

Size-Dependent Spectroscopic Properties and Thermo-chromic Behavior in Poly(substituted thiophene) Nanoparticles

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Polythiophene and its derivatives (PTs) are a class of conjugated polymers, and their electronic, optical, and thermodynamic properties in the bulk solid state have been studied extensively because of their high potential for applications in electronic

and optoelectronic devices, such as field-effect transistors (FETs),^[1,2] light-emitting diodes (LEDs),^[3,4] and solar cells.^[5,6] It is well-known that their spectroscopic properties are closely related to coil-like, planar, and distorted conformations of the polymer chain.^[7–9] In the coil-like conformation, twisted adjacent thiophene rings make the conjugation length short and its distribution broad, resulting in blue-shifted and structureless absorption and fluorescence spectra, as compared to the planar conformation, where the thiophene rings are coplanar and the rotating motion is highly limited, that is, making the conjugation length longer and its distribution narrow. The distorted conformation lies between the flexible coil-like and rigid planar conformations. The difference in conformations also affects their thermodynamics. Distorted polymers easily change their conformation to coil-like, which is accompanied by a color change, as the temperature is elevated (thermochromism), whereas a planar polymer needs a relatively high temperature to induce the change, due to its stiffness.^[10–13] Thus, the spectroscopic and thermodynamic properties of PTs provide information on the structure at a molecular level. By utilizing this notable feature, we have succeeded in demonstrating that a difference in polymer conformations and their spatial arrangements evolves into a difference in the nanometer-scaled surface morphology in poly(3-[2-(*N*-dodecylcarbomoyloxy)ethyl]-thiophene-2,5-diyl), P3DDUT, films (see Figure 1(a) for the chemical structure).^[14,15]

Near-field fluorescence microspectroscopy has revealed that fluorescence spectra at protruding domains were slightly blue-shifted compared with flat areas, and a further blue-shift could be induced more appreciably by a long excitation time. We have concluded that major polymers take a disordered phase in the protruding domain, in which there are some distortions in the main chain (decreasing the conjugation length) and interchain interactions are rather weak, whereas a planar (ordered) conformation giving a longer conjugation is favored in the flat area.^[14] Moreover, we have demonstrated that the P3DDUT films show a nanometer surface protrusion accompanying the blue-shift in the fluorescence spectrum upon near-field excitation: This phenomenon is attributable to a photo-thermally-induced conformational change, such as a planar-to-coil transition.^[15] Thus, we have made it clear that P3DDUT polymer structures at the molecular level are closely related, not only to spectroscopic and thermodynamic properties, but also to nanometer-scaled surface morphology.

Nanoparticles are attractive nanomaterials from both fundamental and technological viewpoints, since they exhibit unique physical and chemical properties, which differ from isolated atoms/molecules and bulk solid states. So far, inorganic semiconductor and metal nanoparticles have been extensively investigated, and their unique properties and phenomena revealed. It is well-documented that the optical properties of semiconductor nanoparticles, such as CdSe, change drastically depending on the particle size, due to quantum confinement of the excitons.^[16,17] An enhancement in catalyses^[18] and a change in thermodynamic properties^[16,19] have also been reported. In contrast, characteristic physical and chemical properties have not been studied well for organic nanoparticles,

