

Self-Assembly of Conjugated Molecules in Drying Solution Coatings

Y. Amano and M. Yamamura
Department of Applied Chemistry,
Kyushu Institute of Technology, Fukuoka, Japan

Presented at the 17th International Coating Science and Technology Symposium
September 7-10, 2014
San Diego, CA, USA

ISCST shall not be responsible for statements or opinions contained in papers or printed in its publications.

INTRODUCTION

Conjugated molecules form dimer, two-dimensional sheet, or rod-like aggregates via π - π interaction in liquid. The nanostructures of self-assembling molecules often impact final film properties after solvent evaporation. For instance, an interlayer stacking of poly(3-hexylthiophene) with an orientation normal to the substrate surface leads to an anisotropic electrical conductivity, resulting in a preferential charge transport along the stacking direction in organic solar cells [1-3]. In order to achieve desirable nanostructures, it is of essential importance to understand the dynamic self-assembling process in the course of drying [4-5]. The photoluminescence (PL) measurement is a simple and robust technique to monitor the molecular self-assembly in solutions. Isolating (monomer) and aggregating molecules emit different PL spectra when an excitation light is irradiated to solutions. The transition from monomer to aggregate generally leads to a decrease in PL intensity, i.e., the concentration quenching, and a shift in PL peak(s), allowing us to distinguish the self-assembling states under different conditions in the solution. However, most of the previous PL studies have been limited to dilute solutions under non-evaporative conditions. The pioneering work by Oku [6] has shown that the liquid-solid phase transition at the evaporating surface significantly changes PL intensities in late drying stages. However, the molecular packing in drying thin liquid films is poorly understood. In this study, we demonstrate the first quantitative evidence that the PL intensities from evaporating solutions show a sharp peak in the intermediate drying stage, whereas those decrease monotonically in non-evaporative case.

EXPERIMENTALS

We used Sulfo-rhodamine G (SRG, Sigma-Aldrich) as a conjugated molecule, which was dissolved in aqueous solutions of sodium carboxymethylcellulose (CMC, Dai-ichi Kogyo Seiyaku) or poly(acrylic

acid)(PAA, Mw = 5,000, Wako Chemical)/ethanol solutions. The average molecular weight (Mw) and the degree of substitution of CMC were 185,000 g/mol and 0.65-0.75, respectively. All chemicals were used as purchased. The PL spectra in a closed optical cell was measured by the fluorescence spectrometer (F-7000, Hitachi High-Tech Science) under non-evaporative conditions. A micropipette was used to coat the specified volume of SRG solution onto the glass substrate. The glass surface was cleaned using a plasma etching device (Meiwafosis, SEDE-GE) for 15 min in vacuum before deposition. A TEM00-mode laser (LasirisTM Green, Coherent; wavelength = 532 ± 1 nm) whose beam intensity obeyed a single Gaussian distribution was held in position at a 45° incidence to the coating. A charge-coupled device (CCD) color camera system (VB-7010, Keyence) with a band-pass filter (580 ± 5 nm) was used to capture the emission signals from the solution at different drying times of every 30 s. The maximum intensity with respect to the background value was analyzed using software (VH analyzer, Keyence) and was used as the characteristic PL intensity. A CCD beam profiler (Beam On, Duma Optronics) was located on the opposite side of the laser at a 45° reflection, and it was used to capture the size and shape of the laser beam reflected from the coating. Simultaneously, film mass was measured using an electronic balance (MSE-3203S-0-00-DE, Sartorius), and was stored in a personal computer at a sampling rate of 2.5 Hz. The base temperature of the substrate was maintained by regulating the current through the heater (MD-10DMFH, Kitazato) located beneath the coating at interspaces of 250 ± 20 μm . All equipment was set up on a vibration isolator (TDI-129-100LM, Sigma Koki) and was covered with a black curtain to prevent outside light from interfering with the measurements. Images of the surface of the dried film were captured using an optical microscope (VH-Z100R, Keyence) and an atomic force microscope.

