Solution-phase laser processing of Π-conjugated polymers: Switching between different molecular states

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Abstract. Liquid-phase laser processing, where the laser-irradiated target material is immersed in water for cooling, has been reported as a promising processing technique for thermally fragile organic materials. Although nanometer-sized particles have been reported to be obtained with the liquid-phase laser processing, the physical property did not change because quantum-mechanical size effect does not exhibit itself in the zero-radius Frenkel excitons. In the present study, we step further to use solution droplets as a target material, where organic molecules are molecularly dispersed in organic solvent and, therefore, expected to easily alter the conformation and the energy state upon laser irradiation. Small volume organic solvent is quickly evaporated upon laser irradiation, letting the bare organic molecule placed in water and rapidly cooled. To prevent the chemical decomposition of the target Π-conjugated molecule, the specimen was resonantly irradiated by a ns-pulse green laser, not by a conventional UV laser.

When the solid state spin-coat film made from MEH-PPV chloroform solution was used as an irradiation target immersed in water, resulting MEH-PPV particles showed similar photoluminescence (PL) like the PL of the spin-coat film and PL of the chloroform solution, including the 0→1, 0→2 vibrational transitions: this indicates that the energy levels were not modified from the spin-coat film. In comparison, when tiny droplets of MEH-PPV chloroform solution (orange color) were suspended in water, laser irradiation gave rise to yellow MEH-PPV particles which showed 550 nm and 530 nm PL (type B), blue-shifted from the spin-coat film PL 580 nm (type A), suggesting a successful phase transition of MEH-PPV polymer to type B. Further solution-phase laser processing left the type B state unchanged. The irreversible phase transition from type A to type B suggests that the type B ground state has lower energy than type A, which is consistent with the blue-shifted PL of type B, provided that the excited state energy is similar between the two states. Thermal annealing up to 200°C of type A state did not give rise to type B state, which indicates that the activation potential between the two states is higher than the thermal energy at 200°C, and that only the proposed solution-phase laser processing enables the system to cross over this potential.

1. Introduction
Laser ablation [1] of solid materials is convenient and efficient technology to fabricate a material with designed chemical composition. Since the technology utilizes a high-photon-energy UV laser to

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decompose the original material into atom clusters, it is inapplicable to fragile organic material whose properties are governed by molecular structure. Liquid-phase laser processing (LLP) was proposed recently [2], where the laser-irradiated solid material is immersed in water in prospect of cooling effect of water in order to avoid degradation of organic materials. Although this technique brought about nanometer-sized particles, the physical and chemical properties of the particles were the same as the original material because no quantum size effect was expected in the case of Frenkel bound excitons with zero Bohr radii. A novel solution-phase laser processing (SLP) is proposed in the present research, where tiny droplets of molecularly dispersed material solution are adopted as the laser-irradiation target and homogeneously suspended in insoluble water. Molecularly-dispersed material is expected to have more possibility to attain a phase transition, free from the binding energy between molecules.

![Figure 1](a) Schematic drawing of SLP processing where a low-photon-energy green pulse laser is irradiated against the target, i.e. polymer solution microdroplets suspended in insoluble water. (b) Resulting polymer particles suspended in water whose SEM image is shown in (c) with a 100 μm scale bar.

Target material is a π-conjugated dye polymer, poly[2-methoxy-5-(20-ethyl-hexyloxy)-pphenylenevinylene] (MEH-PPV), which has strong optical absorption at visible wavelength. Upon resonant irradiation of a green pulse laser, molecular motion is expected to be invoked via the strong electron-phonon coupling of the extended π-conjugated system [3 - 5], leading to a plausible phase transition of the polymer conformation [6]. Low-photon-energy visible pulse laser would be effective to invoke this transition, without any chemical damage of the material.

2. Materials and methods
An aliquot of 200μl MEH-PPV solution in chloroform (CHCl₃), dichloromethane (CH₂Cl₂), chlorobenzene (C₆H₅Cl), or toluene (C₆H₅CH₃), was put in 2 ml distilled water and ultrasonicated for 15 min. After microdroplets of MEH-PPV solution were uniformly suspended in water (turbid appearance due to light scattering), collimated Q-switched Nd/YAG SHG laser (λ=532nm, 2 mJ 5ns pulse, 10Hz, Minilite II, Continuum) was irradiated for typically 30min as a SLP processing (figure 1(a)). The resulting homogeneous suspension (figure 1(b)) was dried on a silicon wafer, vacuum evaporated with gold, and observed by scanning electron microscope (SEM, JSM-6510SLV, JEOL) at lower accelerating voltage of 20kV in order to avoid charging up with incident electrons. The photoluminescence (PL) was observed under a microscope and its spectrum was recorded by a spectrometer attached with a charge coupled device camera with on chip multiplication capability (SP-2358 + PhotonMAX 97EMB, Roper Scientific). The thermal annealing experiment up to 200°C was carried out with the specimen held in a sealed chamber filled with dried N₂ gas.
3. Results and discussions