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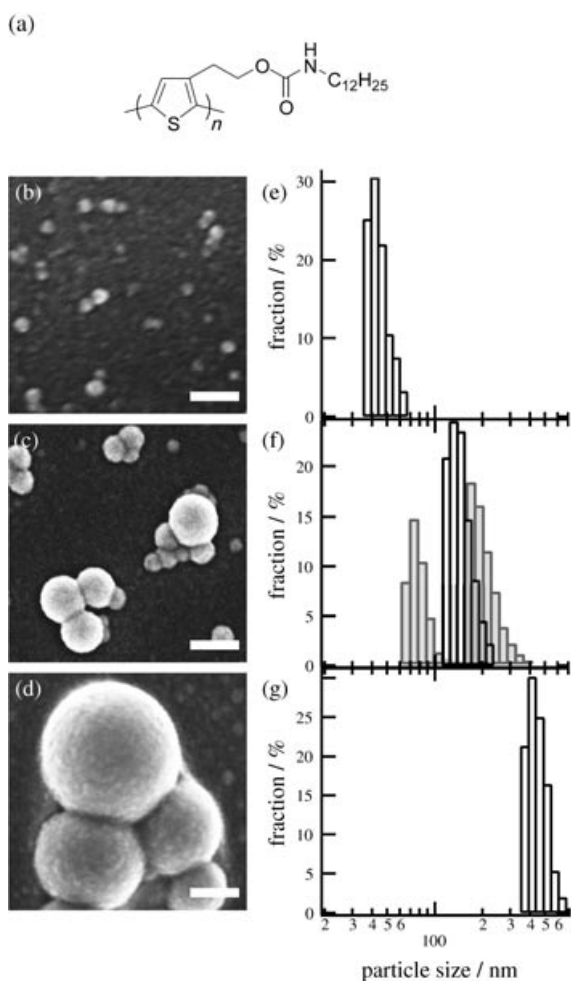


Figure 1. (a) Chemical structure of P3DDUT and (b–g) SEM images of P3DDUT nanoparticles prepared by reprecipitation and DLS size distributions; (b,e) 0.1 wt.-% P3DDUT/THF solution was injected into distilled water at 20°C; (c,f) 1.0 wt.-% at 20°C. Occasionally, reprecipitation resulted in two components, distributed as illustrated by the gray bars in (f); (d,g) 1.0 wt.-% at 80°C.

which is, at least partly, ascribed to the limited number of fabrication methods.

A systematic study of the novel properties of organic nanoparticles was initiated by Kasai et al., who developed a reprecipitation method for preparing organic nanoparticles and found size-dependent and characteristic optical properties in perylene nanoparticles showing blue-shifts in both absorption and fluorescence spectra as the particle diameter decreased from hundreds to tens of nanometers.^[20,21] They have suggested that a change in lattice state due to the increase in surface area makes the Coulombic interaction energies between molecules small, leading to a wider bandgap.^[21] However, the precise mechanism for the size-dependent optical properties is not clear. Therefore, it is now significant and interesting to fabricate P3DDUT nanoparticles, investigate their properties, and discuss a relationship between the size, properties, and polymer conformations at a molecular level.

Herein, we have prepared P3DDUT nanoparticles with various diameters by the reprecipitation method and investigated their spectroscopic properties and thermochromism. We found

a size dependence in absorption and fluorescence spectra and thermochromic behavior, and considered these novel phenomena from the viewpoint of a difference in polymer conformations and spatial arrangements.

Figure 1 shows some SEM images of P3DDUT nanoparticles and their size distributions (measured by dynamic light scattering, DLS). By changing the concentration of the P3DDUT/THF solution, ranging from 0.1 to 1.0 wt% while keeping the water temperature at 20°C, nanoparticles with mean diameters (determined by DLS) ranging from 40 to 140 nm were obtained. The lower concentration provided the smaller nanoparticles. It should be mentioned that nanoparticles obtained from 0.5–1.0 wt% solutions occasionally resulted in a size distribution with two separated components, as shown in Figure 1 (f) (gray line), the reason for this is still not clear. Herein, therefore, the experimental results for the 145 nm particle size are for such polydispersed samples, although the accuracy of the particle size is guaranteed for other particles. P3DDUT solution (1.0 wt.-%) injected into water at temperatures ranging from 20 to 80°C gave monodispersed nanoparticles with mean diameters ranging from 140 to 420 nm.