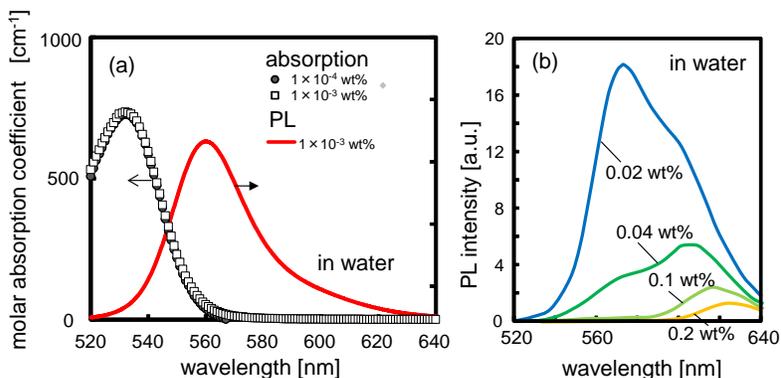


Fig. 1 Light absorption and photoluminescence spectra of aqueous SEG solutions.

RESULTS AND DISCUSSION

A. Non-evaporative case

First, we examined the variation in absorption and emission spectra of aqueous SRG solution in a closed cell for different mass concentrations (c). The wavelength of the excited light was 532 nm. In dilute solutions of $c < 10^{-3}$ wt%, the molar absorption coefficients in the wavelength range of interest match for different concentrations, indicating that the light absorption behavior obeys the Beer-Lambert's law for the monomer state (Fig. 1a). The PL spectra shows a single peak at 560 nm in wavelength. On the contrary, the solution with the higher concentration of $c > 0.02$ wt% exhibits the second peak at a longer wavelength, which is attributed to formation of dimer or higher-order aggregates (Fig. 1b).

The monomer-aggregate transition was further examined by measuring PL intensities at 580 nm for different SRG and polymer concentrations. As depicted in Fig. 2, the emission intensity monotonically decreases with increasing SRG contents, showing a particular concentration quenching arising from the molecular aggregation. Fig. 2 also revealed that the variations in PL intensities were independent of polymer concentrations added in aqueous or ethanol solutions. This is consistent with the negligible light absorption coefficients of CMC/water and PAA/ethanol solutions at 520 ~ 640 nm, i.e., these polymers are optically transparent in the range of wavelengths .

B. Evaporative case

In order to understand how solvent evaporation influences the self-assembly of conjugated molecules,

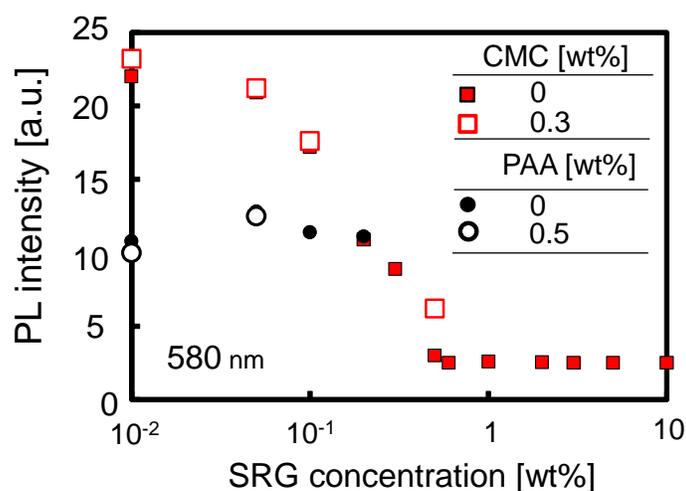


Fig. 2 Variations in PL intensity with SRG concentrations in CMC/water and PAA/ethanol solutions

