

Poly(*N*-isopropylacrylamide)-Tethered Silicate Platelets for Colloidal Dispersion of Conjugated Polymers with Thermoresponse and Photoluminescence Properties

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Poly(*N*-isopropylacrylamide)-tethered nanosilicate platelets (NSP-PNiPAAm) have been synthesized by covalently bonding the polymer onto the surfaces of silicate platelets of nanometer dimension, and this class of nanohybrids has proved to be effective for dispersing water-insoluble conjugated polymers (CPs). Simple pulverization of poly[2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) with NSP-PNiPAAm rendered the powder material dispersible in water, whereupon it displayed thermoresponse properties at 37.5 °C and CP particle size variation between ca. 50 and 100 nm by SEM observation. The same dispersion had a maximum UV-vis absorption at 524 nm and PL emission at 605 nm. The PL emission was significantly higher at 4 °C than at 45 °C. Being coated as a film, it showed an orange emission under an ultraviolet lamp, consistent with the PL measurement. The water-borne process of dispersing the CP in aqueous media by the presence of NSP-PNiPAAm and followed by film formation to demonstrate a unique method of manipulating hydrophobic conjugated polymers in a facile manner.

1. Introduction

In the past decade, poly(*N*-isopropylacrylamide) (PNiPAAm) has attracted a great deal of attention as a thermoresponse polymer. It exhibits a lower critical solution temperature (LCST) and undergoes a coil-to-globule phase transition that is induced by expulsion of water from the polymer chain.¹ Stimulus-responsive polymers have been widely reported as hybrid forms attached to nanomaterials such as wafers,² SiO₂,^{3–5} Au,^{6,7} carbon nanotubes (CNTs),⁸ Fe₃O₄,⁹ and layered silicates.¹⁰ Potential applications of such smart behavior include sensors,¹¹ probes,¹² drug delivery,¹³ and biomaterial separation.¹⁴

Two-dimensional layered silicates have a platelike geometric shape of nanometer thickness and a high aspect ratio. The layered silicates are generally hydrophilic in nature and require organic

modification using ion-exchange agents such as alkylammonium derivatives^{15,16} or phosphonium salts.¹⁷ In our previous studies,¹⁸ oligomeric amines consisting of hydrophobic poly(oxypropylene) segments and multiple amine functionalities were used to exfoliate hydrophilic clays. The original layered clay structure was randomized into individual nanosilicate platelets (NSP). NSP have average dimensions of 80 nm × 80 nm × 1 nm and a charge distribution of 2 × 10⁴ ionic charges per platelet.¹⁹ More recently, we used a living polymerization technique to graft moieties to the NSP surface through covalent bonding to produce PNiPAAm brushes, which exhibited self-assembly and thermoresponse behavior to stimuli at 32–33 °C.²⁰

Conjugated polymers (CPs) with various chemical structures, such as poly(*p*-phenylene)s,^{21–23} poly(*p*-phenylenevinylene)s,²⁴ poly(*p*-phenyleneethynylene)s,²⁵ poly(triacetylene)s,²⁶ polyacetylenes,²⁷ polythiophenes,²⁸ polyanilines,²⁹ polycarbazoles,³⁰ and polyfluorenes,^{31,32} are well documented for their properties and

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applications based on electronic conductivity and in light-emitting devices.^{33,34} Among the diverse applications, the inherent physical properties of the insoluble CPs may limit their further exploitation. Structural modification by attaching sulfonic, carboxylic, or phosphoric acid groups or alkoxy or flexible alkyl chains to the main polymer backbone is the common approach for synthesizing soluble CPs.^{35–37} Recently, we reported a novel mechanism of geometric shape exclusion for the dispersion of nanomaterials such as carbon black (CB),³⁸ CNTs,³⁹ and CPs.⁴⁰ Fine dispersion of CB particles with an average diameter of 40–60 nm was achieved by using platelike clays as a dispersant. The dispersion behavior of the CNTs was significantly improved by simply grinding them with platelike clays before adding solvents, resulting in systems that resembled micelle-like microstructures. The clays were also shown to assist the aqueous dispersion of water-insoluble poly(phenylenevinylene) derivatives, and CP–clay films were demonstrated to produce an orange light emission under ultraviolet exposure.

