



Invited feature article

Correlation of nanodomain morphology and ultrafast fluorescence dynamics in bisdecylsexithiophene-polyethylene oxide copolymer film

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ABSTRACT

Bisdecylsexithiophene rods and polyethylene oxide coils forming alternating copolymer are of photo-physical interest. Nanodomain morphology by means of atomic force microscopy and steady-state/time-resolved fluorescence spectroscopy are correlated. Films, by using drop-casted and spin-coated preparation, consist of drops and terraces with average roughness R_a , maximal height R_{max} , and nanodomain size to be 94.2 and 24.4 nm, 489.1 and 171.7 nm, and 200×400 nm and 1000×1000 nm, forming cylindrical and lamellar aggregates, respectively. The nanodomain aggregate thickness is 8 nm. The ultrafast dynamics of drop-casted and spin-coated films result in two relaxations of 6.9 ps and 12.0 ps, and only one relaxation of 5.3 ps, respectively. The simulation focuses on cylindrical $(12 \times 4$ and $(10 \pm 2) \times (4 \pm 1))$ and lamellar $(12 \times 12$ and $(10 \pm 2) \times (10 \pm 2))$ nanodomains. The aggregate nanodomains and intra-aggregate dynamics correlate as two-parameter drop-casted film and one-parameter spin-coated film.

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1. Introduction

A rod-coil copolymer, as shown schematically in Fig. 1(a), represents technologically important class of multifunctional nanostructured materials in optoelectronics [1], photovoltaics [2], or biomimetics [3], exhibiting spatial ordering of self-organized rod-coil nanodomains of specific morphologies. The importance of the rod-coil copolymers, prepared from hydrophobic π -conjugated rods and hydrophilic flexible coils, originates mainly from their tunable photo-physical properties. The covalent bond connections between rods and coils, forming di-, tri- or multi-block of rod-coil copolymers mediate the formation of a novel class of self-organized materials. The structures of rod-coil copolymers are based on the competition of the free energies of

rod and coil aggregates and of their interface, as well as by packing constraints.

Excitation dynamics is essential in order to relate function and structure of the materials. Polycrystalline films of 6,13-bis(triisopropylsilyl)ethynyl pentacene was characterized by using transient absorption [4,5]. Three channels of dynamics were determined and assigned with time constants of 44 fs, 4.4 ps, and 605 ps corresponding to a thermalization of the hot S_1 excitons, an equilibrium between singlet and triplet excitons, and an internal conversion, respectively [4]. Polyoxometalate containing metal oxygen hybrid rod-coil diblock copolymers were studied as solutions in $CHCl_3$ [6]. The fluorescence decays, spanning from 6.3 to 11.0 ps and from 34 to 67 ps, were assigned as excitation energy transfer in a segment, torsional relaxation, and excitation energy transfer between segments with comparable energy, respectively [6].

In our contribution, the rod-coil copolymer of dimethyl ester of 3,3''''-bisdecyl [2,2'; 5',2''; 5'',2'''; 5''', 2''''; 5''''', 2'''''''] sexithiophene-5,5'''''' - dicarboxylic acid with polyethylene oxide, shortly bd6T-alt-PEO, is investigated. The bd6T-alt-PEO, as shown in Fig. 1(b), is

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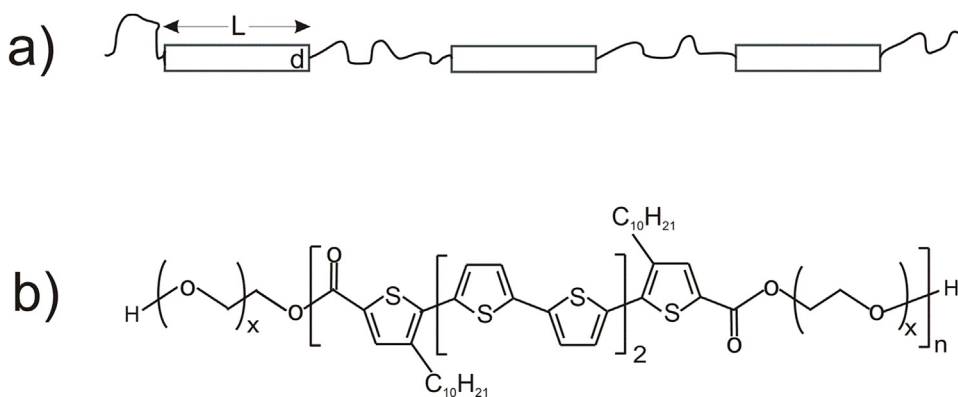


Fig. 1. (a) The rod-coil copolymer illustration with the rod of length L , diameter d and the coil. (b) The molecular structure of dimethyl ester of 3,3''-bisdecyl [2,2'; 5',2''; 5'',2'''; 5''', 2'''''] sexithiophene-5,5''''-dicarboxylic acid with polyethylene oxide (bd6T-alt-PEO).