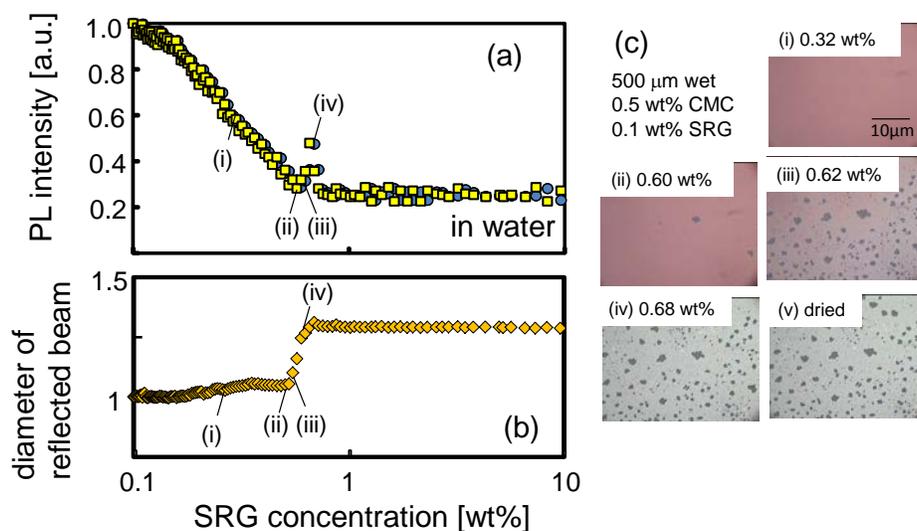


Fig.3 Typical example of in-situ measurements (a) PL intensity, (b) diameter of reflected laser beam spot, and (c) optical microscope images of liquid film during water evaporation.

we conducted in-situ emission intensity measurements during drying. Fig.3 demonstrates a typical example of the variations in (a) PL intensity, (b) normalized diameter of the laser beam reflected from the coating surface, (c) optical microscope images of liquid film surface. The SRG concentrations at different drying times were calculated from film mass data. The measured PL intensity first decreases with increasing SRG concentration because of the concentration quenching in the early evaporation stage. As solvent dries further, the evaporating coating showed a sharp increase in PL intensity at the critical concentration of $C_c \sim 0.6$ wt%, showing a particular "drying-induced emission enhancement" in the intermediate drying stage. The intensity then reduces and eventually reaches a constant value. The laser reflection and optical microscopy measurements reveal that C_c agrees with the concentration, at which the laser scatters at the evaporating surface to expand the beam diameter, and irregular-shaped aggregates form in the liquid. These facts imply that the microscopic surface roughening due to the precipitation of solid aggregates leads to create lateral capillary forces, which, in turn, promote local de-stacking of self-assembling molecules in the vicinity of evaporating surface. To check the hypothesis, we conducted the same measurements in the ethanol solution with a lower surface tension, and found that no peak evolved in ethanol solutions even at high SRG concentrations.

References

[1] Hlaing, H., Lu, X., Hofmann, T., Yager, K.G., Black, C.T., Ocko, B.M., ACS Nano, 5 (2011) 7532-7538

- [2] Ding, G., Wu, Y., Weng, Y., Zhang, W., Hu, Z., *Macromolecules*, 46 (2013), 8638-8643
- [3] Siringhaus, H., Brown P.J., Friend, R.H., Nielsen, M.M., Bechgaard, K., Langeveld-Voss, B.M.W., Spiering, A.J.H., Janssen, R.A.J., Meijer, E.W., Herwig, P., de Leeuw, D.M., *Nature*, 401 (1999) 685-688
- [4] Sanyal, M., Schmidt-Hansberg, B., Klein, M. F.G., Munuera, C., Vorobiev, A., Colsmann, A., Scharfer, P., Lemmer, U., Schabel, W., Dosch, H., and Barrena, E., *Macromolecules*, 44 (2011) 3795-3800
- [5] Schmidt-Hansberg, B., Sanyal, M., Klein, M. F. G., Pfaff, M., Schnabel, N., Jaiser, S., Vorobiev, A., Muller, E., Colsmann, A., Scharfer, P., Gerthsen, D., Lemmer, U., Barrena, E., and Schabel, W., *ACS Nano*, 5 (2011) 8579-8590
- [6] Oku, K., Inasawa, S., Tsuji, Y., and Yamaguchi, Y., *Drying Technology*, 30 (2012) 832-838 (2012)