ELSEVIER

Polymer 41 (2000) 467–472

polymer

Photoconductivity of 3,5-dinitrobenzoates of poly[1-(*p*-methoxyphenyl)penta-1,3-diyn-5-ol] and poly[1-(*p*-*N*,*N*-dimethylaminophenyl)penta-1,3-diyn-5-ol]

S.C. Shim[a,*], M.C. Suh[a], S.C. Suh[a], X.-L. Huang[b], E.K. Suh[b]

[a]*Department of Chemistry, Korea Advanced Institute of Science and Technology, 373-1 Kusung-Dong, Yusung-Gu, Taejon 305-701, South Korea*
[b]*Department of Physics & Semiconductor Physics Research Center, Chonbuk National University, Chonju 561-756, South Korea*

Received 8 December 1998; received in revised form 25 January 1999; accepted 24 February 1999

Abstract

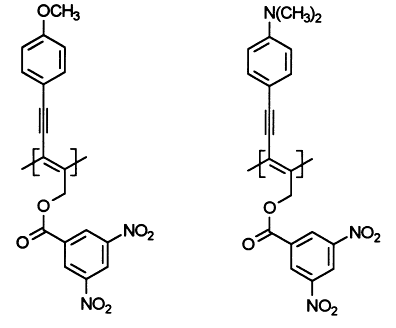
The 3,5-dinitrobenzoates of poly[1-(*p*-methoxyphenyl)penta-1,3-diyn-5-ol] and poly[1-(*p*-*N*,*N*-dimethylaminophenyl)penta-1,3-diyn-5-ol] [DN-1,4-PMDO and DN-1,4-PDDO] showed high photoconductivity due to the conjugated main chain and the electron donating and accepting side chains. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Photoconductivity; Polyacetylene; Metathesis

---

1. Introduction

There has been a lot of interest in photoconductivity of polymers, such as poly[2-((3,5-dinitrobenzoyl)oxy)ethyl methacrylate] [1], poly[1-(4-nitrophenyl)-2-(3-thienyl) ethane] [2], poly{(2-(3,5-dinitrobenzoyl)oxy)ethyl dipropargylacetate} [3], poly(2′-ethylmethacryl 4,5,7-trinitro-9-fluorenone-2-carboxylate) [4] and also other carbazole containing polymers [5–7]. Several research groups have attempted to synthesize photoconducting polymers which have electron accepting groups and fully conjugated backbone. However, only a few examples of these polymers have been reported [2,3] due to the obvious reasons that most of the common polymerization methods such as free radical, anionic, and cationic polymerization are not satisfactory because the chain reaction is quenched by free-radical inhibition processes or electron-transfer reactions [4] (Scheme 1).



DN-1,4-PMDO **DN-1,4-PDDO**

Another serious problem can arise when electron acceptors are introduced into the polyconjugated polymers for the efficient charge-transfer complex formation. Most of the polyconjugated polymers which have highly efficient electron accepting groups become insoluble in organic solvents [8].

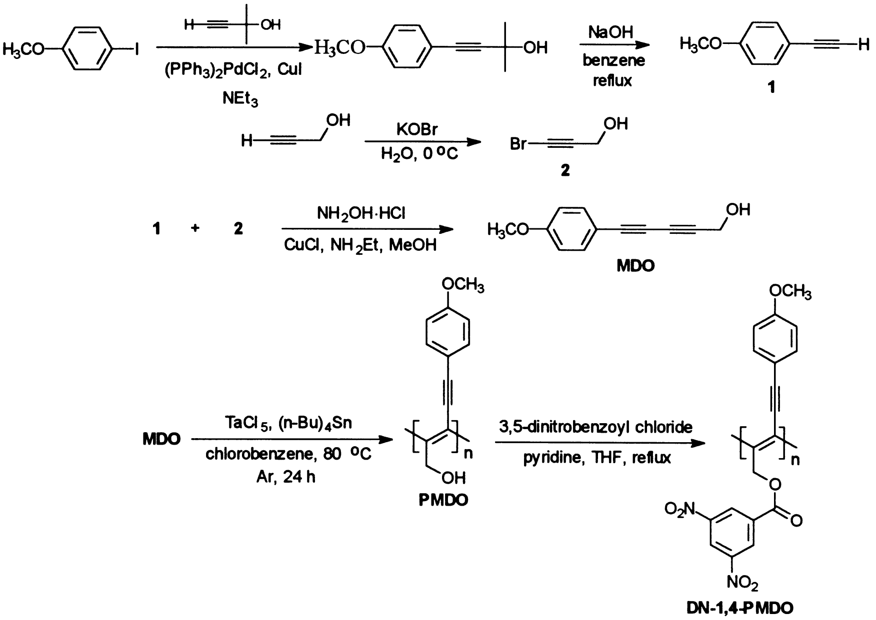
In our previous work, we reported a series of polyacetylene derivatives which have fully conjugated backbone; poly(1-phenylpenta-1,3-diyn-5-ol) [9], poly(2,4-hexadiyn-1,6-diol) [10], poly[1-(2-methoxyphenyl)penta-1,3-diyn-5-ol] [11,12], poly[(Z)-1-methoxy-4-phenyl-1-buten-3-yne] [13], poly(1,4-diphenyl-1-buten-3-yne) [14], and poly[5-(2-pyridyl)-2,4-pentadiyn-1-ol] [15]. They showed good solubility in common organic solvents and their pendant groups were easily modified to introduce electron accepting groups [16].

