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Colloids of semiconducting polymers for high-performance, environment-friendly polymer field effect transistors

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ABSTRACT

Considering the recent rapid growth of polymer field effect transistor (PFET) techniques and environmental pressure to avoid the use of toxic organic solvents in industrial processes, it is very important to develop colloids of semiconducting polymers in non-toxic solvents. Herein, we demonstrate the fabrication of surfactant-free, emulsion-dispersed nanoparticles of donor–acceptor copolymers. By optimizing the deposition methods of such semiconducting polymer colloids, high mobility (2.7 cm^2/Vs) PFETs were fabricated via environmentally benign processes. Systematic analyses on the crystalline nature of the colloid-processed films revealed that the well-developed edge-on lamella structure comparable to that of the bulk polymer, was preserved during the colloid-fabrication processes.

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1. Introduction

In the polymer industry, the use of toxic organic solvents can be a serious issue due to the attendant additional environmental costs at the mass-production stage. Consequently, tremendous effort has been directed toward switching from solvent-based to water-borne polymer systems, especially in the fields of adhesives, thermoplastics, textiles, paints, and biomedical applications [1–2]. Such systems may be denoted as polymer colloids, where polymer microparticles or submicroparticles are dispersed in environmentally benign solvents such as water or alcohols. For example, in the field of conducting polymer colloids, conducting polymers such as polypyrrole or polyacetylene are sterically stabilized by water-soluble polymeric stabilizers that are physically adsorbed on the outer surface of the conducting polymer microparticles [3]. The conductivity of films prepared with such colloids is usually lower than that of films prepared using bulk polymer powders due to the presence of the electrically insulating polymeric stabilizer and the increased number of resistive interparticle contacts [3]. Nonetheless, the demand for these conducting polymer colloids is increasing because of the environmental pressure to avoid the use of toxic organic solvents [4].

In the field of semiconducting polymers, however, efforts to fabricate polymer colloids to meet the trend toward greener polymer technologies have been limited [5–7]. This can be attributed in part to the fact that the colloids of semiconducting polymers usually exhibit very low charge carrier mobility. For example, Zhou and coworkers demonstrated that colloids of poly-3(-hexylthiophene) could be dispersed in water either with or without the assistance of a surfactant, and relatively higher mobility was obtained from the colloids without surfactant, presumably due to better interparticle charge transport [7]. Although this result is very interesting, the mobility was still remarkably low compared to that of bulk poly-3(-hexylthiophene). This may be attributed to the generally poor charge transport within the microparticles of semiconducting polymers that assemble very quickly in hydrophilic environments. Note that in the field of traditional polythiophene-based polymer field effect transistors (PFETs), it is well known that slow formation of the polymer domain is a critical factor for achieving better intermolecular interactions [8].

Based on these considerations, we attempted to fabricate colloids of novel semiconducting polymers, represented by donor–acceptor conjugated polymers. Unprecedentedly high performance, with charge carrier mobilities higher than 10 cm^2/Vs, has been achieved with these polymers, mostly having diketopyrrolopyrrole (DPP) or isoindigo (IID) as an electron acceptor [9–13]. More importantly, these polymers have exhibited high performance even in the case of thin films with low crystallinity [14].

Such interesting characteristics were observed especially for the donor–acceptor copolymers with strongly planar backbone structures [15]. Therefore, it is anticipated that these novel polymers should be able to maintain high mobility even in the form of (sub)microparticles constructed without sufficient time for self-assembly.

On this basis, we demonstrate herein a simple method for the fabrication of polymer colloids to achieve high mobility (>2 cm^2/Vs) PFETs. Polymer colloids were prepared in butyl acetate (BA) or ethyl acetate (EA) by a simple emulsion dispersion method based on a donor–acceptor copolymer that has a torsion-free, planar backbone structure, i.e., diketopyrrolopyrrole–thienothiophene (DPP–TT) [16]. According to previous reports, BA and EA can be categorized as relatively greener solvents comparable to ethanol [17,18], and therefore, the prepared colloids of the semiconducting polymer adequately satisfy the requirements of the colloid technique (also see Table S1). The submicroparticles of DPP–TT were fully characterized by employing scanning tunneling microscopy (FE-SEM) and grazing incident X-ray diffraction (GIXD). By optimizing the methodology for deposition of the submicroparticle film, high mobility (2.7 cm^2/Vs) PFETs are achieved from polymer colloids for the first time.

2. Experimental

2.1. Materials

The procedure for synthesis of DPP–TT is documented in a previous report. 16 BA, EA, and chloroform were purchased from Sigma–Aldrich and used without further purification. Molecular weight of DPP–TT used in this work was Mn = 34,200, Mw = 57,800.