Figure 2(a) shows the absorption spectra of P3DDUT nanoparticles with various mean diameters dispersed in water at

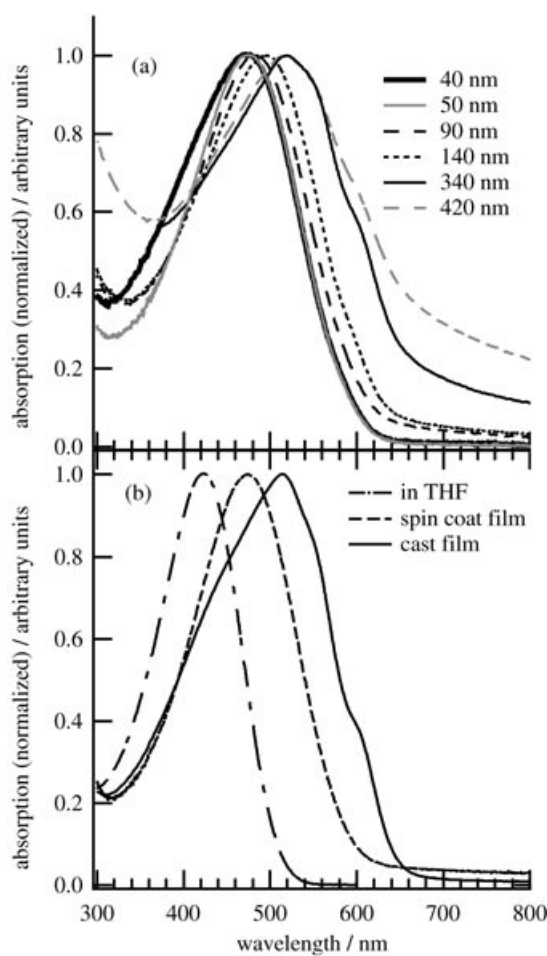


Figure 2. (a) Absorption spectra of P3DDUT nanoparticles with various mean diameters dispersed in water; (b) absorption spectra of a P3DDUT/THF solution, a spin-coated film, and a cast film.

room temperature. The nanoparticles with mean diameters of 340 and 420 nm showed absorption spectra with a peak at 520 nm and shoulders at 560 and 610 nm. On the other hand, nanoparticles smaller than 140 nm had structureless spectra. The peak wavelengths of the nanoparticles shifted from 500 to 470 nm, as the diameter decreased from 140 to 40 nm. It is interesting to note that the absorption spectra of nanoparticles depend on their diameter; that is, the smaller nanoparticles show a further blue-shifted spectrum. For a comparison, absorption spectra of P3DDUT in tetrahydrofuran (THF) and in the bulk solid states, such as cast and spin-coated films, are shown in the Figure 2(b). A cast film had an absorption spectrum with a peak at 515 nm and shoulders at 560 and 610 nm; resembling that of 340 and 420-nm sized nanoparticles. These shoulders originate from a vibronic coupling, since their energy splitting of 1400 cm^{-1} corresponds to the ring vibration of the thiophene ring.^[22] On the other hand, a spin-coated film showed a structureless spectrum with a peak at 475 nm, thereby resembling nanoparticles smaller than 140 nm. An absorption spectrum similar to that of 40 nm sized nanoparticles, having short wavelength components around 400 nm, could not be obtained from either cast or spin-coated films.

The excitation spectra of P3DDUT nanoparticles showed a similar size dependence to the absorption spectra. Figure 3 displays the absorption and excitation spectra of P3DDUT nanoparticles, with various mean diameters, dispersed in water. The detection wavelength of excitation spectra was 630 nm. Although in the excitation spectrum of the 420-nm sized nanoparticles, wavelengths of the peak ($\approx 520\text{ nm}$) and shoulder ($\approx 560\text{ nm}$) resemble those in the absorption spectrum, there are some differences between the two spectral shapes that are attributable to the scattering effect [Figure 3(a)]. In general, for a large colloidal solution with a strong absorption, the absorption appears to shift from its actual position to longer wavelength because of light scattering and anomalous dispersion of the refractive index.^[23] On the other hand, the excitation spectra of nanoparticles smaller than 140 nm are almost identical to the absorption spectra. This indicates that distortion of the absorption spectrum due to the scattering effect can be excluded for nanoparticles smaller than 140 nm.