In this study, we report the important role of electron donating groups and charge transporting materials for photoconductivity by investigating 3,5-dinitrobenzoate of (1,4)-PMDO (DN-1,4-PMDO) and (1,4)-PDDO (DN-1,4-PDDO) which have characteristic acetylene pendant groups as examples.

---

[*] Corresponding author. Tel: +82-42-869-2815; fax: +82-42-869-2810.
E-mail address: scshim@sorak.kaist.ac.kr (S.C. Shim)

0032-3861/00/$ - see front matter © 1999 Elsevier Science Ltd. All rights reserved.
PII: S0032-3861(99)00164-0

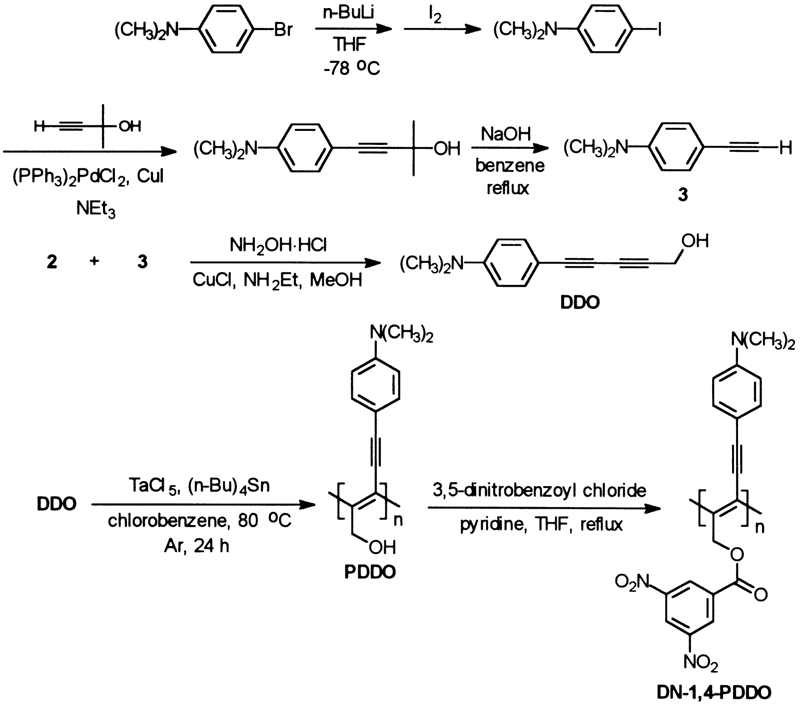


Scheme 1.

2. Experimental section

2.1. Instruments

Proton and ^{13}C NMR spectra were recorded on Bruker AM-300 and Bruker AM-200 spectrometers with chemical shifts being referenced against TMS as an internal standard or the signal of the solvent $CDCl_3$. Mass spectra were determined at 70 eV with a Hewlett–Packard 5985A GC/MS interface by the electron impact (EI) method. High resolution mass spectra were determined with JEOL JMS-DX 303 mass spectrometer. FT-IR spectra were recorded on a Bomem MB-100 or EQUINOX 55 FTIR (Bruker Co.) spectrophotometer in KBr pellet or NaCl cell. UV–Vis absorption spectra were recorded on a Shimadzu 3100S spectrophotometer. The average molecular



Scheme 2.

weight of polymer was determined in chlotoform solution by a Waters GPC-150c with a calibration curve for polystyrene.

