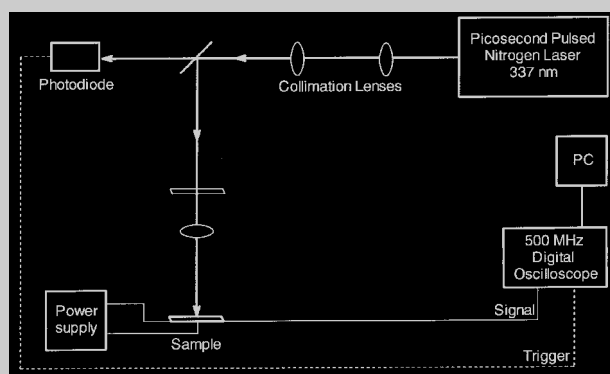


Full Paper: Xerographic photoconductivity of 3,5-dinitrobenzoates of poly[1-(*p*-methoxyphenyl)penta-1,3-diyne-5-ol], poly[1-(2'-methoxyphenyl)penta-1,3-diyne-5-ol] and poly[1-(*p*-*N,N*-dimethylaminophenyl)penta-1,3-diyne-5-ol] [DN-1,2-PMDO, DN-1,4-PMDO and DN-1,4-PDDO] is dependent on the electron donating side chains. From the transient photoconductivity signal on a sub-nanosecond time scale, a plausible mechanism for the charge carrier generation and charge transporting properties of these polymers is proposed.

Block diagram of experimental setup for the measurement of time resolved photoconductivity.



Photoconductivity of Some Metathesis Polymerized Polyacetylenes

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Introduction

Synthesis and properties of conducting polymers such as poly(phenylenevinylene),^[1] polythiophene,^[2] poly(*p*-phenylene),^[3] polyacetylenes^[4,5] have attracted much attention in recent years in view of the electric conductivity, electroluminescence and nonlinear optical properties. Since the discovery of photoconduction in poly(vinylcarbazole),^[6] many photoconducting polymers have been synthesized and characterized.^[7–9] However, polyacetylenes have not been extensively studied in this field because of synthetic difficulties and poor stability.

The understanding of photoconducting polymers at transient time scale is very informative for the mechanism of charge carrier generation, charge transporting property, and for designing new materials such as organic photoreceptors (OPC) etc.^[19] The peak potential of transient signal represents the amount of charge carrier generation and the lifetime implies charge carrier recombination rate.

We have recently reported synthesis of various polyacetylene derivatives^[10–16] by metathesis polymerization method and investigated steady state photoconducting properties of these materials.^[5] When electron accepting groups are introduced as polymer side chains, photocon-

ductivity of the polymers increases drastically, suggesting new formation of charge transfer complexes. Introduction of electron donating substituents also changes photoconductivity to a great extent. We, therefore, investigated nanosecond transient photoconductivity varying the electron donating side chains to give insight into the mechanism of photoconductivity of some polyacetylenes.

Experimental Part

General Procedures

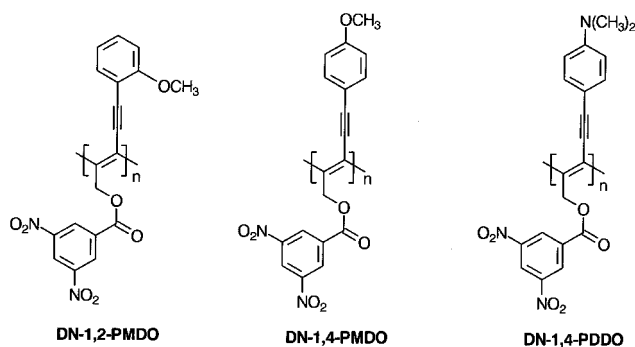
¹H and ¹³C NMR spectra were recorded on Bruker AM-400 and Bruker AM-300 spectrometers. UV-vis absorption spectra were recorded on a Shimadzu 3100S spectrophotometer. FT-IR spectra were obtained by Bomem MB-100 or EQUINOX 55 FTIR (Bruker Co.) spectrophotometer. Mass spectra were determined at 70 eV with 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. The average molecular weight of polymer was determined in chloroform solution by a Waters GPC-150c with a calibration curve for polystyrene. For transient photoconductivity measurements, picosecond N₂ laser (Laser Photonics) and 500 MHz digital oscilloscope (HP 54520A) were utilized.