Figure 4 shows fluorescence spectra of P3DDUT nanoparticles, with various mean diameters, dispersed in water, measured with excitation at 480 nm. The concentration of the nanoparticle suspensions was adjusted by making the maximum absorbance less than 0.2, to avoid the reabsorption effect. It is obvious that the fluorescence spectra also showed a blue-shift as the diameter of the nanoparticles decreased.

So far, several mechanisms have been proposed for size-dependent spectroscopic properties in nanoparticles: 1) quantum confinement; 2) light scattering; and 3) lattice softening. Quantum confinement is well-documented for inorganic semiconductor nanoparticles, such as CdSe.^[16,17] Their absorption and fluorescence spectra show a size dependence when the particles are comparable to, or smaller than, the exciton Bohr radius. The conjugated length of polyalkylthiophenes has been estimated at 2.1 nm, which corresponds to $\approx 5\text{--}6$ repeating thiophene units,^[24] whereas the size of the present nanoparti-

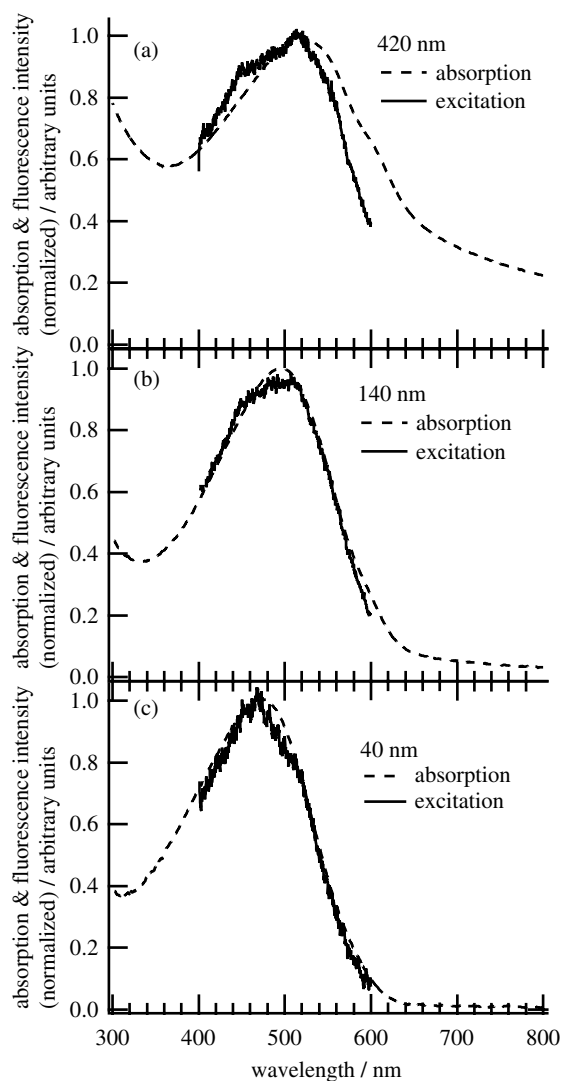


Figure 3. Absorption and excitation spectra of P3DDUT nanoparticles, with various mean diameters, dispersed in water: (a) 420, (b) 140, and (c) 40 nm. The detection wavelength of the excitation spectra was 630 nm.

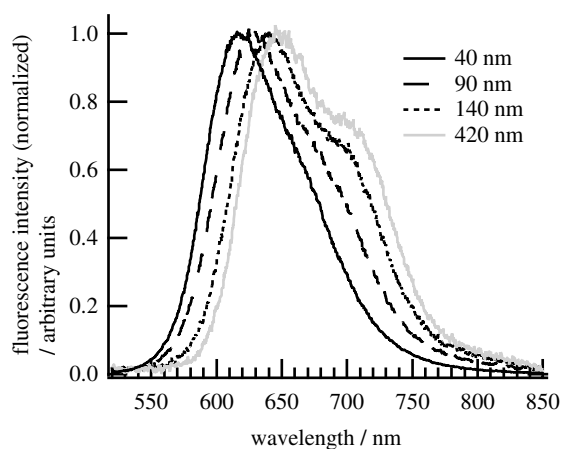


Figure 4. Fluorescence spectra of P3DDUT nanoparticles, with various mean diameters, dispersed in water. The excitation wavelength was 480 nm.