In the literature, there have only been a few reports about both the thermoresponsive properties and photoluminescence (PL) sensitivities of macromolecules,^{41,42} conjugated polymers,^{43,44} and polypeptides.⁴⁵ Furthermore, the hydrophobic conjugated polymers are generally modified by covalent bonding with organic moieties rather than a dispersing method. Herein, we report the first study on the thermoresponsive and PL-sensitive functions of poly[2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) by using a physical–geometric approach or non-covalent bonding force. Both NSP-PNiPAAm and MEH-PPV have been physically pulverized to form an NSP-PNiPAAm/MEH-PPV mixture, and the mixed powder showed aqueous dispersion with thermoresponsive PL sensitivity. The mixture has been characterized by ultraviolet–visible (UV–vis) and PL spectrophotometer to demonstrate the aqueous dispersion property, thermoresponsive behavior, and PL responsiveness.

2. Experimental Section

2.1. Materials. The conjugated polymer (CP) poly[2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV), a weight-average molecular weight (M_w) of 51 000, was purchased from Aldrich Chemical Co. The MEH-PPV is insoluble in water and has a rigid chemical structure. Copper(I) chloride (CuCl, 95%, Acros) was successively washed with glacial acetic acid (Fisher Scientific) and ethanol and then dried under vacuum. 2-Hydroxyethyl acrylate (HEA; 97%, Acros) was distilled before use. 2-Bromo-2-methylpropionyl bromide (98%, Acros), 3-aminopropyltriethoxysilane (APTES, TCI) and *N,N,N',N'',N'''*-penta-methyldiethylenetriamine (PMDETA, 99%, TCI) were used as received. *N*-Isopropylacrylamide (NiPAAm, 99%, Acros) was purified by recrystallization from *n*-hexane and dried under

vacuum. Sodium montmorillonite (Na⁺-MMT), a sodium form of smectite aluminosilicate, was obtained from Nanocor Co. These naturally occurring clays have a 2:1 layered silicate/aluminum oxide structure in which two tetrahedral sheets sandwich an edge-shared octahedral sheet. The commercially available clay has exchangeable Na⁺ counterions with a cationic exchange capacity of 120 mequiv/100 g and an average of 8–10 sheets in a primary stack. The size of individual platelets in the polydisperse MMT primary stack is estimated to be 80–100 nm in width and 1 nm in thickness.^{46,47} NSP were obtained by delaminating the layered Na⁺-MMT using an exfoliation process developed by our research group,⁴⁸ and NSP-PNiPAAm was prepared according to the reported procedures.²⁰ A linker with bromide and triethoxysilane functionalities was grafted onto the NSP clay surfaces at a weight ratio of 1/5 (linker/NSP). Subsequent atom-transfer radical polymerization (ATRP) afforded NSP-PNiPAAm brushes.²⁰ The product of hybrids of PNiPAAm tethered to NSP had an organic/inorganic fraction of 67/33, a degree of polymerization of 1370, and a narrow molecular weight distribution (1.21 polydispersity or M_w/M_n). Moreover, the NSP-PNiPAAm showed thermoresponsive LCST behavior at 32–33 °C and controllable formation of nanodomain 3D networks of high regularity.

2.2. Preparation of NSP-PNiPAAm/MEH-PPV in Aqueous Dispersion and as a Film. The NSP-PNiPAAm/MEH-PPV hybrid was prepared as follows. Mixtures of NSP-PNiPAAm (1 mg) and MEH-PPV (1 mg) were thoroughly ground in an agate mortar and pestle. The sides of the mortar were occasionally scraped down with the pestle during grinding to ensure thorough mixing. The powder mixture was washed from the mortar and pestle using deionized water so as to obtain a solid content of 1 mg MEH-PPV in 5 g of water. During the dispersion, the vessel was immersed in an ice bath (ca. 4 °C), and the contents were stirred by means of a magnetic bar. The NSP-PNiPAAm/MEH-PPV hybrids were prepared at NSP-PNiPAAm/MEH-PPV weight ratio of 1/0, 0/1, 1/1, 2/1, 3/1, and 4/1. NSP-PNiPAAm/MEH-PPV films were prepared by dropping 0.1 wt % NSP-PNiPAAm/MEH-PPV solution onto 5 × 5 mm glass substrates and drying at 80 °C.

