# Charge Transport Properties of PEG Substituted Phthalocyanine Polymers

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## Abstract

Phthalocyanine polymers substituted with polyethylene glycol (PEG), PPEGPc, were synthesized and characterized by photoelectrochemistry. Thin film of phthalocyanine polymer was coated on a conductive ITO glass using a mixture of soluble PPEGPc in DMF. The PPEGPc film coated ITO electrode showed photocurrent of 3-16 mA/cm$^3$ in a liquid electrolyte system containing hydroquinone. Phthalocyanine polymers substituted with polyethylene glycol showed higher photocurrent generation compared to that with unsubstituted polymer, suggesting that PEG units facilitate transport of generated charge carrier. Solid state PPEGPc photoelectrochemical cell, fabricated by using PPEGPc as charge generation materials and benzidine as a charge transport material, showed photo current of 0.04 ~ 0.27 mA/cm$^3$ under applied potential of 10V. Photocurrent generation was highly dependent on the PEG chain length, indicating that ethylene oxy groups in PEG participate charge transport. The photocurrent in solid state ($i_{p,s}$) was correlated to that in liquid cell ($i_{p,l}$) with a linear relationship of $i_{p,s} = 0.025 + 0.015 \times i_{p,l}$. Optimization of photocurrent generation in PPEGPc was attempted by varying the bridging group, PEG chain length, and end group of the polymer.

## Introduction

Phthalocyanines and their polymers have gained sustained interests for their photo conductivity, 3rd order nonlinear optical properties, and other optoelectronic properties.[1] A number of phthalocyanine polymers involving various metals have been reported and showed higher thermal stability than polymers containing other photoconducting chromophores. However, the solubility of phthalocyanine polymers in organic solvent is very poor in general. Such a low solubility has limited characterization and practical application of phthalocyanine polymers. In this respect, synthesis and characterization of soluble phthalocyanine polymers are important for application of phthalocyanine compounds. Several attempts to increase solubility of phthalocyanines and their polymers by introducing solubilizing groups have been reported. For example, phthalocyanines substituted with long alkyl chains have been reported to afford soluble and ordered phthalocyanine analogues.[2] However these low molecular weight phthalocyanines have weak mechanical strength and poor film forming properties. In our previous studies,[3-4] we have reported synthesis of phthalocyanine polymers from tetramerization of benzenetetracarboxylic acid dianhydride and urea in the presence of $Ti(OBu)_4$ and $(NH_4)_2MoO_4$. These bridged phthalocyanine polymers showed increased solubility in organic solvent such as DMF and DMSO.

In this presentation we report synthesis and photoelectrochemical characterization of PEG substituted phthalocyanine polymers. In addition, we report the effect of PEG groups on carrier transport properties of organic photoconductors based on PPEGPc.

## Experimental Section

### Materials

3,3',4,4'-Benzophenonetetracarboxylic dianhydride (96%, BTDA, 16.1 g) was dissolved in a mixture of tetramethylsulfone (TMS, 120ml) and xylene (20ml) at room temperature and stirred for 1hr. To the above mixture was added poly(ethyleneglycol)monomethyl ether (PEGM350, Mw 350, 8.7 g) and the reaction mixture was stirred at 50°C. After 3 hrs of stirring, the temperature of the reaction medium was elevated to 80°C, followed by addition of titanium tetrabutoxide (5.13g), urea (24 g), and ammonium molybdate (0.2g). The temperature of the reaction mixture was elevated to 160°C, at which deep green color was developed. The mixture was stirred at 180°C for 12 hrs and then cooled to room temperature. Precipitated polymer product was filtered, washed with acetone and a mixture of methanol and water (1: 1, *v/v*), and dried in vacuum to give 30 g of P(TiO-BTDA-P350)im. FT-IR (KBr, cm$^{-1}$); 960 (Ti-N), 1101, 1157 ($CH_2$-O-$CH_2$), 1249, 1299 (aromatic C=C, C-H), 1361(C-O str.), 1524 (aliphatic C-H), 1661 (C=N), 1724 (C=O str.), 1772 (CONH), 3421 (N-H). $^1$H-NMR (300MHz, DMSO-$d_6$, ppm); 3.10 (s, $OCH_3$), 3.14~3.54 (m, $OCH_2CH_2$), 7.38~8.28(m, aromatic C-H). Hydrolysis and subsequent alkylation with octanol at 90 –100°C afforded P(TiO-BTDA-P350)Oct, in 70 % yield. FT-IR (KBr, cm$^{-1}$); 948 (Ti-N), 1098, 1245, 1289 ($CH_2$-O-$CH_2$), 1353 (C-O str.), 1408, 1454 (aliphatic C-H), 1613 (C=N), 1727 (C=O str.), 2876 (-$OCH_3$). $^1$H-NMR (300MHz, DMSO-$d_6$, ppm); 3.15 (s, $OCH_3$), 3.29~4.31 (m, $OCH_2CH_2$), 7.16~8.39 (m, aromatic C-H). Similar reactions with a mixture containing 3,3',4,4'-dipenylsulfonetetracarboxylicacid dianhydride (DSDA), different Mw of poly-(ethyleneglycol)monomethyl ether (PEGM164, Mw 164; PEGM750, Mw 750), or octanol afforded PEG or octyl substituted phthalocyanine polymers in 50–90 % yields.