studied as a solution in toluene and as solid films on plate prepared by using drop-casted (DC) and spin-coated (SC) techniques. The main focus is on fluorescence dynamics correlated with nano-domain morphologies. Steady-state and time-resolved fluorescence spectroscopies, atomic force microscopy (AFM), as well as computational modeling are instrumental. The fluorescence is interpreted by computational modeling of one-exciton optical absorption spectra of bd6T-alt-PEO copolymer forming nano-domain morphologies. The time-resolved fluorescence of bd6T-alt-PEO is solved by the master equation of one-exciton states probabilities, describing their radiative emission and non-radiative relaxation. The steady-state fluorescence spectra are calculated by integrating the simulated time-resolved fluorescence. The interpretations of the AFM images are based on thermodynamics of free energy during the DC and SC processes of the rod-coil nano-domains formation.

2. Experimental

The copolymer synthesis was performed by condensation reaction of alkylated dimethylester of oligothiophene dicarboxylic acid with PEO, resulting in bd6T-alt-PEO copolymer [7]. The molecular weight of bd6T-b-PEO, as shown in Fig. 1(b), was approximately 15 000 a.u. The value of x denotes the EO monomer number in the PEO blocks of approximately 350. The value of n for bd6T-b-PEO was almost mono-dispersed with a value of approximately 12. The solution of copolymer in toluene was prepared by ultrasonic dissolution for one hour within the concentration range of 0.01–4.00 g dm^{-3} .

The thin solid films for steady-state fluorescence spectroscopy were prepared from the solution of 1 g dm^{-3} concentration and deposited on 1 mm thick square quartz plate, with a number of drops 1, 3, 10, and 40 for the DC and SC preparation techniques separately. The SC technique was based on dropping of 15 drops of the solution on the plate which was spinned at 100 rpm revolution on a spin-coater. The DC technique was the same, without using the spin-coater. In both preparation cases, each drop contained 15 μL of the solution which was deposited one by one at room temperature and was evaporated and dried by infrared lamp. Since the steady-state fluorescence spectroscopy is more sensitive than the time-resolved fluorescence spectroscopy, the higher concentration of 4.00 g dm^{-3} was used in the later case. The solution of 4.00 g dm^{-3} concentration in toluene was deposited on 1 mm thick circular quartz plate.

The AFM (SPM Solver P47H, NT-MDT) was performed in semi-contact tapping mode. The DC and SC films were deposited on silicon wafer surface at room temperature. Note that the silicon wafer is naturally covered with a thin layer of SiO_2 , providing the

same surface chemistry as quartz surface. The AFM single crystal silicon tips had a spring constant of approximately 11.8 N/m and a curvature radius of approximately 10 nm. For each sample, at least four areas were imaged, the images were line-fitted, and the average roughness (R_a) and maximum height roughness (R_{max}) were determined on $5 \times 5 \mu\text{m}$ area.

The steady-state fluorescence excitation and emission spectra were performed (Jobin – Yvon SPEX Fluorolog-3) with the 450 W Xe lamp, the 90° configuration, the square cuvettes with the 5 mm excitation and 10 mm emission pathways, the entrance and exit slits of 1 mm, the integral time of 1 s, and the three scans averaged. The thin films on the quartz plates were placed at the cuvette slot at the incident angle of 45° .

The time-resolved fluorescence spectroscopy was performed with Ti:sapphire oscillator (CDP TiF50)/pump laser (COHERENT Verdi) and up-conversion system (CDP FOG100) [8]. The laser system provided the output power of 300 mW, the repetition rate of 80 MHz, the pulse length of 150 fs, the wavelength of 800 nm, and second harmonic generation wavelength of 400 nm, which was used for excitation. The time resolution of the up-conversion system was estimated to be 250 fs [9]. The fluorescence signal was collected from the opposite side of the solution sample in transmission mode by using an achromatic lens. The film samples were measured in the same way, collecting signal from the direction of interface between quartz surface and the copolymer film. To minimize a degradation process, the samples containing either the solution or the films were constantly rotated during the measurements. The wavelength dependence of time-resolved fluorescence spectroscopy was examined at the wavelengths of 490, 500, 510, 520, 540, 560, 580, and 600 nm. The fluorescence spectroscopy, both steady-state and time-resolved were performed at $20 \pm 1^\circ\text{C}$ in ambient conditions.

3. Results and discussion

The nanodomains of rod-coil copolymer were directly visualized as surface morphology by using AFM. Since the nanodomain morphology is driven by free energy thermodynamics the rod-coil copolymer film formation is based on the preparation condition. The main focus was to correlate the morphologies of rod-coil, core-corona, micelle self-organized copolymer nanodomains through their electronic states by using steady-state and time-resolved fluorescence spectroscopies.

3.1. Morphology

During the DC process, the copolymer solution was deposited on the plate surface and the self-organized process followed

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