cles ranges from 40 to 420 nm. Therefore, it is unlikely that quantum confinement is responsible for the size dependence observed in P3DDUT nanoparticles. The light scattering of colloidal nanoparticles sometimes gives incorrect absorption spectra by conventional measurements. This apparent absorption includes a light-scattering loss, which is dependent on particle size and shape.^[25,26] However, we can exclude the scattering effect as the origin of the size dependence because the fluorescence and excitation spectra also depend on the particle size. Lattice softening has been suggested for organic nanocrystals, such as perylene^[21] and pyrazoline,^[27] as mentioned above. It was proposed that an increase in surface area results in lattice softening, which makes intermolecular interactions weaker and modifies the bandgap, leading to size-dependent absorption and fluorescence properties. As mentioned above, we have demonstrated that, in P3DDUT films, polymer conformations and spatial arrangements are closely related not only to spectroscopic and thermodynamic properties, but also to nanometer-sized surface morphology. Therefore it is likely that lattice softening is responsible for our size-dependent spectroscopic properties in P3DDUT nanoparticles.

Three classifications of polymer conformations of polythiophene derivatives have been proposed. First, there is a coil-like conformation,^[12,13,28] in which distortion and bending at the C–C bond between adjacent thiophene rings exist, making the conjugation length short and its distribution broad. Therefore, coil-like polymers exhibit a blue-shifted and structureless absorption spectrum, such as that in solution or in molten state. From the absorption spectrum in solution [Figure 2(b)], it is supposed that P3DDUT adopting the coil-like conformation exhibits an absorption spectrum with a peak around 415 nm. An assembly of coil-like polymers forms an amorphous phase. Second, there is a planar conformation in which the thiophene rings are coplanar.^[12,13,28] Polymers adopting a planar conformation tend to form a π -stacked aggregate and are found in a crystalline phase. Rotation of the thiophene rings is highly limited for planar polymers, due to intermolecular interactions which make the conjugation length long and its distribution narrow. Therefore, planar polymers exhibit a red-shifted absorption spectrum with vibronic structure. P3DDUT adopting a planar conformation exhibits an absorption spectrum with a peak at 515 nm and shoulders at 560 and 610 nm, which is often observed for cast and annealed films.^[10] Third, there is a distorted conformation which lies between the flexible coil-like and rigid planar conformations.^[12,29] This conformation possesses some degree of freedom, allowing partial distortions in the main chains, however its conjugation length is longer than that of coil-like polymers. These polymers form a quasicrystalline phase, in which the interchain distances are longer and the intermolecular interactions weaker than those in the crystalline phase.

The absorption spectra of nanoparticles larger than 340 nm exhibit a peak and shoulders at 520, 560, and 610 nm, respectively. Therefore, it is considered that polymers adopting a planar conformation are the major component in nanoparticles larger than 340 nm. As the nanoparticles get smaller, the absorption spectrum becomes blue-shifted and structureless,

which indicates that the smaller nanoparticles consist of polymers adopting a more distorted conformation. In particular, 40 nm nanoparticles have a larger absorbance in the short wavelength region around 415 nm, indicating that coil-like polymers are included much more than other large particles.

