

# Effect of Coating and Drying Process on the Optical Properties of Pi-conjugated polymers

Masahiro Yamaguchi,<sup>1\*</sup> Yoshiko Tsuji,<sup>1,2</sup> and Yukio Yamaguchi<sup>1</sup>

1. Department of Chemical System Engineering, The University of Tokyo,  
7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan
2. Environmental Science Center, The University of Tokyo,  
7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan

Presented at the 16<sup>th</sup> International Coating Science and Technology Symposium,  
September 9-12, 2012, Midtown Atlanta, GA<sup>1</sup>

## 1. Introduction

Low-cost manufacturing and using solution-processing to form polymer films is desirable. However intrinsic difficulty of evaluating the amorphous structure inhibit the development of electronic devices consisting of functional polymers. In this work, we focus on the relation between optical properties and molecular vibration of amorphous conductive polymers which show blue-shift of photoluminescence(PL) by UV irradiation.

## 2. Experimental details

In this study, we used two CNPPV derivatives which have the same main backbone and different side chains : poly(5-(2-ethylhexyloxy)-2-methoxy-cyanoterephthalylidene) (CN1) and poly(2,5-di(hexyloxy)cyanoterephthalylidene) (CN3). CN1 films show PL blue-shift by UV irradiation under ambient temperature and CN3 films show PL blue-shift at over 100 °C. Thin films of CNPPV derivatives (about 50 nm thick) were spin-coated on the cleaned glass slide substrates from 0.1 wt% chloroform solutions under ambient atmosphere. Films were photoirradiated with a UV-LED (Keyence, UV-400) on a

---

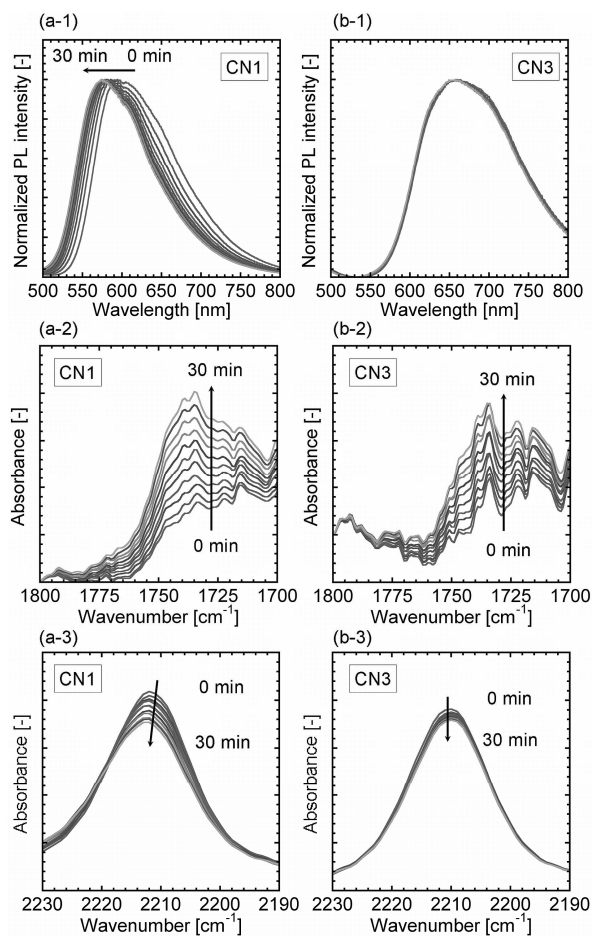
<sup>1</sup> Unpublished. ISCST shall not be responsible for statements or opinions contained in papers or printed in its publications.

heater for 10 to 50 min. The temperature of the substrate heater was controlled between -20 and 240 °C. The intensity of the UV light source was 1.7 mW/cm<sup>2</sup>. Meanwhile original powder, re-precipitated powder, drop casted film and spin-coated films were prepared to evaluate the effect of drying rate in coating process. The optical properties were measured by a UV-vis spectrometer (Hitachi, U-4100) and fluorescence spectrophotometer (Jasco, FP-6300). Chemical properties during UV irradiation were measured by FT-IR spectroscopy (Perkin-Elmer, Spectrum One) using CNPPV films with a thickness of about 1 μm drop-cast on KBr pellets. A system allowing simultaneous measurement of FT-IR and PL spectra was used. A UV-LED and photonic multichannel analyzer (Hamamatsu, PMA-11) were introduced into the FT-IR spectrometer, and *in situ* measurement of PL and FTIR spectra during photoirradiation were obtained at ambient temperature.