Materials

2-Iodoanisole, 4-iodoanisole, 4-bromo-*N,N*-dimethylamino-benzene, 2-methyl-3-butyn-2-ol, iodine, bis(triphenylphosphine)palladium(II) chloride, copper(I) iodide, triethylamine, diethylamine, TaCl₅, and other organometallics as cocatalysts were obtained from Aldrich Chemical Co. and used without further purification. Solvents were purified by standard methods,^[17] care being taken to remove moisture completely from 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).

Synthesis

DN-1,2-PMDO, DN-1,4-PMDO and DN-1,4-PDDO (Scheme 1) were prepared according to the literature methods.^[5]



Scheme 1.

Xerographic Measurements

ITO glass plate coated with polymer layer was placed into the xerographic measurement equipment and charged positively by corona charging apparatus (the distance between the charger and substrate was 2.5 cm; induced power was 15000 V) for exactly 30 sec. The sample on the conducting plate was charged by a corona up to the saturated surface potential, and then the change of the surface potential was observed by monitoring the discharge voltage. After 60 sec, UV light (RUL 350 nm lamps, Southern New England Ultraviolet Co.) was irradiated on the surface of the polymer film charged to suitable potential within the range of +550 to +650 V using corona charger. The details of these xerographic measurements were reported elsewhere.^[5, 18]

Transient Photoconductivity Measurements

The experimental set-up for transient photoconductivity measurements is shown in Figure 3. The excitation source was N₂ laser (337 nm) with the pulse width of 0.8 ns (FWHM). The bias voltages applied in the experiment were varied from 0 V to 3 V from DC power supply. Neutral density filters were used to change the excitation beam intensity, and a convex lens was used to focus the excitation beam. The transient photoconductivity signal was measured with

50 Ω terminated 500 MHz digital oscilloscope. Since the resolution of the digital scope was about 1 ns with the sampling rate of 1 GHz, transient photoconductivity signal in nanosecond time resolution could be detected with the set-up. The instrumental response function of the detection system was obtained by measuring the excitation pulse with picosecond response photodiode (Newport 818BB-20).

Results and Discussion

FT-IR spectra give many important information on the structure of polymers as shown in Figure 1. When the monomer was polymerized by metathesis polymerization method, the stretching vibration band (2209 cm⁻¹, ν(C≡C)) of the monomer was almost vanished and ν(C=O) bands were generated near 1728 cm⁻¹ after esterification with 3,5-dinitrobenzoate as shown in Figure 1 (b) and 1 (c).

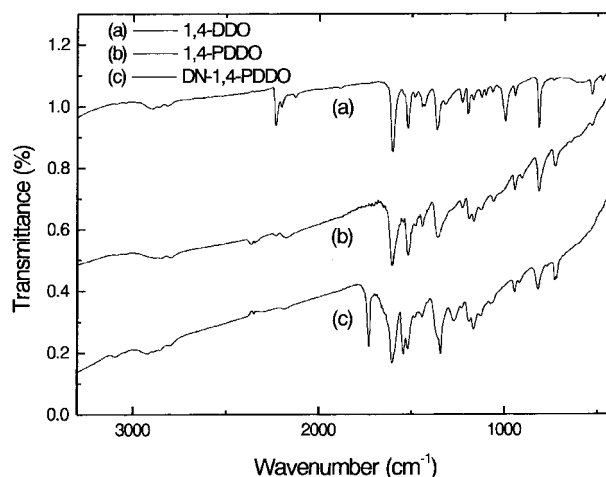


Figure 1. FT-IR spectra of 1,4-DDO, 1,4-PDDO, and DN-1,4-PDDO.

The UV-vis absorption spectra of the polymers are shown in Figure 2. When methoxy phenyl substituents were replaced by *N,N*-dimethylaminophenyl moiety (DN-1,4-PDDO), a large red-shift and a significant increase of absorption intensity was observed compared to those of DN-1,n-PMDO. This shift is probably due to the effective charge-transfer complex formation between *N,N*-dimethylaminophenyl and 3,5-dinitrobenzoate moieties through strong push-pull interaction.