2.2. Materials

4-Iodoanisole, 4-bromo-*N,N*-dimethylaminobenzene, 2-methyl-3-butyn-2-ol, iodine, bis(triphenylphosphine)palladium(II) chloride, copper(I) iodide, triethylamine, diethylamine, $TaCl_5$, and other organometallics as cocatalysts were obtained commercially from Aldrich Chemical Co. and used without further purification. Solvents were purified by standard methods [17], care being taken to remove moisture as completely as possible for the polymerization solvent (chlorobenzene). Solvents of reagent grade were used for chromatography without further purification. A chromatography column of silica gel was prepared with Kieselgel 60 (70–230 mesh).

2.3. Synthesis of monomers

2.3.1. Synthesis of 1-(p-methoxyphenyl)penta-1,3-diyn-5-ol [(1,4)-MDO]

(1,4)-MDO was prepared according to the known procedure as shown in Scheme 2 [11,16].

2.3.2. Synthesis of 1-(p-N,N-dimethylaminophenyl)penta-1,3-diyn-5-ol [(1,4)-DDO]

2.3.2.1. 4-Iodo-N,N-dimethylaniline. *n*-BuLi (30 ml of 2.5 M *n*-BuLi solution, 75 mmol) was added to a solution of 4-bromo-*N,N*-dimethylaniline (12 g, 60 mmol) in THF (200 ml) under nitrogen atmosphere at −78°C for 20 min. I_2 (15.2 g, 60 mmol) dissolved in THF (100 ml) was then added to this solution slowly. The temperature of mixture was elevated to RT after addition of I_2 solution and maintained at that temperature for 1 h. After evaporation of solvents, the reaction mixture was extracted with diethyl ether and separated by silicagel column chromatography using *n*-hexane/diethyl ether (30/1, v/v) as an eluent to give 4-iodo-*N,N*-dimethylaniline in 95% yield. ^{1}H NMR (δ??$CDCl_3$) 7.45 (d, 2H), 6.47 (d, 2H), 2.90 (s, 6H) ppm. ^{13}C NMR (δ??$CDCl_3$) 150.0, 137.5, 131.7, 114.7, 40.4 ppm.; HRMS (M^+) calcd. for $C_8H_{10}N_1I_1$ 246.9860, found 246.9869.

2.3.2.2. 2-Methyl-4-(4-N,N-dimethylaminophenyl)-3-butyn-2-ol. 2-Methyl-3-butyn-2-ol (4.70 ml, 48.6 mmol) was added to a solution of bis(triphenylphospine)palladium(II) chloride (568 mg, 0.81 mmol), copper(I) iodide (309 mg, 1.62 mmol), and 4-Iodo-*N,N*-dimethylaniline (10 g, 40.5 mmol) in triethylamine (200 ml) under nitrogen atmosphere. The mixture was heated to 40°C and maintained at that temperature for several hours. After evaporation of solvents, the reaction mixture was extracted with ether and separated by silica gel column chromatography using *n*-hexane/diethyl ether (1/1, v/v) as an eluent to give 2-methyl-4-(*p-N,N*-dimethylaminophenyl)-3-butyn-2-ol in 50% yield (Scheme 2). ^{1}H NMR (δ? $CDCl_3$) 7.27 (d, 2H), 6.58 (d, 2H), 2.94 (s, 6H), 2.08 (s, 1H), 1.59 (s, 6H) ppm. ^{13}C NMR (δ??$CDCl_3$) 150.1, 132.7, 111.8, 109.6, 91.5, 82.9, 65.7, 40.2, 31.7 ppm.

2.3.2.3. 4-Ethynyl-N,N-dimethylaniline. The mixture of 2-methyl-4-(*p-N,N*-dimethyl-aminophenyl)-3-butyn-2-ol (4 g, 19.7 mmol) and sodium hyroxide (1.97 g, 62.5 mmol) in benzene (100 ml) was refluxed for several hours. After extraction with diethyl ether and removal of solvent under the reduced pressure, the mixture was filtered through a silica gel column using *n*-hexane/diethyl ether (1/1, v/v) as a eluent to give 4-ethynyl-*N,N*-dimethylaniline in 99% yield. ^{1}H NMR (δ??$CDCl_3$) 7.36 (d, 2H), 6.60 (d, 2H), 2.98 (s, 1H), 2.96 (s, 6H) ppm. ^{13}C NMR (δ??$CDCl_3$) 150.3, 133.1, 111.6, 108.7, 84.8, 74.7, 40.0 ppm.