2.3. Characterization. Aqueous dispersions of the NSP-PNiPAAm/MEH-PPV hybrid were analyzed by ultraviolet–visible spectrophotometer (Perkin-Elmer Lambda 20 UV–vis spectrophotometer). The UV–vis absorbance of hybrid solutions was examined at 4 and 45 °C. The UV–vis transmittance of hybrid solution was monitored at 524 nm. During the measurement of UV–vis transmittance, hybrid solution was controlled in a temperature gradient that ramped from 25 to 50 °C. Both solutions and films of the NSP-PNiPAAm/MEH-PPV hybrid were analyzed by a photoluminescence spectrophotometer (LS45/55 spectrophotometer). Because of the inherent optical property of MEH-PPV, the PL emission spectrum was examined at excitation wavelength of 524 nm. The light-emitting phenomenon was observed under illumination with a hand-held ultraviolet (UV) lamp, UVGL-85 (365 nm, 6 W, 115 V, 60 Hz, 0.12 A). The LCST of NSP-PNiPAAm/MEH-PPV was observed by field emission scanning electronic microscopy (FE-SEM, Zeiss EM 902A) at 80 kV.

3. Results and Discussion

Conjugated polymers are generally water-insoluble and require substantial side-chain chemical modification to improve their solubility for processing. Recently, we reported a physical–geometric approach to control the degree of aggregation of nanomaterials such as CB, CNTs, and CPs through geometric-shaped

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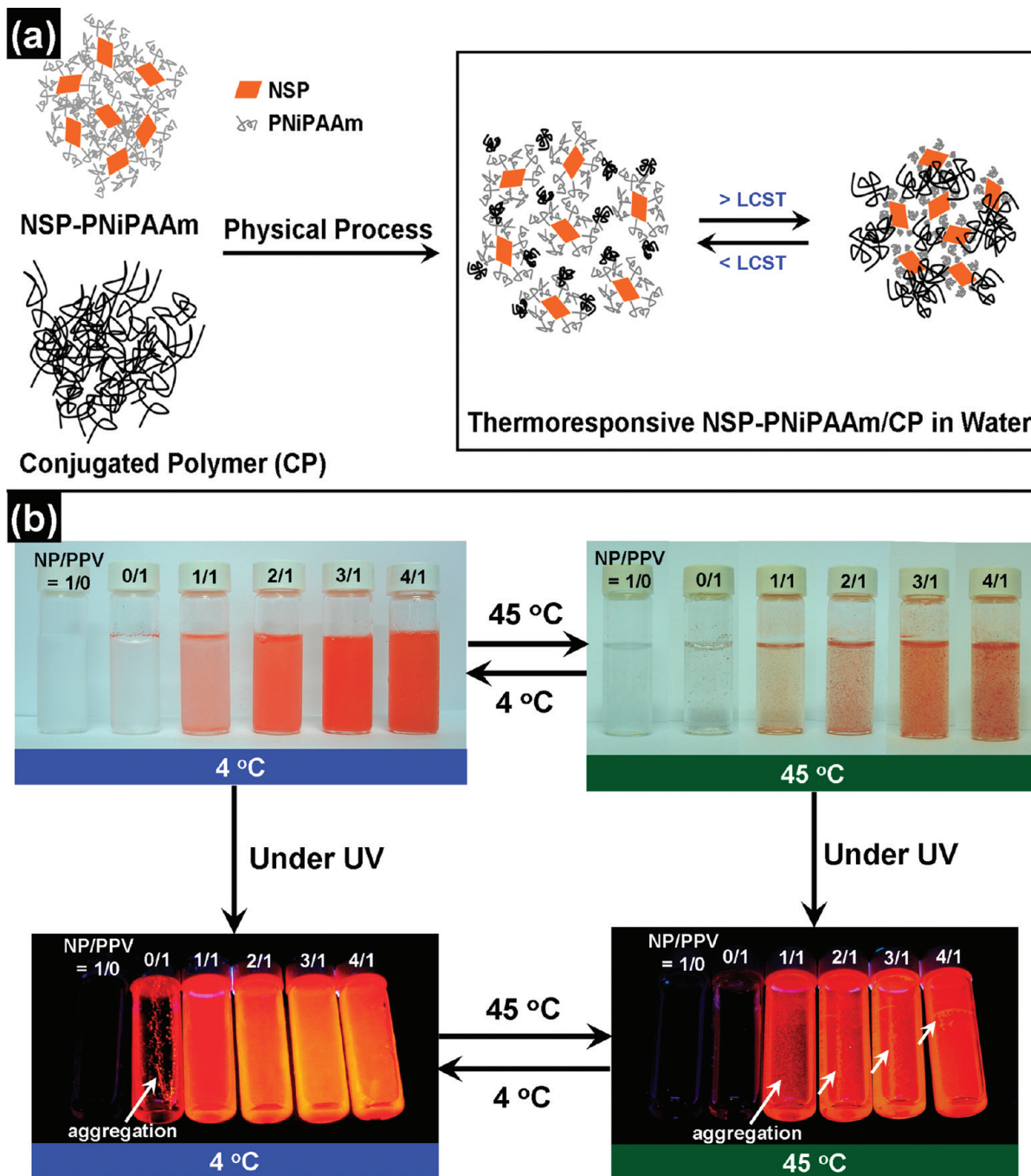