### 3. Results and Discussion

#### 3-1. In situ IR measurement

Figure 1(a-1) shows the PL spectra of CN1 films drop-cast on KBr substrates following UV irradiation for between 0 and 30 min at ambient temperature obtained using the simultaneous FT-IR and PL measurement system. Figure 1(a-2) and (a-3) show FT-IR spectra of CN1 films measured simultaneously with the PL spectra shown in Fig. 1(a-1). When films were irradiated with UV light, the intensity of the peak corresponding to the C=O stretching mode at around 1740 cm<sup>-1</sup> increased as reported in our previous paper.<sup>[1]</sup> The intensity of the peak corresponding to the C-N stretching mode at around 2210 cm<sup>-1</sup> decreased and the peak shifted to slightly higher energy when the blue shift of the PL maximum was observed. Figure 1(b-1) shows the PL spectra of CN3 films. The PL maximum appeared at 657 nm and

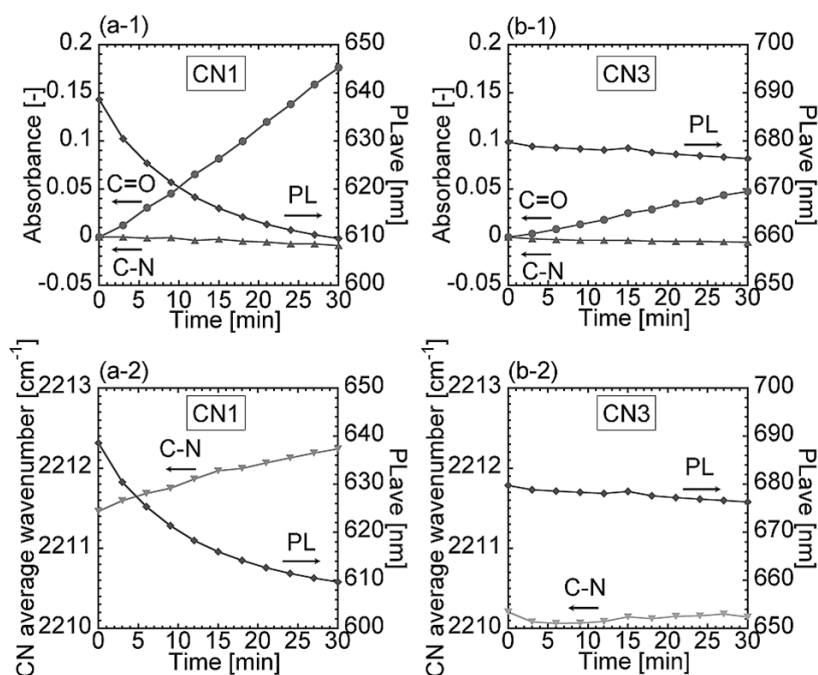


**Fig. 1.** *In situ* PL and IR measurements for (a) CN1 and (b) CN3 films drop-cast on KBr substrates. (a-1, b-1) Normalized PL spectra, (a-2, b-2) FT-IR spectra of C=O, and (a-3, b-3) FT-IR spectra of C-N.

did not shift because of substrate temperature is below 100 °C. Figure 1(b-2) and (b-3) shows the FT-IR spectra of CN3 films measured simultaneously with the above PL spectra. When the films were irradiated with UV light, the intensity of the peak corresponding to the C=O stretching mode around 1740 cm<sup>-1</sup> increased similar to that of the CN1 films, even though there was considerable discrepancy in the PL peak shift between CN3 and CN1. On the other hand, for the peak corresponding to the C-N stretching mode around 2210 cm<sup>-1</sup>, the intensity decreased slightly and the peak position did not exhibit a blue shift.