Annealing the nanoparticles makes the size-dependence in their absorption spectra distinct, and provides a detailed insight concerning polymer structure in the nanoparticles. The nanoparticle suspensions were heated to $\approx 95^\circ\text{C}$ and then cooled at a rate of 1°Cmin^{-1} . Figure 5 shows the absorption

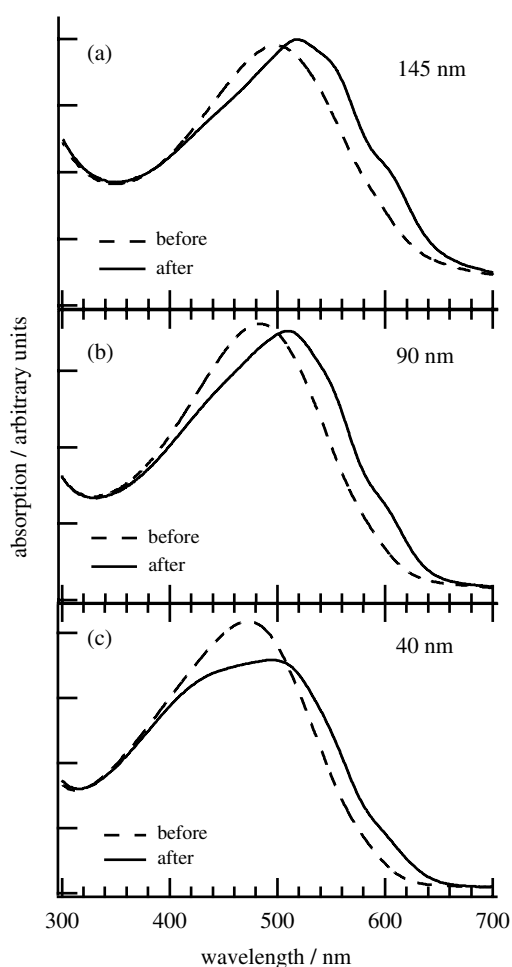


Figure 5. Absorption spectra of P3DDUT nanoparticles dispersed in water before and after annealing: (a) 145, (b) 90, and (c) 40 nm.

spectra before and after annealing. Since the optical densities at 300–350 nm attributed to scattering show no change upon annealing, it is considered that the change of the particle size is negligibly small. The absorption spectrum of 145-nm sized nanoparticles shows a red-shift and the appearance of vibronic structure upon annealing. After the annealing, the spectral shape of the 145 nm sized nanoparticles was identical to that of other, larger ones. In addition, this spectral change upon annealing is similar to that of bulk spin-coated films.^[30] These results indicate that planar and distorted conformations are included in the larger particles, and that a certain level of the distortion is relaxed into the planar conformation upon anneal-

ing. As the particles become smaller, the absorbance of the short wavelength components (around 415 nm) become larger, while the vibronic structures at 560 and 610 nm become less distinct. In particular, 40-nm particles exhibit a distinct shoulder not at 560 and 610 nm, but around 415 nm after annealing, which indicates that they include distorted and coil-like polymers much more than other, larger particles, and a lot of distorted conformations still remain after annealing. Such behavior upon annealing is different from that observed in bulk films.^[10,30] These results explain the size-dependent absorption and fluorescence spectra, that is, the amount of structural distortion increases with decreasing particle size. Accordingly, we propose one model for the internal structure of P3DDUT nanoparticles: The surface layer consists of distorted and coil-like conformations, to reduce the surface free energy, whereas the inner region forms an ordered phase with more planar conformations. As the nanoparticle size decreases, the relative amount of surface layer in the particle increases, and the characteristic properties attributed to polymer conformations appear.^[16,31,32] Of course, further investigations, including X-ray crystallography, are needed for the precise description of the inner structure.