Figure 1. (a) Conceptual illustration of thermoresponsive NSP-PNiPAAm/MEH-PPV in water. (b) Thermoresponsive dispersion of NSP-PNiPAAm/MEH-PPV in water (1 mg of MEH-PPV in 5 g of water) at weight ratio of NSP-PNiPAAm/MEH-PPV = 1/0, 0/1, 1/1, 2/1, 3/1, and 4/1 weight ratios under temperature cycle and UV exposure.

exclusion.^{38–40} When pulverized together in a physical mixture, the two materials altered their inherent aggregating behaviors and mutually affected their solvation capacities. The mixture of NSP-PNiPAAm and MEH-PPV showed a greatly improved solvation in water, whereas pristine MEH-PPV is nondispersible. The fine dispersion of CP by the presence of NSP-PNiPAAm and demonstrated a thermoresponsive optical properties are conceptually described in Figure 1. The visual images in Figure 1b reveal that the NSP-PNiPAAm/MEH-PPV mixture at 3/1 and 4/1 weight ratios were dispersible as opposed to the aggregation of MEH-PPV without NSP-PNiPAAm. The difference in dispersion can be witnessed by the naked eyes, with a red solution being obtained in the former cases and an apparent solid aggregate in the latter. The

same mixture also shows thermoresponsive behavior which stems from the attachment of PNiPAAm to the NSP surface. Under thermal cycling between 4 and 45 °C, the aqueous dispersion of NSP-PNiPAAm/MEH-PPV showed reversible thermoresponsive aggregation due to the expulsion of water from the PNiPAAm hydrogen-bonding interaction.

Considering both the aqueous dispersion and thermoresponsive property, the NSP-PNiPAAm/MEH-PPV dispersions were examined by UV–vis spectrometry. As shown in Figure 2a, the MEH-PPV dispersion at 4 °C is greatly affected by the amounts of NSP-PNiPAAm added. The absorbance at 524 nm becomes more intense on increasing the amounts of NSP-PNiPAAm, implying improvement of the MEH-PPV dispersion. A control experiment