The photodischarge results of DN-1,n-PMDO and DN-1,4-PDDO were obtained in the presence and absence of triphenylamine (TPA) as shown in Figure 4 and Table 1. TPA was mixed into polymers as charge transporting materials (CTM) to overcome the low transporting property of the hole in the polymer films. DN-1,4-PDDO having efficient electron donating moiety (*N,N*-dimethylphenyl-) [M5, M6] shows higher photoconductivity than DN-1,n-PMDO having a methoxyphenyl moiety as the elec-

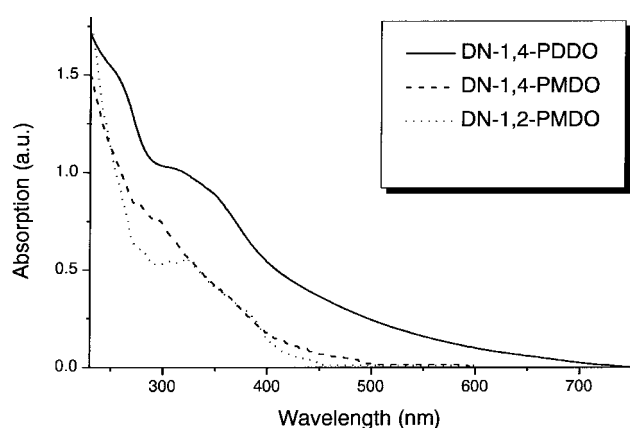


Figure 2. UV-vis absorption spectra of DN-1,2-PMDO, DN-1,4-PMDO, and DN-1,4-PDDO.

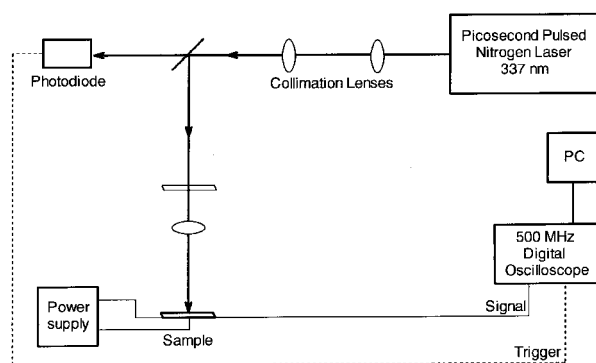


Figure 3. Block diagram of experimental setup for the measurement of time resolved photoconductivity.

tron donor [M1, M2, M3 and M4], indicating that DN-1,4-PDDO forms charge transfer (CT) complexes much more effectively than DN-1,n-PMDO. Triphenylamine (TPA) mixed polymers [M2, M4 and M6] showed higher photoconductivity, indicating that TPA can form extra charge transfer complexes with electron accepting moiety and the trapped charge carriers in the polymers can be transported through the help of TPA. DN-1,4-PDDO, in particular, shows a large difference between TPA doped [M6] and undoped systems [M5], indicating that there are much more trapped charge carriers per unit volume in DN-1,4-PDDO than in DN-1,n-PMDO.

Transient photoconductivity results of each polymer with varying light intensity or external electric field are

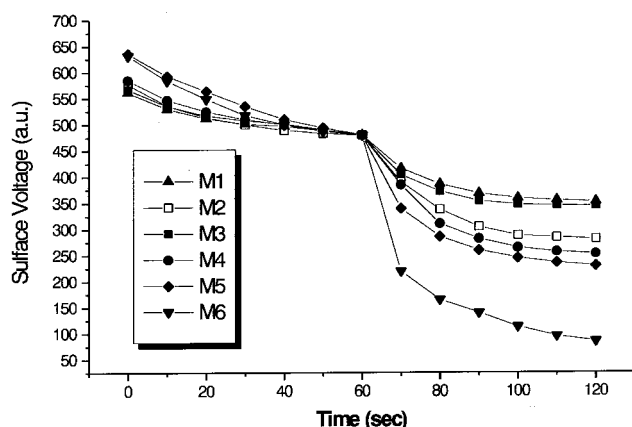


Figure 4. Photodischarge curves of M1, M2, M3, M4, M5, and M6.