3.1. Conventional liquid-phase laser processing

For comparison, conventional LLP processing was tried first, with a solid phase irradiation target: MEH-PPV spin-coat film made from chloroform solution. The apparent color of the resultant suspension in water did not change before and after the LLP processing. The photon energies of the PL main peak and its vibronic subpeaks were similar with those of MEH-PPV chloroform solution (figure 2(a)), which indicates that the electronic state of MEH-PPV was unchanged. We name this PL as type A, in this paper.

![Figure 2](image)

**Figure 2.** Comparison of PL spectra. (a) spin-coat film (solid line) and LLP processed spin-coat film (dashed line) made from chloroform solution. (b) spin-coat film (solid line) and SLP processed particle before (dashed line) and after the annealing (dotted curve, diminished by 0.12 times), made from chloroform solution. (c) spin-coat film (solid line) and SLP processed and annealed particle (dashed line) made from chloroform solution. Completely overlapped two dotted curves are a spin-coat film, and SLP processed / annealed particle, made from dichloromethane solution. (d) Solution PL dissolved in dichloromethane (solid line), chlorobenzene (dotted line), chloroform (dashed-dotted line), and toluene (dashed line).
3.2. Solution-phase laser processing

In SLP processing, microdroplets of MEH-PPV chloroform solution were uniformly suspended in water and used as a laser irradiation target. Since tiny volume of volatile solvent chloroform are expected to rapidly evaporate upon laser irradiation, insoluble MEH-PPV polymer will be cooled and form tiny particles in water. After SLP processing, the apparent color of the suspension was changed from orange to yellow for chloroform, toluene, and chlorobenzene solution, while the color was already yellow in the case of dichloromethane solution.

The resulting homogeneous suspension was found to be composed of 5μm MEH-PPV particles by the SEM observation (figure 1(c)). The size of the particles seemed to be homogeneous and no aggregation was observed, which is a promising feature for application.

The PL was blue-shifted from that of spin-coat film (figure 2(b)): two new peaks emerged at 550 nm and 530 nm. We call this PL as type B, in the following. The PL intensity was increased after thermal annealing up to 200°C, with intensity profile unchanged. When dichloromethane was used as the starting solvent, the spin-coat film and the SLP processed particles both showed the identical type B spectrum as shown in figure 2(c) dotted curve. Dichloromethane solution of MEH-PPV also showed type B PL, whereas chloroform and toluene solution showed type A PL, as shown in figure 2(d). Chlorobenzene solution showed PL with maximum in between: it may be a mixture of many states because it also seemed to show both type A and type B PL.

In all cases, SLP processing forced the specimen into type B state irreversibly, which suggests that type B state has lower (ground state) energy than type A state (figure 3). This interpretation is consistent with the fact that type B state PL was blue-shifted from that of type A state, provided that the excited state energy is similar between the two states. The activation potential between the two states should be higher than the thermal energy at 200°C, because thermal annealing up to 200°C of type A state did not give rise to type B state. The fact that dichloromethane solvent can induce this transition suggests that this transition may reflect some conformational change of MEH-PPV polymer itself, not a change of the packing of polymer molecules in the particles. This is not a solvatochromism, because the PL showed type B spectrum even after dichloromethane evaporated completely from the spin-coat film by thermal annealing: instead, the transition can be induced by dichloromethane solvation and is irreversible.

![Diagram](image)

**Figure 3.** (a) Schematic model of the phase transition. SLP processing irreversibly converts the MEH-PPV type A state to type B state which has lower ground state energy. This stabilization is consistent with the blue-shifted PL of type B state. The activation potential $E_a$ between the two states is higher than the thermal energy $kT$ at 200°C.
In figure 2, every PL of type B is accompanied with type A peaks. It may mean that these spectra are mixture of type B and type A state. In fact, with shorter term SLP processing of chloroform solution, type A peaks remained as major components, larger than type B peaks, which suggests that the two states type A and type B belong to different electronic states and that they coexist in the same specimen with a ratio dependent on the degree of SLP processing.