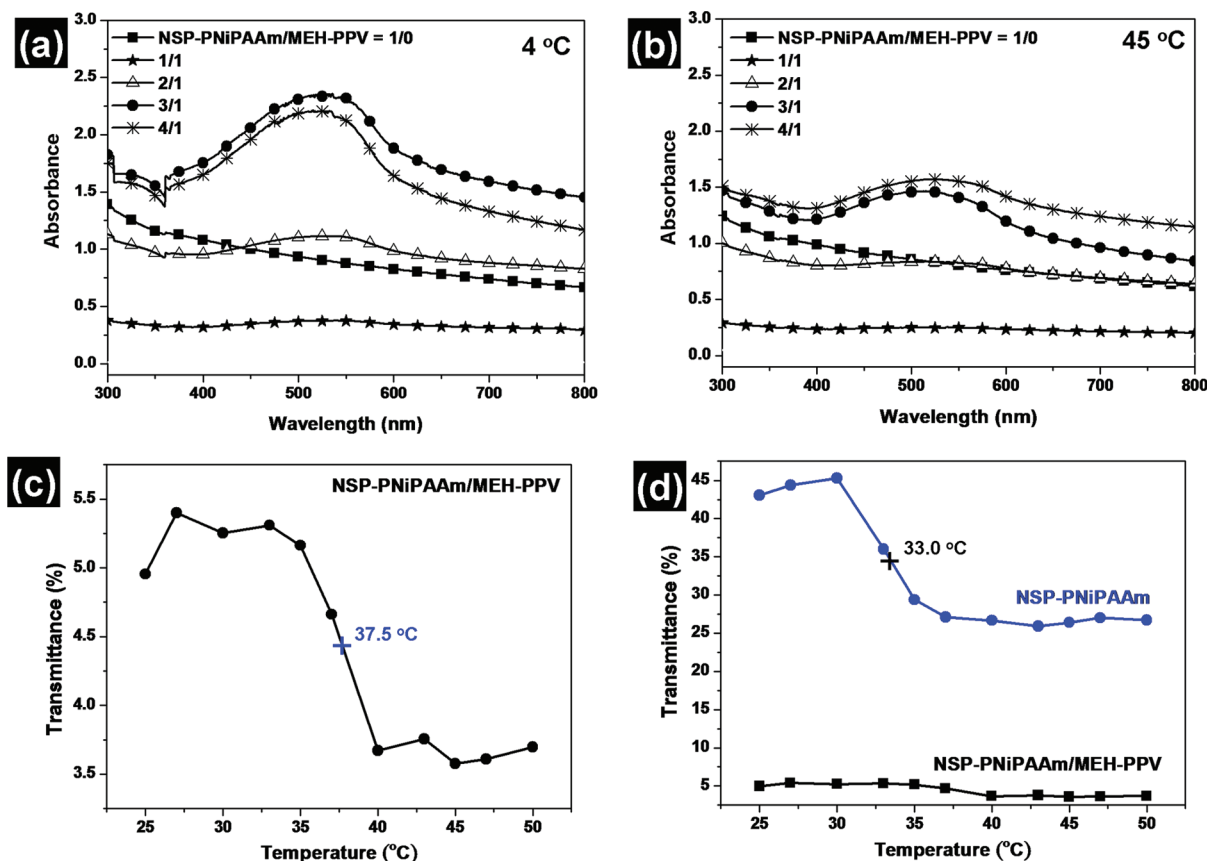


Figure 2. NSP-PNiPAAm/MEH-PPV dispersed in water at different weight ratio for UV-vis absorbance (a, b) and transmittance (c, d).

(NSP-PNiPAAm/MEH-PPV = 1/0) indicated that the UV-vis absorbance stemmed fully from MEH-PPV in the water. For comparison, the same set of MEH-PPV dispersion at 45 °C exhibited a similar trend but weak absorbance due to aforementioned LCST of NSP-PNiPAAm that aggregates at elevated temperatures (Figure 2b).

According the definition of LCST, the thermoresponsive behavior can be precisely identified by temperature dependence of UV-vis transmittance at 524 nm. The NSP-PNiPAAm/MEH-PPV hybrid at 4/1 weight ratios was dispersed in water and has a solid content of 0.08 wt % NSP-PNiPAAm and 0.02 wt % MEH-PPV. The UV-vis transmittance of hybrid solution was monitored from 25 to 50 °C. As shown in Figure 2c, the hybrid has a higher UV-vis transmittance at 25 to 30 °C, indicating the solution has a better dispersion in water than that after the transition temperature of 37.5 °C or LCST. At the elevated temperature, the solution transparency suddenly reduced due to the drop of particle aggregation through the expulsion of water from the PNiPAAm chains in the hybrids. Compared to the NSP-PNiPAAm (Figure 2d), the LCST of NSP-PNiPAAm/MEH-PPV (37.5 °C) is similar to that of NSP-PNiPAAm (33.0 °C). The LCST phenomenon of the dispersion can also be characterized by FE-SEM. Below the LCST (37.5 °C), the NSP-PNiPAAm/MEH-PPV dispersed very well in the water (Figure 3a, inset) and spin-coated into film that exhibited a morphology with ca. 50 nm particle size (Figure 3b). In contrast, the dispersion at the temperature above LCST rendered the film with the observable larger particle size of ca. 100 nm (Figure 3c,d). The temperature difference altered the particle size of MEH-PPV due to the temperature-responded aggregation. For comparison, NSP-PNiPAAm itself revealed a smooth surface at both temperature of 25 °C (Figure 3e) and 80 °C (Figure 3g) in the absence of CPs. Without the association

with MEH-PPV, the NSP-PNiPAAm film morphologies failed to demonstrate the surface differences perhaps due to the NSP predominance in controlling the aggregation.