2.3.2.4. 3-Bromo-2-propyn-1-ol. 3-Bromo-2-propyn-1-ol was obtained in 90% yield as a viscous liquid from propargyl alcohol by the same method used for 5-bromo-4-pentyn-1-ol.[13] ^{1}H NMR (δ??$CDCl_3$) 4.26 (s, 2H), 2.15 (s, 1H) ppm; ^{13}C NMR (δ??$CDCl_3$) 78.1, 51.6, 45.7 ppm.

2.3.2.5. (1,4)-DDO. (1,4)-DDO was prepared by the Chodkiewicz and Cadiot coupling of 4-ethynyl-*N,N*-dimethylaniline and 3-bromo-2-propyn-1-ol in 70% yield. m.p. 124.5°C. ^{1}H NMR (δ, $CDCl_3$) 7.34(d, 2H), δ 6.57(d, 2H), δ 4.38(s, 2H), δ 2.97(s, 6H), δ 1.58(s, 1H) ppm, ^{13}C NMR (δ, $CDCl_3$) 150.7, 133.9, 111.6, 107.4, 80.5, 79.5, 77.4, 77.0, 76.6, 71.3, 71.2, 51.8, 40.0 ppm; HRMS (M^+) calcd for $C_{13}H_{13}N_1O_1$ 199.0997, found 199.1024.

2.4. Polymerization

All the procedures for the preparation of the catalyst system and polymerization reaction were carried out under dry argon atmosphere. A typical procedure is as follows: A suspension of $TaCl_5$ (120 mg, 0.33 mmol) and 0.1 M solution of $(n\text{-Bu})_4Sn$ in chlorobenzene (3.30 ml, 0.33 mmol) was stirred at 80°C for 15 min and chlorobenzene (21 ml) solution of (1,4)-DDO (2 g, 10.0 mmol) was added with continuous stirring at 80°C for 24 h. Methanol was added to the reaction mixture followed by suction filtration to obtain (1,4)-PDDO and the product was purified by Soxhlet extraction to give (1,4)-PDDO (1.5 g, 75%) and the product was dried overnight under vacuum at 50°C. PMDO were polymerized by the same method.

2.5. Preparation of 3,5-dinitrobenzoate of (1,4)-PMDO (DN-1,4-PMDO), 3,5-dinitrobenzoate of (1,4)-PDDO (DN-1,4-PDDO)

The THF solution of 3,5-dinitrobenzoyl chloride (46.1 g, 200 mmol) was added to a solution of (1,4)-PMDO ($\overline{M}_w = 4375$, 7.45 g, 40 mmol on the –OH) and pyridine (16.1 ml, 200 mmol) in THF. The mixture was heated to 50°C and kept at the temperature for 48 h. The reaction

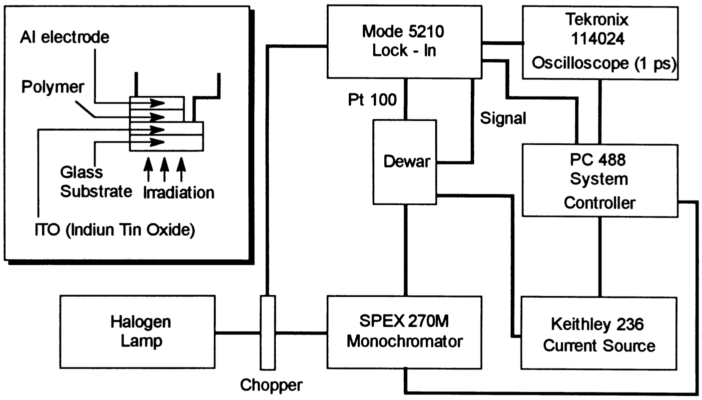


Fig. 1. Photoconductivity measurement equipment.

mixture was poured into a large excess of methanol followed by suction filtration to obtain DN-1,4-PMDO. The product was subjected to Soxhlet extraction with methanol for 12 h to remove residual pyridinium salt and low molecular weight fractions. The polymers were dried overnight under vacuum at 50°C (polymer yield: 97%). DN-1,4-PDDO was obtained by the same reaction condition as that of DN-1,4-PMDO in 95% yield.