Figure 6 shows the temperature-dependent absorption spectra of P3DDUT nanoparticles, with various mean diameters, dispersed in water. These measurements were carried out below 100 °C, to avoid boiling the water. Although all nanoparticles showed a temperature dependence of the spectral shape, it should be noted that the smaller particles showed a more drastic change. In the case of 40-nm particles, the absorption peak at 473 nm observed at room temperature gradually decreased, and a new band appeared at \approx 415 nm as the temperature increased. The observed spectral changes were reversible, as the spectral shape after cooling down is quite similar to the original one, shown in Figure 5. The absorption maximum wavelength was plotted as a function of temperature (Figure 7). It is obvious that the transition temperature, at which a drastic color change was observed, became lower as the nanoparticles became smaller. As the particle size increased (40, 50, and 80 nm) the transition temperature shifted to a higher temperature (60, 75, and 90 °C, respectively). Other, larger nanoparticles did not show any drastic spectral change within this temperature range. This size dependence of the transition temperature is also shown in fluorescence spectral change (Figure 8). For comparison, the absorption spectral change of a spin-coated film is shown in Figure 7. The spectral peak of the film was at 495 nm at room temperature and the thermochromic transition appeared at a temperature higher than 100 °C. Previously, it had been revealed that the thermochromism of a polythiophene derivative film is attributable to the thermally induced distortion in the main chains; the distortion makes the conjugation length shorter.^[10-13,28] Therefore, it is reasonable that the thermochromism of nanoparticles is also attributable to the conformational change induced by the temperature change, while the transition temperature is different from the bulk film and dependent on its size. A conventional method for controlling the transition temperature of polythiophene derivatives is to modify their chemical structure, for ex-

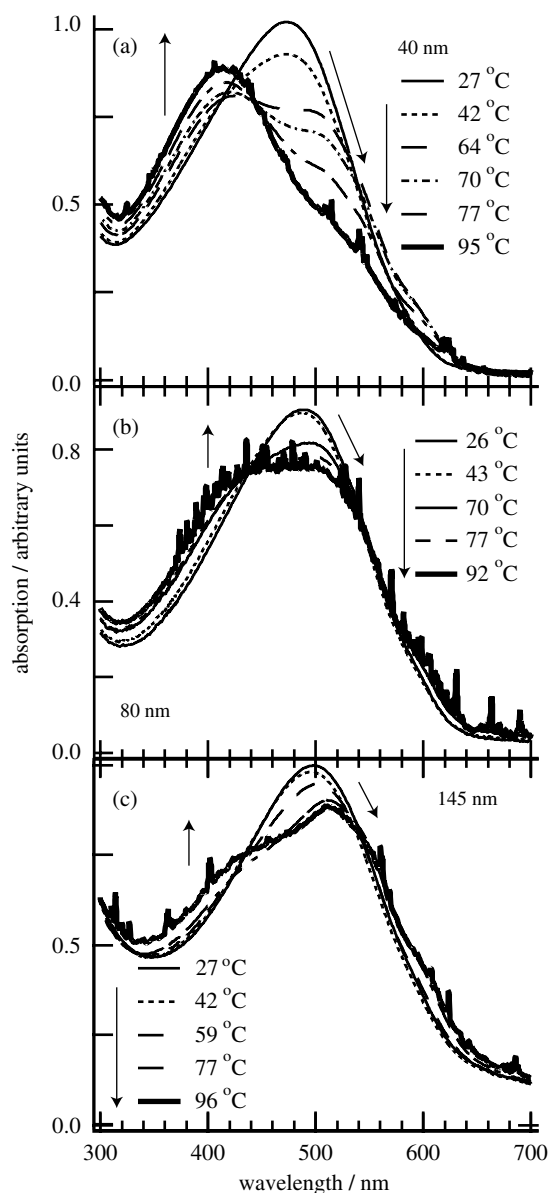


Figure 6. Temperature-dependent absorption spectra of P3DDUT nanoparticles dispersed in water with various mean diameters: (a) 40 nm, (b) 80 nm, and (c) 145 nm.

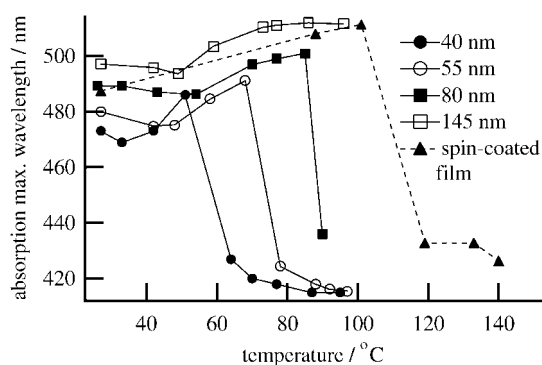


Figure 7. Temperature dependence of the absorption maximum wavelength of P3DDUT nanoparticles dispersed in water, and a spin-coated film.