The NSP-PNiPAAm/MEH-PPV dispersion showed a compounded property of thermoresponsive at the transition temperature of 37.5 °C from NSP-PNiPAAm and the photophysical performance of MEH-PPV. At 4 °C under illumination from a UV lamp, the NSP-PNiPAAm/MEH-PPV dispersions showed good dispersion with orange light emission, and the intensity of the emission was increased in the presence of NSP-PNiPAAm due to the enhanced degree of dispersion (Figure 1b). However, the NSP-PNiPAAm/MEH-PPV displayed aggregation with weak emission above the LCST or at 45 °C. The photophysical property of PNiPAAm/MEH-PPV was further examined by PL spectroscopy. The PL was manifested at an excitation wavelength of 524 nm which corresponded to the inherent MEH-PPV properties. As shown in Figure 4a, the PL intensity of the NSP-PNiPAAm/MEH-PPV dispersion (at 4 °C) increased with the increasing amount of NSP-PNiPAAm, which is nicely consistent with the UV-vis results. When the same dispersion was heated to 45 °C, however, the intensity of PL from the MEH-PPV decreased due to the LCST behavior of the NSP-PNiPAAm (Figure 4b), which stemmed from expulsion of water from the PNiPAAm chains. The overall effect is that MEH-PPV mixed with NSP-PNiPAAm displays the compounded thermoresponsive-photoluminescence sensitivity.

For the practical application, NSP-PNiPAAm/MEH-PPV films were prepared from the corresponding solutions and shown to have UV-vis and PL properties. In a control experiment with NSP-PNiPAAm film (Figure 4c), no UV-vis or PL features were detected. This result was confirmed in that UV exposure and visual observation showed no emission (inset in Figure 4c). On the