In order to evaluate the electronic transition energy and the vibrational energy, PL spectra were replotted with the photon energy as abscissa, and deconvoluted into different vibrational transitions (figure 4). PL spectra were fitted mathematically as a superposition of Gaussian peaks at photon energy $E_\nu$, with linewidth $\Delta E$:

$$I_{pl}(E) = \sum I_i \exp \left[ -\frac{(E - E_i)^2}{\Delta E_i^2} \right]$$  \hspace{1cm} (1)

Since the Lorentzian function form was not fitted well with the PL spectrum, Gaussian function was adopted successfully. This fact suggests that the present inhomogeneous linewidth may be governed by static and dynamic, i.e. transient polymer deformation due to vibrational mode, disorders, similar to the case of energy transitions lower than the band gap of pseudo-isocyanine dye J-aggregate [7, 8].

The spin-coat film made from MEH-PPV chloroform solution and that from toluene solution both showed type A emission (figure 4(a) and (c), respectively) which are well reproduced in the photon energy range above 1.85eV by a superposition of two Gaussian peaks, corresponding to $0\rightarrow0$ ($E_{A0}$) and $0\rightarrow1$ ($E_{A1}$) vibrational transitions [9]. Discrepancy around 1.8eV suggests that it is due to a small contribution of additional $0\rightarrow2$ vibrational transition. From this decomposition, the electronic transition energy was deduced to be 1.93eV and the vibrational energy was 0.17eV, consistently between two specimens (table 1(a)). In the case of the spin-coat film made from MEH-PPV dichloromethane solution (figure 4(b)), type B emissions at $E_{B1}=2.26eV$ and $E_{B2}=2.35eV$ showed up.
accompanying type A emissions, $E_{A0}$, $E_{A1}$, $E_{A2}$ as minor components. The spacing $E_{B1}$ to $E_{B2}$ is 0.09eV, smaller than the vibrational energy 0.17eV, suggesting that type B emissions $E_{B1}$ and $E_{B2}$ have origins different from type A emissions.

After SLP processing, the same PL spectrum resulted for all the particles made from chloroform, dichloromethane, and toluene solution (figures 4(d), (e), and (f), respectively). Majority of the PL belongs to type B emissions $E_{B1}$ and $E_{B2}$, although minor components $E_{A0}$, $E_{A1}$, and $E_{A2}$ remained, with the observed PL spectrum well-reproduced by the superposition of $E_{A0}$ and $E_{B1}$ five components.

Judging from figure 4, relative intensities $E_{A1} / E_{A0}$, $E_{A2} / E_{A0}$ of the deconvoluted components are different among different solvents, whereas they are similar between the spin-coat film and the SLP particles made from the same dichloromethane solvent. This observation suggests that the electron-phonon coupling is sensitive to the solvent and that it memorizes the change even after the

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**Figure 4.** Deconvolution of PL spectra into different vibrational transitions. The abscissa is expressed in photon energy so as to show clearly the equispaced energies among different vibrational transitions ($E_{A0}$, $E_{A1}$ and $E_{A2}$). Decomposed peaks are drawn by dashed or dashed-dotted lines. The mathematical superposition of these decomposed peaks is expressed as thick solid curves which overlap the original PL spectra shown by dotted lines. (a)-(c): spin-coat films, (d)-(f): SLP processed particles. (a), (d): made from chloroform solution, (b), (e): from dichloromethane solution, (c), (f): from toluene solution.
solvent is evaporated: one of the candidates of this “memory” effect is the conformational change of the polymer molecule.

4. Conclusion
A novel visible laser processing technique, where \( \pi \)-conjugated polymer solution droplets suspended in insoluble water were photoexcited resonantly by a low-photon-energy green pulse laser, was demonstrated to yield polymer particles with altered photoluminescence, which is indicative of phase transition of the polymer conformation. The final state was the same among laser processing of polymer in different original solvents, chloroform, toluene, dichloromethane. The electronic ground state of the resultant polymer particles is expected to have lower energy than the original state, which is consistent with the blue-shift of the photoluminescence after this laser processing, and also consistent with this irreversible phase transition upon the laser processing. Thermal annealing up to 200 °C did not give rise to this phase transition, which indicates that the activation potential between the two states is higher than the thermal energy at 200 °C, and that only the proposed solution-phase laser processing enables the system to cross over this potential and to transit to the same state, irrespective of the molecular environment defined by surrounding solvents.

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