2.6. Photoconductivity measurements

The DN-1,4-PMDO and DN-1,4-PDDO films were prepared by spin casting on a photo-resist spinner. A glass slide (fused silica) coated by ITO was placed on the spinner head and viscous 1,2-dichloroethane polymer solutions were dropped on the substrate. The thickness of the spin cast films was controlled by the spinning rate and measured on an Alpha Step 200 of Tenkor Instruments. The glass plate coated by conductive layer and polymer layer is placed on the aluminum deposition tool to make electron injection electrode. The device set made by these procedures was mounted onto the photoconductivity measurement equipment.[18,19] The details are shown in Fig. 1.

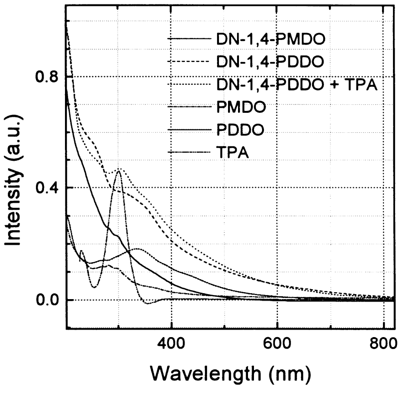


Fig. 2. Solid-state UV–Vis absorption spectra of DN-1,4-PMDO and DN-1,4-PDDO (film thickness: ~1400 Å).

3. Results and discussion

Synthesis and characterization of DN-1,4-PMDO $[\overline{M}_w = 4375\ (\overline{M}_w/\overline{M}_n = 1.25)]$ have been reported elsewhere [16]. DN-1,4-PDDO $[\overline{M}_w = 8376\ (\overline{M}_w/\overline{M}_n = 1.32)]$ which has a strong electron-donating substituent was prepared to increase the photoconductivity of the polymers.

The UV–Vis absorption spectrum (Fig. 2) of DN-1,4-PMDO film showed continuous absorption from UV into the visible region with a gradual slope suggesting the efficient formation of intramolecular charge-transfer complexes. Absorption edge was detected near 4000 Å. When substituents were replaced by *N*,*N*-dimenthylaminophenyl moiety (DN-1,4-PDDO), the absorption was much more red-shifted than that of DN-1,4-PMDO, and absorption edge was also very much shifted to ~6000 Å. This can be attributed to the more effective charge-transfer complex formation by the strong push-pull interactions between *N*,*N*-dimethylaminophenyl and 3,5-dinitrobenzoate moieties. When triphenylamine (TPA) was dispersed into

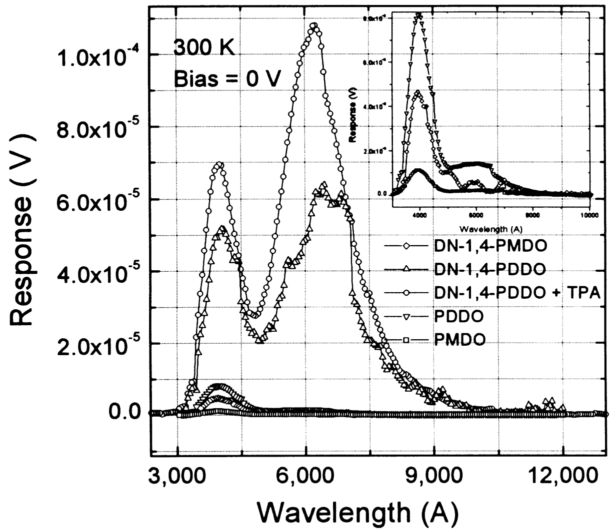
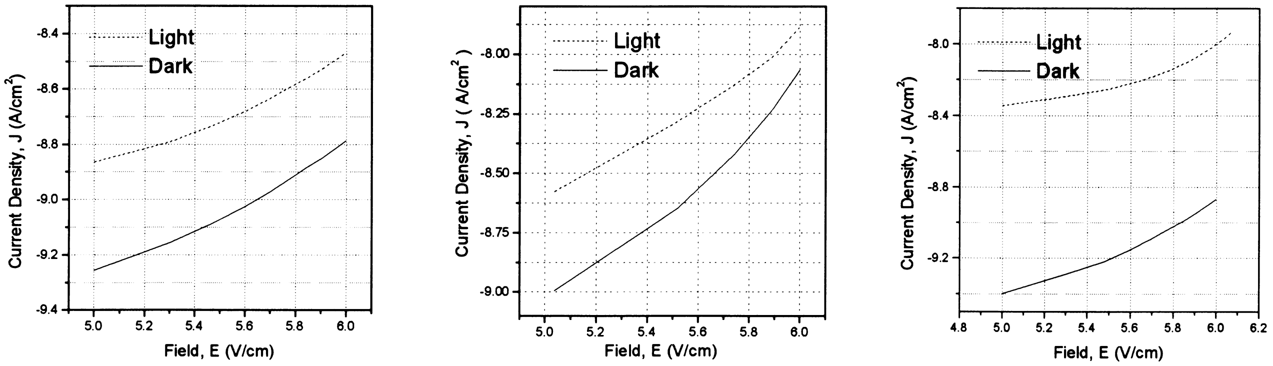