presented in Figure 5, 6 and 7. All of the polymers show linear dependence of peak potentials on the light intensity and external field, indicating that the probability of the charge carrier generation is influenced by the external field and the number of photons following the Onsager model.^[20] The decay times of each polymer are shown in Table 2, 3, 4 and 5, respectively. The lifetime of DN-1,2-PMDO with 1.81 V/cm of external field showed 312–319 ns and there is not much change by variation of the light intensity (Table 3). DN-1,4-PMDO shows 297–324 ns of the lifetime with 2.26 V/cm and there is no dependence of life time on the light intensity (Table 4). DN-1,4-PDDO shows somewhat different lifetime depending on the light intensity. It shows relatively shorter lifetimes (125–153 ns) than DN-1,n-PMDO, indicating that there are many recombination processes in this polymer (Figure 5, Table 5). The peak potentials of the polymers show linear dependence on the external electric field and DN-1,4-PDDO shows much higher peak potentials than DN-1,n-PMDO under the same conditions (Figure 7). From these observations and xerographic results, it is concluded that DN-1,4-PDDO can generate much more charge carriers per unit volume than DN-1,n-PMDO when it is irradiated, and these excessively generated charge carriers may easily be recombined. Thus, DN-1,4-PDDO shows relatively short lifetimes and great dependence on the charge transporting TPA. In general, DN-1,n-PMDO shows relatively low peak potential and

Table 1. The composition and photodischarge results of undoped and TPA doped polymers.

| Material | Polymer/mg | TPA/mg | Solvent/ml | $V_{t=70s} - V_{t=60s}$ |
|----------|----------------|--------|------------------------|-------------------------|
| M1 | DN-1,2-PMDO 50 | – | 1,2-dichloroethane 0.8 | 64 |
| M2 | DN-1,2-PMDO 50 | 5 | 1,2-dichloroethane 0.8 | 90 |
| M3 | DN-1,4-PMDO 50 | – | 1,2-dichloroethane 0.8 | 76 |
| M4 | DN-1,4-PMDO 50 | 5 | 1,2-dichloroethane 0.8 | 95 |
| M5 | DN-1,4-PDDO 50 | – | 1,2-dichloroethane 0.8 | 140 |
| M6 | DN-1,4-PDDO 50 | 5 | 1,2-dichloroethane 0.8 | 260 |

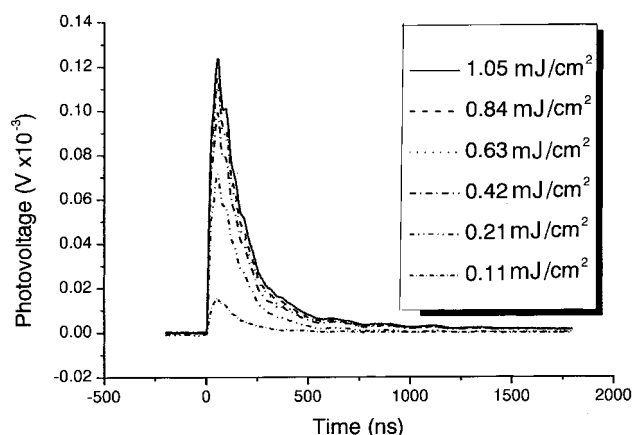


Figure 5. Transient PC of DN-1,4-PDDO with 1.41 V/cm varying light intensity.

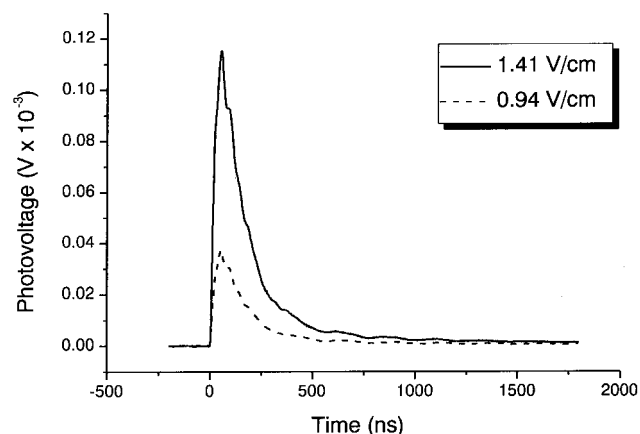


Figure 6. Transient PC of DN-1,4-PDDO with a light intensity of 0.837 mJ/cm² by variation of the external electric field. The decay time is 0.94 V/cm – 152 ns and 1.41 V/cm – 144 ns, respectively.