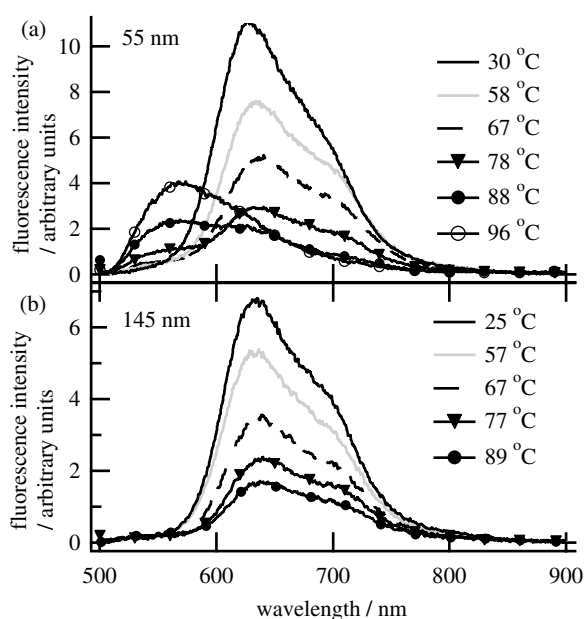


Figure 8. Temperature dependence of fluorescence spectra of P3DDUT nanoparticles dispersed in water: (a) 55 nm and (b) 145 nm. The excitation wavelength was 480 nm.

ample, by changing regioregularity or a substituent in the side chains, which affects polymer stiffness and intermolecular interactions.^[13,33] It is noteworthy that, for P3DDUT nanoparticles, the transition temperature, as well as the absorption and fluorescence spectra, can be controlled without any modification to the chemical structure.

In conclusion, we have succeeded in preparing P3DDUT nanoparticles ranging from 40 to 400 nm by a simple reprecipitation method, and have investigated their spectroscopic properties and thermochromic behavior. It was found that the absorption, fluorescence, and the thermochromic transition temperature are clearly size-dependent. The results of this study prove the usefulness of conjugated polymer nanoparticles, and their characteristic properties, which are based on the molecular conformation, will receive further attention.

Experimental Section

The synthesis of P3DDUT has been described elsewhere.^[10] A THF (Nacalai Tesque, Spectro-Grade, used without further purification) solution of P3DDUT (250 μ L) was injected into vigorously stirred distilled water (10 mL) by using a microsyringe. Polymers began to form nanoparticles immediately, and a water suspension of P3DDUT nanoparticles was obtained. The diameter of the nanoparticles was controlled by controlling the water temperature and the concentration of injected P3DDUT/THF solution.

To evaluate the size and shape of the nanoparticles, the suspension was dropped on a glass substrate and was observed by a scanning electron microscope (SEM: FEI, DB235). The size distribution was evaluated by a dynamic light scattering system (Otsuka electronics, DLS-7000). Absorption and fluorescence spectra were measured by a UV/Vis spectrometer (Shimadzu, UV-3100PC) and spectrofluorometer (Hitachi, F4500), respectively, using a quartz cell with a 1-cm optical path length. For the measurements of the

temperature dependent absorption and fluorescence spectra, a ceramic heater was attached to the outside of the quartz cell and a thermocouple was inserted into the suspension.

Bulk films were prepared from a P3DDUT/THF solution by both spin-coating and by casting onto glass coverslips. The spin-coated films were prepared from solution (1 wt.-%) at 1500 rpm. The cast films were prepared from solution (0.2 wt.-%) in a saturated solvent atmosphere. All glass coverslips were washed with detergent solution before the film preparation.

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