### Preparation of Polymer Films

PPEGPc (10 ~ 20 wt %) was dissolved into DMF and stirred for 2 hrs at room temperature. The resultant solution was filtered using membranes of 0.45 µm pore size attached to a Teflon syringe, and the solution was coated on a substrate (ITO, wafer, or slide glass) by a spin-coater with a spin rate of 1000-2000 rpm. The PPEGPc solution coated substrate was dried at 100 °C for 12 h in a vacuum oven to give homogeneous film with surface roughness less than 0.01 µm. Solid-state photoelectrochemical cell was fabricated by using PPEGPc as charge generation materials. The cell was consisted of multi layers of Al/ PPEGPc/ charge transport layer/ITO. A charge transport layer (CTL) was coated on top of the PPEGPc by using a THF solution of benzidine (40 wt %) and polycarbonate (60 wt%).

### Instruments

The surface roughness of a polymer film was measured on an α step (TENCOR instrument) and AFM (PSI). UV spectra were obtained from a Guided Wave model 260 (Guided Wave, Inc., USA). Photoelectrochem-ical properties of PPEGPc coated ITO electrodes were investigated using a Xe lamp (Oriel) and a potentiostat (EG&G Princeton Applied Research, Model 273A). Detected photocurrent was normalized by dividing area and thickness of the phthalocyanine polymer film.

## Results and Discussion

### Synthesis of Phthlaocyanine Polymers

A general scheme for synthesis of PPEGPc is summarized in Figure 1. The polymer was deep blue green in color with a metallic glint and soluble in DMF, THF, and DMSO up to 15 wt%. It was noteworthy that the phthalocyanine polymer with carbonyl bridging groups showed higher solubility in DMF than the sulfur dioxide group. Solubility of the polymers are summarized in Table 1.

The solubility of PPEGPc has allowed us to prepare thin films by solution process. Thin films cast from the solution of PPEGPc in DMF were homogeneous without particular morphology as examined by scanning electron microscope. Absorption spectra of the PPEGPc film coated on ITO glass were characterized by appearance of Q band centered at 650 ~ 700 nm.

### Photocurrent Generation of Phthalocyanine Polymer Films in Contact to a Liquid Cell

Irradiation of an ITO glass coated with PPEGPc film resulted in photocurrent generation (3-16 mA/cm$^3$) in a liquid electrolyte system containing hydroquinone as a carrier quenching species. The current generation was repetitive by a light/dark switching under the bias potential of 0.6V (vs. Ag/AgCl). Such a current generation can be rationalized by a redox process of hydroquinone,[5] which can quench the photo generated hole carrier from PPEGPc film.

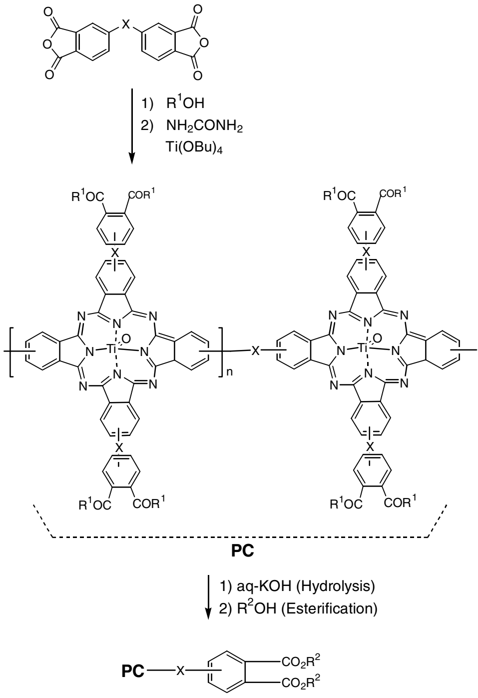

*Figure 1. Synthesis of PPEGPc (X : C=O or SO$_2$).*

**Table. 1. Solubility of PPEGPc**

| PPEGPc | X | R$^1$, R$^2$ | CHCl$_3$$^a$ | DMF$^a$ |
|---|---|---|---|---|
| P(BTDA-PA)Oct | C=O | H, Octyl | + | ++ |
| P(BTDA-P350)ca | C=O | PEGM350,OH | + | ++ |
| P(BTDA-P350)Oct | C=O | PEGM350, Octyl | +++ | +++ |
| P(DSDA-P350)ca | SO$_2$ | PEGM350,OH | + | ++ |
| P(DSDA-P350)Oct | SO$_2$ | PEGM350, Octyl | + | +++ |

$^a$ Solubility less than 1%(g/g) +:1~5% ++:5~10% +++:above 10%.