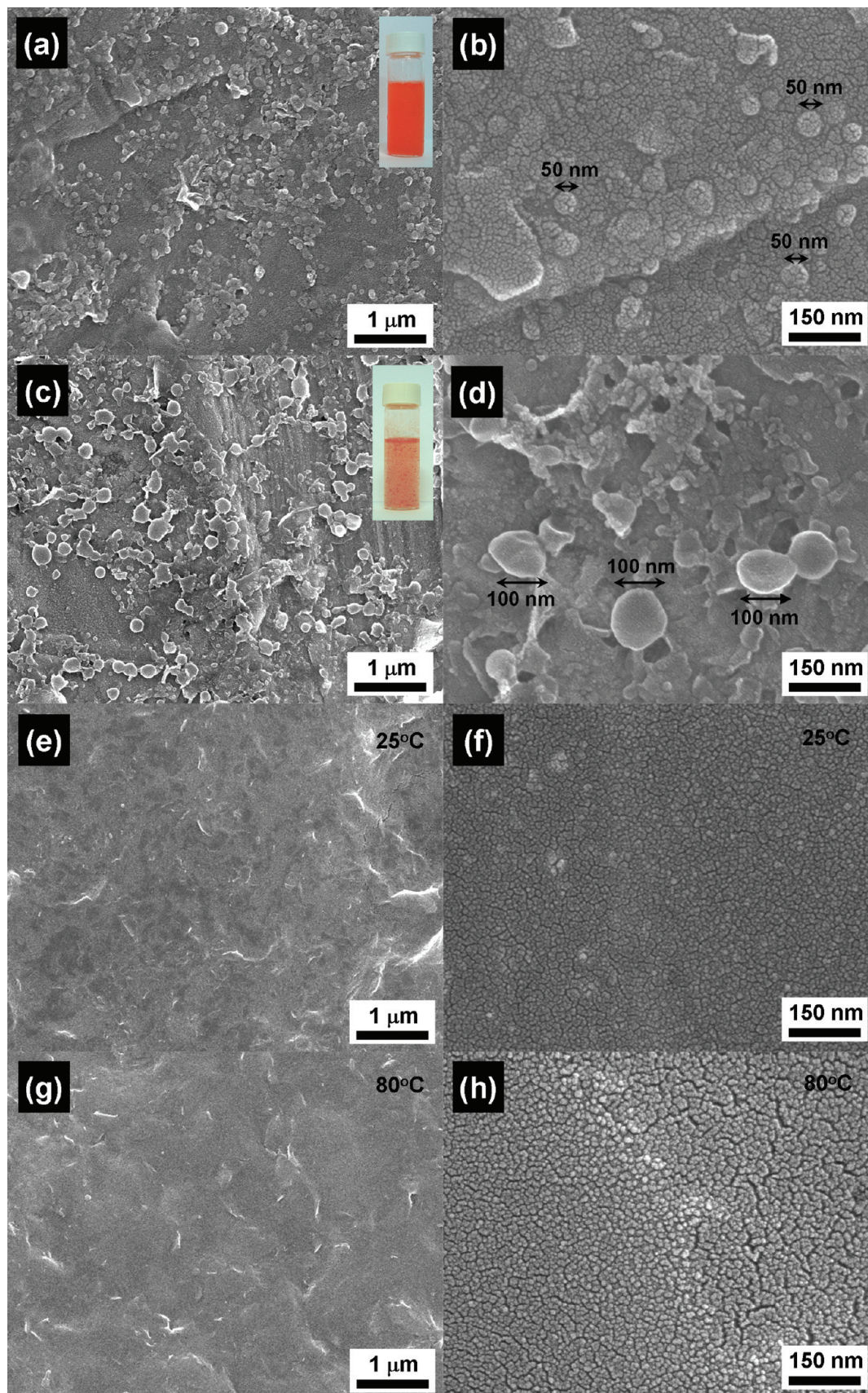


Figure 3. FE-SEM images of NSP-PNiPAAm/MEH-PPV dispersed in water and then dried at 25 °C (a, b) and 80 °C (c, d) and surface of NSP-PNiPAAm coating at 25 °C (e, f) and 80 °C (g, h).

contrary, NSP-PNiPAAm/MEH-PPV film has a maximum absorption at $\lambda_{\text{max abs}} = 485 \text{ nm}$ and a maximum emission at $\lambda_{\text{max em}} =$

605 nm (Figure 4d). Comparing the UV-vis results for the solution and film, the absorbance shows a blue shift from 524 nm