Fig. 3. Photocurrent vs wavelength (photoaction spectra) of DN-1,4-PMDO and DN-1,4-PDDO (applied field: 0 V/cm).



(a) (b) (c)

Fig. 4. *I–V* curves of (a) DN-1,4-PMDO (thickness = 682.5 nm), (b) DN-1,4-PMDO (thickness = 504 nm), and (c) DN-1,4-PDDO dispersed with TPA (thickness = 543 nm); applied field = $\pm 10^6$ V/cm.

DN-1,4-PDDO matrix, the absorption pattern did not change significantly suggesting that TPA does not work as an effective electron-donor. The thickness of all the polymer films used was ~1400 Å.

The photoaction spectra shown in Fig. 3 are in good agreement with the UV–Vis spectra. The PMDO having a weak electron-donating group without a strong electron-accepting group showed weak photocurrent (PC) spectra as a whole. Only one single peak is detected near 4000 Å. The generation of signal can be ascribed to the formation of polaron, soliton, bipolaron, etc. from the polymer main- and side chains. If the 3,5-dinitrobenzoate moieties are introduced to this polymer, some other peaks are generated near 5000 and 6000 Å. The response of DN-1,4-PMDO, however, is not stronger than that of PDDO. In the case of PDDO, which does not have 3,5-dinitrobenzoates showed weak PC although the response is somewhat stronger than that of PMDO and DN-1,4-PMDO. There is one intense peak near 4000 Å and a shoulder near 6000 Å. The shoulder near 6000 Å is probably due to the charge- transfer complex formation between *N*,*N*-dimethylaminophenyl moiety and polymer backbone. Introduction of 3,5-dinitrobenzoate moieties to PDDO enhanced the PC signal significantly, especially the peak near 6000 Å. The enhancement of PC signals is due to the two kinds of strong interactions: i) interaction between highly electron-accepting substituents and polymer backbone (~4000 Å), ii) interaction between strong electron acceptor and highly electron-donating moieties (~6000 Å). The shape of PC signal of DN-1,4-PDDO changed to be smooth when the TPA (charge transporting material) was dispersed into polymer matrix because this material can act as a detrapping agent of trapped electrons from main- and side- chains of DN-1,4-PDDO (e.g. carbonyl group, nitro group, defect sites such as bent position of polymer backbone, etc).

The field (*E*) dependence of current density (*J*) for polymers tested with positive bias is almost linear indicating the presence of space charge perturbation (Fig. 4). [18,19] It is

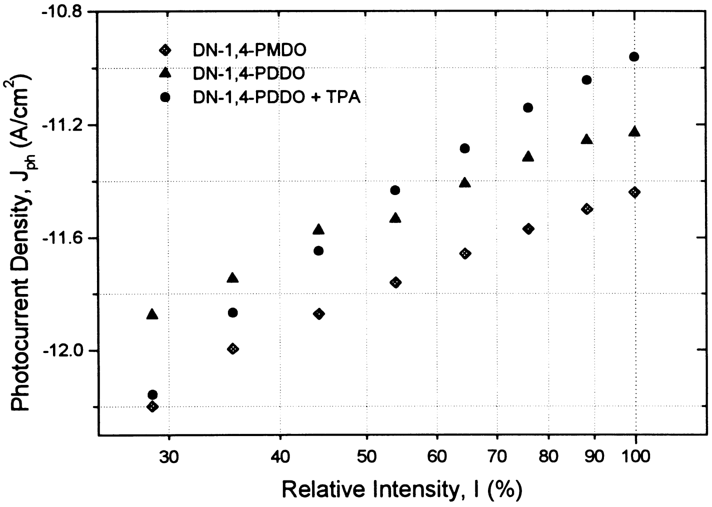


Fig. 5. Light intensity dependence of the photocurrent of polymers tested.