Interestingly photocurrent generation was dependent on the substituents of the polymer. Thus higher photo-current was generated when the phthalocyanine polymer was modified by PEG group than the unmodified polymer (P(BTDA-PA)Oct). It was more effective when the polymer end groups were octyl, as summarized in Table 2. There was significant photocurrent increase for PPEGPc bridged with sulfur dioxide group (X = SO$_2$). Thus further studies were carried out using sulfur dioxide bridged PPEGPc.

In order to study the effect of PEG on photocurrent generation, different chain length of PEG was incorporated into the polymer. PPEGPc substituted with low molecular weight PEG (Mw 164), P(DSDA-P164)Oct, showed higher photocurrent generation than the unmodified polymer, P(BTDA-PA)Oct. However, the increase was much less than that of P(DSDA-P350)Oct. Similar result was obtained from P(DSDA-P164)ca as compared with P(DSDA-P350)ca. Furthermore PPEGPc substituted with high molecular weight PEGM (Mw 750), P(DSDA-P750)Oct, showed much less photocurrent generation than that of P(DSDA-P350)Oct, as summarized in Table 3.

**Table. 2. Photocurrent generation of carbonyl and sulfur dioxide bridged PPEGPc films in liquid cells.**

| PPEGPc | Thickness (μm) | $i_{p,l}$ (mA/cm$^3$) |
|---|---|---|
| P(BTDA-PA)Oct | 1.03 | 2.7 |
| P(BTDA-P350)ca | 0.43 | 3.0 |
| P(BTDA-P350)Oct | 0.54 | 3.3 |
| P(DSDA-P350)ca | 0.32 | 11 |
| P(DSDA-P350)Oct | 0.3 | 16 |

**Table. 3. Photocurrent generation of sulfur dioxide bridged PPEGPc substituted with different Mw of PEGM in liquid cells.**

| PPEGPc | Thickness (μm) | $i_{p,l}$ (mA/cm$^3$) |
|---|---|---|
| P(DSDA-P164)ca | 0.54 | 3.3 |
| P(DSDA-P164)Oct | 0.57 | 3.5 |
| P(DSDA-P350)ca | 0.32 | 10.9 |
| P(DSDA-P350)Oct | 0.3 | 16 |
| P(DSDA-P750)Oct | 0.75 | 3.1 |

The above result strongly indicates that PEG groups in the polymer affect carrier transport generated from the polymer. In particular the ethylene oxide unit in PEG seemed to play an important role for transport of charge carrier, since the photocurrent was highly dependent on the chain length of PEG. Such an effect may be attributed to the effective carrier transport by the ethylene oxy group, which could host hole carrier by electron donating oxygen atom. If so, the hole carrier generated from phthalocyanine ring could be transported through ethylene oxy group and transferred to hydroquinone molecules, which are then subjected to oxidation.

### Photocurrent Generation of Phthalocyanine Polymer Films in a Double Layered Solid Cell

In order to estimate the charge generation property of PPEGPc films in contact to solid type charge transport layer, all solid type photo conductors were assembled using benzidine as a charge transporting material. Irradiation of the solid type cell resulted in photocurrent generation higher than 40 μA/ cm$^3$ under the external potential of 10 V. Such a current generation could be originated from charge generation of phthalocyanine polymer, followed by a charge transport to benzidine molecules dispersed in charge transport layer. Interestingly, the photocurrent for the solid state cell was also highly dependent on bridging group as well as PEGM substitution as summarized in Table 4.

