyanobenzene. Hole mobility may be reduced in the 1:1 alternating copolymer relative to the homopolymer,[36] but at the same time it is suggested that the efficiency of photogeneration of charge-carriers in dopant-free poly(VCz-alt-FN) is also reduced based on the present result of the I_s^{th} value; the free energy change in the electron-transfer process yielding an ion-pair is $\sim$ 0.3 eV more positive for poly(VCz-alt-FN) than for PVCz.

REFERENCES

1. P. J. Melz, R. B. Champ, L. S. Chang, C. Chiou, G. S. Keller, L. C. Liclican, R. R. Neiman, M. D. Shattuck, and W. H. Weiche, Photogr. Sci. Eng., 21, 73 (1977).
2. Y. Hayashi, Natl. Tech. Report, 22, 818 (1976).
3. D. M. Pai and J. Yanus, Photogr. Sci. Eng., 27, 14 (1983).
4. N. Sato, K. Seki, and H. Inokuchi, J. Chem. Soc., Faraday Trans., 77, 1621 (1981).
5. K. Seki, Mol. Cryst. Liq. Cryst., 171, 255 (1989).
6. K. Seki, in Optical Techniques to Characterize Polymer Systems, edited by H. Baessler (Elsevier Science Publishers, Amsterdam), in press.
7. F. I. Vilesov, A. A. Zagrubskii and D. A. Sukhov, Soviet Phys. Solid State, 11, 2775 (1970).
8. M. Fujihira and H. Inokuchi, Chem. Phys. Lett., 17, 554 (1972).
9. M. Fujihira, T. Hirooka and H. Inokuchi, Chem. Phys. Lett., 19, 584 (1973).
10. S. Hashimoto, S. Hino, K. Seki and H. Inokuchi, Chem. Phys. Lett., 40, 279 (1976).
11. C. B. Duke, W. R. Salaneck, T. J. Fabish, J. J. Ritsko, H. R. Thomas and A. Paton, Phys. Rev., B18, 5717 (1978).
12. W. R. Salaneck, CRC Crit. Rev. Solid State Mat. Sci., 12, 267 (1985).
13. A. Inami, K. Morimoto, and Y. Murakami, Nippon Kagaku Zasshi, 85, 880 (1964); K. Morimoto and H. Mitsuda, J. Polym. Sci., B, 5, 27 (1967).
14. E. Gipstein, W. A. Hewett, and O. U. Need, J. Polym. Sci., A-1, 8, 3285 (1970).
15. M. Stolka, D. M. Pai, D. S. Renfer, and J. F. Yanus, J.`Polym. Sci., Polym. Chem. Ed., 21, 969 (1983).
16. F. Iinuma, H. Mikawa, and Y. Shirota, Polym. J., 13, 641 (1981).
17. Y. Shirota, M. Yoshimura, A. Matsumoto and H. Mikawa, Macromolecules, 7, 4 (1974).
18. Y. Shirota, K. Takemura, H. Mikawa, T. Kawamura and K. Matsuzaki, Macromol. Chem., 3, 913 (1982).
19. K. Tada, H. Higuchi, M. Yoshimura, H. Mikawa, and Y. Shirota, J. Polym. Sci., Polym. Chem. Ed., 13, 1737 (1975).
20. W. Zeng and Y. Shirota, Polym. J., 21, 511 (1989).
21. T. Wada and R. Oshima, Kobunshi Ronbunshu, 41, 377 (1984).
22. F. C. De Schryver, L. Moens, M. Van der Auwerear, N. Boens, L. Monnerie, and L. Bokobza, Macromolecules, 15, 64 (1982).
23. T. Hirooka, K. Tanaka, K. Kuchitsu, M. Fujihira, H. Inokuchi and Y. Harada, Chem. Phys. Lett., 18, 390 (1973).
24. R. M. Schaffert, IBM J. Res. Develop., 15, 75 (1971).
25. Jap. Patent S47-37431
26. A. Priola, G. Gatti, and S. Cesca, Makromol. Chem., 180, 1 (1979).
27. Y. Shirota, K. Fukuhara, F. Iinuma, and H. Mikawa, Denshishashin Gakkaishi, 20, 136 (1982).
28. K. Okamoto, A. Itaya, and S. Kusabayashi, J. Polym. Sci., Polym. Phys. Ed., 14, 869 (1976).
29. K. Okamoto, S. Kusabayashi, and H. Mikawa, Bull. Chem. Soc. Jpn., 46, 2324 (1973).
30. G. Pfister and D. J. Williams, J. Chem. Phys., 61, 246 (1974).

31. H. J. Haink, J. E. Adams, J. Huber, Ber. Bunsenges. Phys. Chem., 78, 436 (1974).
32. B. Ruscic, B. Kovac, L. Klasinc, H. Gusten, Z. Naturforsch., A33, 1006 (1978).
33. H. Kanega, Y. Shirota, and H. Mikawa, J. Chem. Soc., Chem Commun., 1984, 158.
34. Y. Shirota, T. Kakuta, H. Kanega, and H. Mikawa, J. Chem. Soc., Chem. Commun., 1985, 1201.
35. Y. Shirota, Y. Matsumoto, H. Mikawa, K Seki, and M. Inokuchi, Chem. Phys. Lett., 97, 57 (1983).
36. S. R. Turner and D. M. Pai, Macromolecules, 12, 1 (1979).