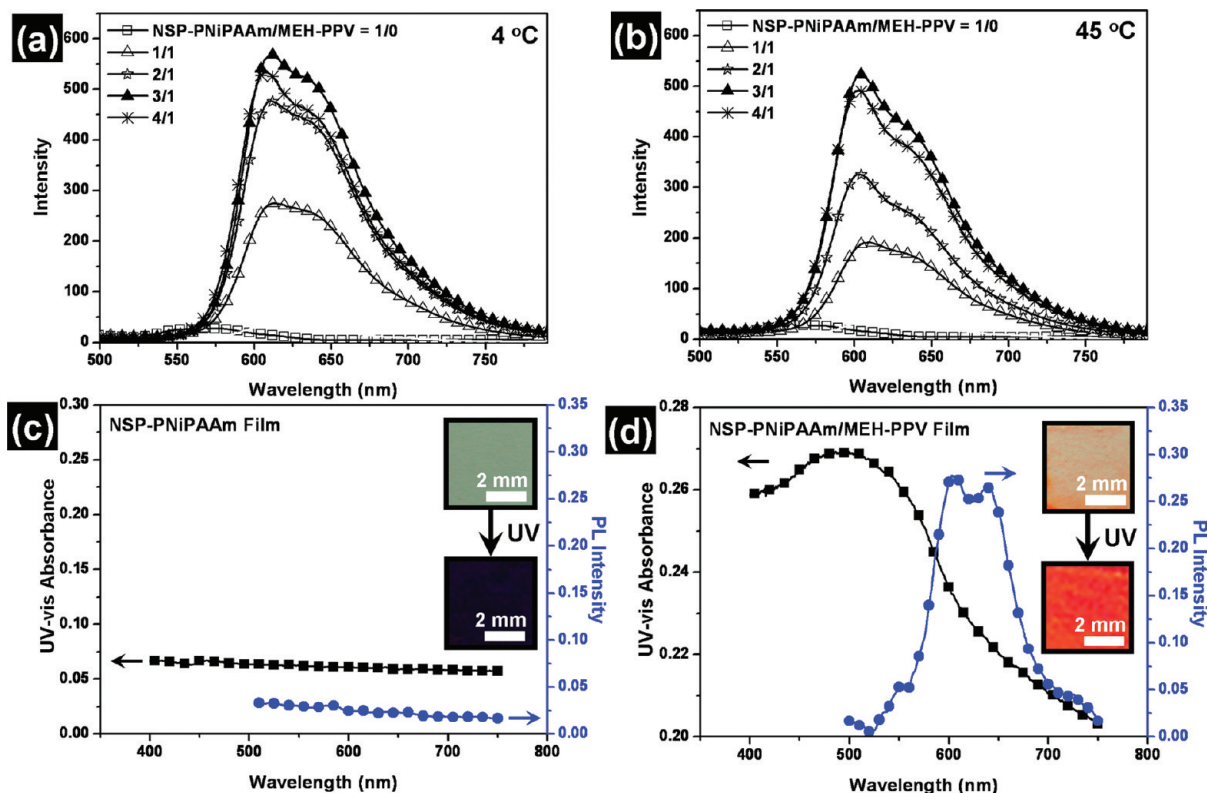


Figure 4. NSP-PNiPAAm/MEH-PPV dispersed in water at different weight ratio for PL emission (a, b) and their corresponding films at weight ratio of NSP-PNiPAAm/MEH-PPV = 3/1 and their optical properties (c, d).

(aqueous dispersion) to 482 nm (solid film) due to the influence of the conjugated length.⁴⁹ The inset in Figure 4d shows that the film exhibited a noticeable orange light emission when illuminated with a UV lamp. This orange emission is exactly correlated to the PL at 605 nm.

The thermoresponsive behavior seen for aqueous dispersion of CP in the presence of the NSP-PNiPAAm may be rationalized in terms of noncovalent bonding forces and the expulsion of water from the PNiPAAm chains. The CP is hydrophobic and only soluble in organic media. In water, the polymers are aggregated or precipitated due to molecular-coil entanglement. The aqueous dispersion, thermoresponsive behavior, and PL sensitivity of the hybrid must therefore stem from the NSP, PNiPAAm, and MEH-PPV. Both visual observation and UV-vis absorbance confirmed the behavior of the NSP-PNiPAAm/MEH-PPV mixtures in aqueous dispersion. As illustrated conceptually in Figure 1a, the initial grinding of two distinctly different materials of nanometer dimensions may have homogenized these materials on the micrometer scale. Upon dispersal in water, the strong noncovalent bonding force between NSP-PNiPAAm and water molecules could further preclude the polymer self-aggregation. The mutual interactions through noncovalent bonding forces, such as ionic charges on the clay surface, van der Waals forces, and π - π stacking for CP entanglement attraction, as well as the platelike geometric shape blockage, could all together influence the aggregation of the pristine CP. Below LCST, the NSP-PNiPAAm showed a good solubility in water because both PNiPAAm chains and NSP are hydrophilic. The well dispersion of NSP-PNiPAAm consequently assisted the dispersion of MEH-PPV in contacting

with NSP. Above LCST, the PNiPAAm chains behave as hydrophobic moieties and aggregate together with MEH-PPV in water. Furthermore, the thermoresponsive behavior is induced by the PNiPAAm through a mechanism involving expulsion of water from the PNiPAAm chains, and the PL performance shows a strong correlation with the LCST behavior. The overall effect is that the CP becomes dispersible and thermoresponsive without the need for tedious chemical modification of the CP molecules. The results also imply the “green” process may be developed and generalized for other hydrophobic polymers.

4. Conclusion

By simply pulverizing MEH-PPV with NSP-PNiPAAm, the resulting powder mixture became dispersible in water and demonstrated both solution thermoresponsive behavior and film photoluminescence. The NSP-PNiPAAm/MEH-PPV mixture displays thermoresponsive dispersion at the critical temperature of 37.5 °C and has photoluminescence at 605 nm. The corresponding films have been prepared and still maintain their UV-vis and PL properties. The compounded properties of thermoresponsive behavior and its correlation with PL sensitivity in aqueous dispersion are the results of fine mixing among the thermoresponsive PNiPAAm chains on NSP and MEH-PPV with light-emitting behavior. The thermoresponsive PL sensitivity of CPs in the presence of NSP-PNiPAAm provides a smart material, prepared by an organic solvent-free process, for biomedical and sensor applications.

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