**Table 4. Photocurrent generation of PPEGPc substituted with different Mw of PEGM in solid state double layered structure.**

| PPEGPc | Thickness (μm) | $i_{p,s}$ (μA/ cm$^3$) |
|---|---|---|
| P(BTDA-P350)ca | 1.41 | 41 |
| P(BTDA-P350)Oct | 1.06 | 70 |
| P(DSDA-P164)ca | 0.68 | 164 |
| P(DSDA-P164)Oct | 0.87 | <1 |
| P(DSDA-P350)ca | 0.72 | 175 |
| P(DSDA-P350)Oct | 0.63 | 273 |
| P(DSDA-P750)Oct | 0.84 | <1 |

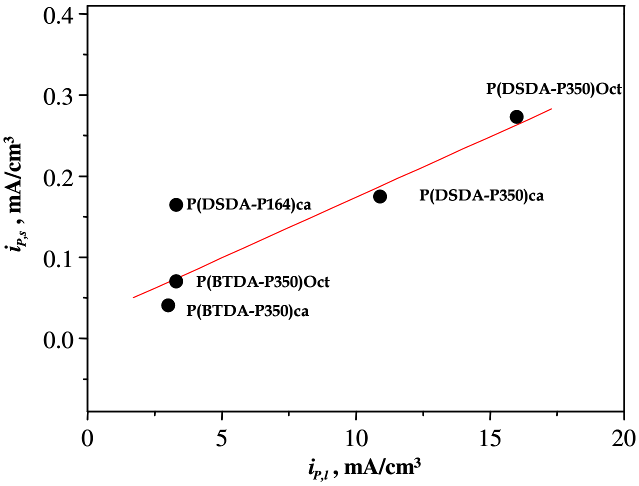

*Figure 2. Plot of the photocurrent at solid state ($i_{p,s}$) against that of liquid state ($i_{p,l}$).*

The intensity of solid state photocurrent was low but the effect of polymer structure on the current generation was quite well correlated to that of liquid state. Figure 2 shows linear correlation of the photocurrent at solid state ($i_{p,s}$) against that of liquid state ($i_{p,l}$), resulting the following relationship (eqn 1) with a correlation factor of 0.85.

$$i_{p,s} = 0.025 + 0.015 \times i_{p,l} \qquad (1)$$

Such correlation between solid and liquid state strongly suggests that the PEG effect for photoconduction in solid state applies similarly in liquid state. Since the photocurrent generation is dependent on PEG, ethylene oxy group seemed to participate in the transport of hole carrier, which could be transported to CTL, by plasticizing and ordering effect. PEG groups induce ordering of polymer as estimated from XRD. Several peaks were observed from PEG substituted polymer, while no peaks were observed from octyl substituted polymer, indicating that ordering of phthalocyanine polymer was increased in the former. Such ordering may facilitate carrier transport, generating higher photocurrent.

Plasticization by PEG is also important in solid medium, in which carrier transport is subjective to polymer segmental motion and free volume around the carrier. Further studies on this transporting mechanism will hopefully identify the interesting problem of the increased photo current generation in PPEGPc.

## Conclusion

Phthalocyanine polymers substituted with polyethylene glycol showed higher photocurrent generation in both liquid and solid type photocell, compared to that with unsubstituted polymer. Photocurrent generation was highly dependent on the PEG chain length, indicating that ethylene oxy groups in the PEG participate charge transport. The photocurrent in solid state ($i_{p,s}$) was correlated to that in liquid cell ($i_{p,l}$) with a linear relationship of $i_{p,s} = 0.025 + 0.015 \times i_{p,l}$. Optimization of photocurrent generation in the PPEGPc was achieved by varying bridging group, PEG chain length, and end group of the polymer.

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## References

1. *"Phthalocyanines. Properties and Applications"* Eds by C.C. Leznoff and A. B. Lever, Vol 2-4, VCH Publisher, New York, 1993.
2. J. F. Van Der Pol, E. Neeleman, J.W. Zwikker, R. J. M. Nolte, W. Drenth, J. Aerts, R. Visser, S. J. Picken, *Liq. Cryst.* **6**, 577 (1989).
3. (a) J. Lim and E. Kim, *J. Korean Society for Imaging Science*, **3**, 24**,** (1997). (b) *ibid*, **4**, 13 (1998).
4. D. S. Han, Y.-J. Li, E. Kim, *Synthetic Metals*, **101**, 62 (1999).
5. W. J. Buttner, P. C. Reike, and N. R. Amstrong, *J. Phys. Chem.*, **89**, 1116 (1985).

## Biography

Eunkyoung Kim received her B.S. degree in Chemistry from Yonsei University at Seoul (Korea) in 1982, a master degree in Chemistry from Seoul National University at Seoul (Korea) in 1984, and Ph.D. in Chemistry from University of Houston in 1990. Since 1992 she has been working in the Korea Research Institute of Chemical Technology at Taejon, Korea. Her work has primarily focused on the development of functional polymers, including photochromic polymers, photoconductive polymers, and charge transport issues. She is a committee member of the Korean Society for Imaging Science and Technology.