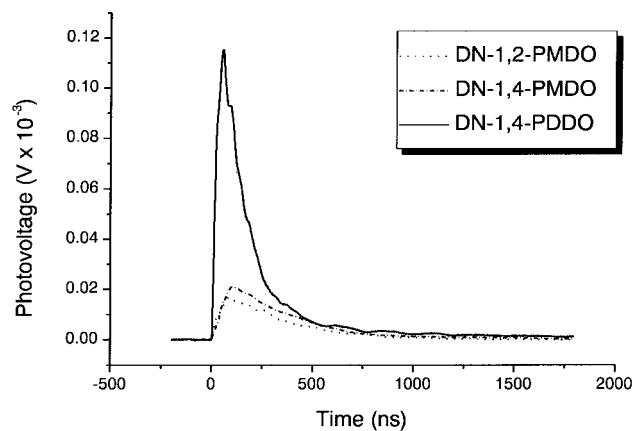


Figure 7. Transient PC of DN-1,2-PMDO, DN-1,4-PMDO and DN-1,4-PDDO. The data plotted were taken at room temperature and with an electric field of 1.41 V/cm. The light intensity was 0.84 mJ/cm².

Table 2. Peak potentials and decay times of DN-1,2-PMDO, DN-1,4-PMDO and DN-1,4-PDDO with 1.41 V/cm of external field and 0.84 mJ/cm² of light intensity.

| | DN-1,2-PMDO | DN-1,4-PMDO | DN-1,4-PDDO |
|------------------|-----------------------|-----------------------|-----------------------|
| Peak potential/V | 1.69×10^{-2} | 2.10×10^{-2} | 11.6×10^{-2} |
| Decay time/ns | 314 | 329 | 144 |

Table 3. Peak potentials and decay times of DN-1,2-PMDO with 1.81 V/cm of external field and varying light intensity.

| Light intensity (mJ/cm ²) | Peak potential/V | Decay time/ns |
|---------------------------------------|-----------------------|---------------|
| 1.046 | 33.3×10^{-3} | 319 |
| 0.837 | 24.4×10^{-3} | 315 |
| 0.628 | 18.4×10^{-3} | 319 |
| 0.418 | 14.5×10^{-3} | 312 |
| 0.209 | 5.66×10^{-3} | 313 |

Table 4. Peak potentials and decay times of DN-1,4-PMDO with 2.26 V/cm of external field and varying light intensity.

| Light intensity (mJ/cm ²) | Peak potential/V | Decay time/ns |
|---------------------------------------|-----------------------|---------------|
| 0.837 | 45.6×10^{-3} | 324 |
| 0.628 | 41.9×10^{-3} | 300 |
| 0.418 | 29.7×10^{-3} | 322 |
| 0.209 | 16.3×10^{-3} | 344 |
| 0.105 | 7.31×10^{-3} | 297 |

Table 5. Peak potentials and decay times of DN-1,4-PDDO with 0.94 V/cm of external field and varying light intensity.

| Light intensity (mJ/cm ²) | Peak potential/V | Decay time/ns |
|---------------------------------------|-----------------------|---------------|
| 1.046 | 4.00×10^{-2} | 153 |
| 0.837 | 3.74×10^{-2} | 152 |
| 0.628 | 3.70×10^{-2} | 143 |
| 0.418 | 3.04×10^{-2} | 140 |
| 0.209 | 2.19×10^{-2} | 131 |
| 0.105 | 1.58×10^{-2} | 125 |

longer decay time and no dependence of the decay time on the light intensity. On the other hand, DN-1,4-PDDO shows linear dependence of decay time on the light intensity, high peak potential, and relatively fast decay time, indicating the better charge generation efficiency of DN-1,4-PDDO, and lower mobility of this polymer causes fast decay time of photocurrent. As charge transporting materials such as TPA are introduced into DN-1,4-PDDO, better photoconducting behavior is observed coinciding with xerographic results.

Conclusions

The steady state and transient photoconductivity of some polyacetylenes, both doped with TPA and undoped poly-

mer, was measured and a plausible mechanism for the charge carrier generation and carrier lifetime is proposed. DN-1,4-PDDO having efficient electron donating groups such as *N,N*-dimethylaminophenyl group shows better charge generation efficiency but shorter decay time than DN-1, n-PMDO because of the efficient charge transfer complex formation and relatively low mobility. When TPA, a charge transporting material, is doped into DN-1,4-PDDO, better photoconductivity is observed due to the transportation of excessive charge carriers generated upon photoexcitation.

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