The variation of FT-IR absorption intensity of the carbonyl and cyano peaks over time obtained in conjunction with the arithmetic average of wavelength of PL peak for UV-irradiated CN1 films shown in Fig. 1(a1-a3) are summarized in Figure 2(a-1). The intensity of the carbonyl absorption increased and that of the cyano one decreased with increasing UV irradiation time. Fig. 2(a-2) summarizes the variation of the arithmetic average of wavenumber of IR absorption peak corresponding to cyano stretching mode over time in conjunction with the PL wavelength for UV-irradiated CN1 films. There is a frequency shift of the cyano peak from 2211.5 to 2212.2 cm<sup>-1</sup> as the PL underwent a blue shift. Figure 2(b-1) and (b-2) show the result of CN3 films shown in Figs. 1(b1-b3). Although the intensity of the carbonyl peak increased and that of the cyano one decreased with increasing UV irradiation time similar to the UV-irradiated CN1 films, there was no frequency shift observed for the cyano peak, and the PL wavelength barely changed. These results suggest

that the CNPPVs were photooxidized by UV irradiation, which caused the number of carbonyl groups to increase and cyano groups to decrease. However, the increase or decrease in the number of these functional groups was unrelated the blue shift of PL. In contrast, the PL maxima only exhibited a blue shift when a change in the frequency of the cyano absorption was observed for

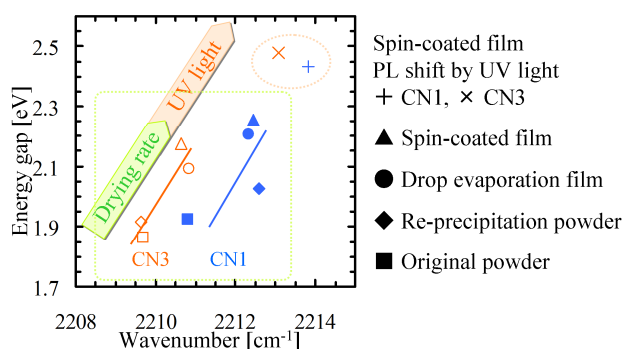


**Fig. 2.** Variation of (a) the intensity of FT-IR absorptions from C=O and C-N bonds, and (b) the position of the C-N wavenumber of CN1 and CN3 films drop-cast on KBr substrates following UV irradiation at ambient temperature. PL wavelength are also indicated.

the photooxidized CNPPVs. Such a blue shift of PL has been attributed to a general decrease in intermolecular interaction that is a result of increased intermolecular distance. The widening interchain distance is caused by the different equilibrium interchain distances of PPV derivatives with and without cyano groups.

### 3-2. Effect of drying rate

Figure 3 shows the relation between cyano wavenumber and energy gap of samples which underwent different drying rate of solution: original powder, re-precipitated powder, drop evaporation film and spin-coated film. The increase of drying rate induced the blue shift of cyano wavenumber and the widening energy gap. This correlation is



**Fig. 3. The relation between cyano wavenumber and energy gap of samples which underwent different drying rate.**

understood as follows, high drying rate induces the conformation of polymer chains being far from equilibrium states, which result in shortening effective conjugation length. The wavenumber of cyano groups and energy gap of spin casted film without UV irradiation were smaller than the spin-coated films which is UV irradiated under sufficient temperature. This is because generated carbonyl groups by UV irradiation induced wider inter-chain distance than the inter-chain distance in disordered structure formed by high drying rate without chemical reactions.

### 4. Conclusions

Both generating carbonyl groups with UV irradiation under sufficient thermal energy and forming disordered structure by high drying rate play the same role on the shortening effective conjugation length which governs the polymer properties. The correlation between process and properties of amorphous polymer chains were summarized by the wavenumber of cyano group attached to polymer backbone.

Reference: [1] Y. Kuzuoka and Y. Yamaguchi, *Synthetic Metals* 158, 489-496 (2008).