also shown that the current value increases both in dark and illuminated states as the electric field (*E*) increased although their slopes are smaller than 1. Kang et al. reported that all the slopes should be greater than 1 if there are space charge-perturbed photocurrents associated with a large population of trapped charge. In the case of DN-1,4-PDDO dispersed with TPA, the slope is only 0.38 indicating that there is only a little of space charge effect. The order of space charge effect of theses polymers was DN-1,4-PDDO > DN-1,4-PMDO > DN-1,4-PDDO mixed with TPA. A 2 nA of photocurrent increase was observed during illumination of DN-1,4-PDDO mixed with TPA at the field = 10^6 V/cm. This is 7 times larger value than that of DN-1,4-PMDO.

A linear dependence of light intensity was observed for three samples tested (Fig. 5). DN-1,4-PMDO and DN-1,4-PDDO showed similar slopes. However, DN-1,4-PDDO mixed with TPA showed higher dependence on the light intensity than DN-1,4-PMDO and DN-1,4-PDDO due to the efficient hole transporting properties of TPA.

4. Conclusions

Introduction of 3,5-dinitrobenzoate moieties into PDDO enhanced the PC signal significantly, especially the peak near 6000 Å. The enhancement of PC signals is due to two kinds of strong interactions: (i) interaction between highly electron-accepting substituents and polymer backbone (~4000 Å); (ii) interaction between strong electron acceptor and electron-donating moieties (~6000 Å). The order of space charge effect of theses polymers was DN-1,4-PDDO > DN-1,4-PMDO > DN-1,4-PDDO mixed with TPA. DN-1,4-PDDO mixed with TPA showed higher dependence on the light intensity than DN-1,4-PMDO and DN-1,4-PDDO.

Acknowledgements

This investigation was supported by the Ministry of Education (BSRI-97-3406) and the Korea Advanced Institute of Science and Technology.

References

[1] Ohkawa H, Furuichi T, Oshima R, Uryu T. Macromolecules 1989;22:2266.

[2] Greenwald Y, Cohen G, Poplawski J, Ehrenfreund E, Speiser S, Davidov D. J Am Chem Soc 1996;118:2980.

[3] Lee J-H, Park J-W, Oh J-M, Choi S-K. Macromolecules 1995;28:377.

[4] Turner SR. Macromolecules 1980;13:782.

[5] Natansohn A, Flaisher H. J Polym Sci: Polym Lett Ed 1984;22:579.

[6] Chang DM, Gromelski S, Rupp R, Mulvaney JE. J Polym Sci: Polym Chem 1977;15:571.

[7] Hu CJ, Oshima R, Seno M. Macromolecules 1988;21:1536.

[8] Kunugi Y, Miller LL, Maki T, Canavesi A. Chem Mater 1997;9:1061.

[9] Lee HJ, Shim SC. J Chem Soc: Chem Commun 1993;:1420.

[10] Lee HJ, Shim SC. J Polym Sci: Polym Chem 1994;32:2437.

[11] Lee HJ, Suh MC, Shim SC. Synth Met 1995;71:1763.

[12] Lee HJ, Suh MC, Shim SC. Synth Met 1995;73:141.

[13] Suh MC, Shim SC. Macromolecules 1995;28:8707.

[14] Shim SC, Suh MC, Kim DS. J Polym Sci: Polym Chem 1996;34:3131.

[15] Suh MC, Shim SC. Chem Mater 1997;9:192.

[16] Jeong BM, Suh MC, Shim SC. Synth Met 1997;89:73.

[17] Perrin DD, Armerigo WLF. Purification of laboratory chemicals. Oxford: Pergamon Press, 1988.

[18] Kang ET, Ehrlich P, Bhatt AP, Anderson WA. Macromolecules 1984;17:1020.

[19] Harrison MG, Grüner J, Spencer GCW. Phys Rev B 1997;55:7831.