2.2. Characterization

Optical images were obtained with a digital camera (Lumix DMC-LX5, Panasonic). SEM images were obtained via FE-SEM (Sigma/Carl Zeiss) with a Schottky Field Emitter. The GIXD measurements were performed at the PLS-II 9A U-SAXS beamline of Pohang Accelerator Laboratory (PAL) in Korea. The X-rays coming from the in-vacuum undulator (IVU) were monochromated (E = 11.06 keV) using Si(1 1 1) double crystals, and were focused at the detector position using a K-B focusing mirror system. The horizontal and vertical beam sizes were 300 (H) μm and 30 (V) μm, respectively. The incidence angle (α_i) was adjusted to 0.13°, which is above the critical angle. GIXD patterns were recorded with a 2D CCD detector (Rayonix, SX-165). The diffraction angles were calibrated using precalibrated sucrose (Monoclinic, P21) and the sample-to-detector distance was approximately 225 mm. The electrical characteristics of the transistors were measured with 4156A Precision semiconductor parameter analyzers (Agilent Technologies).

3. Results and discussion

Fig. 1(a) shows the chemical structure of the semiconducting polymer, DPP–TT, used as a polymeric semiconductor in this work. A scrutiny of the chemical structure shows that the lactam moiety in the DPP segment should exhibit a strong electron-withdrawing effect and high electron affinity. Furthermore, because the thiophene unit is attached to the DPP unit, it is expected that close (2.1 Å) intramolecular hydrogen bonding between the carbonyl oxygen of DPP and the nearest thiophene hydrogen would be operative, facilitating backbone planarity [19]. Consequently, in contrast with the traditional polythiophene-based semiconducting polymers, in the case of DPP–TT, the formation of reasonably high

crystalline ordering can be expected, even in the form of colloidal particles. The colloids of DPP–TT were fabricated by the dispersion of polymer powder in BA or EA by sonication at room temperature. The UV–Vis absorption spectra of colloidal solutions of DPP–TT in BA are summarized in Fig. 1(b) as a function of sonication time. After ∼50 min, no further changes in the absorption spectra were observed; therefore, 50 min was selected as the standard dispersion time in this study. Similar experiments were also performed using EA, whose results are also summarized in the Fig. S1. As shown in Fig. 1(b), typical dual band absorption spectra were obtained for all of the prepared colloidal solutions: band I (600–1000 nm) and band II (300–500 nm), implying that the polymer structure is well preserved in the colloidal solutions. Notably, the position of the maximum absorption of the polymer colloids dispersed in BA is slightly (∼8 nm) red-shifted relative to that of the solution of the polymer perfectly dissolved in chloroform. This means that DPP–TT undergoes some degree of crystalline ordering in the form of submicroparticles during the dispersion processes.

To characterize the submicroparticles of DPP–TT and their resulting films, morphological analyses were performed as summarized in Fig. 2. The typical size of the submicroparticles dispersed in BA (Fig. 2(a)) was ∼300 nm. However, these submicroparticles quickly formed microclusters when cast on the substrate and subsequently annealed (200 °C for 30 min) as depicted in Fig. 2(b). This fast interparticle-aggregation phenomenon can be attributed to the surfactant-free fabrication process used for the current colloidal solutions. In other words, because no surfactant or ligand (which can inhibit interparticle interaction) was used, it was not possible to achieve well-aligned arrays of submicroparticles. However, the focus of this study is to achieve high charge carrier mobility, and therefore, the observed presintering phenomenon is not an issue. Moreover, because of the efficient interparticle aggregation, thermal annealing was not mandatory. Only negligible enhancement of the PFET performance was obtained as a result of thermal annealing, which is discussed in the following section. Fig. 2(c) and (d) respectively show optical microscope (top view) and FE-SEM (side view) images of the device after depositing Au electrodes onto the films of submicroparticles. The final PFET device structure with bottom-gate and top-contact geometry is illustrated in Fig. 2(e). Interestingly, Fig. 2 demonstrates that the films cast from the colloids of DPP–TT retain reasonably good (continuous, smooth) film properties even though the colloidal solution consisted of submicroparticles. Notably, however, on the nanoscale, these films are quite rough due to the presence of interparticle nonhomogeneity as highlighted by the AFM image presented in the Fig. S2.

The transfer and output data for PFETs employing DPP–TT cast from BA and EA are presented in Fig. 3. The results for the device fabricated using chloroform are also shown in the Fig. S3 for comparison. As the gate and dielectric layers of the PFET, a SiO$_2$ (100 nm)/Si++ wafer was used after treating the surface with octyltrichlorosilane prior to semiconductor deposition. After semiconductor deposition, all the devices were annealed at 200 °C for 30 min. However, it should be noted that the colloid-based PFETs exhibited only slight enhancement of the charge carrier mobility as a result of thermal annealing, which can be attributed to the efficient interparticle aggregation at the stage of film formation. As shown in Fig. 3(a)–(d), both BA- and EA-based PFETs showed typical p-channel transfer/output characteristics. The field effect mobility values of the pristine BA-based devices were as high as 2.7 cm^2/Vs at the peak value, with an average of 2.52 cm^2/Vs, calculated in the saturation regime. The EA-based devices yielded slightly lower peak mobility value of ∼0.6 cm^2/Vs with average value of 0.51 cm^2/Vs. In each case, ten independent devices were fabricated and measured to obtain statistical values. The comparatively poor performance of the EA-based PFETs might be related to