

Temperature Responsive Poly(N-isopropylacrylamide-*block*-styrene) Block Copolymer Coatings with Tunable Hydrophilicity

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ABSTRACT

Responsive polymers have been explored for both fundamental and applied studies due to their ability to undergo conformational and chemical changes upon receiving an external stimulus. In this work, we report the wetting behavior of thermoresponsive poly(N-isopropylacrylamide-*block*-styrene) diblock copolymer films, below and above the lower critical solution temperature of poly(N-isopropylacrylamide) studied using contact angle measurements. The water contact angle determined for the 2 wt% films at 27°C is found to be 24° and 57° at 40°C. Though the water contact angle showed a systematic increase with increasing temperature, it never crossed to the hydrophobic domain. This infers that the PNIPAM chains lie in the corona of the poly(N-isopropylacrylamide-*block*-styrene) micelles. Here, we show that a temperature tunable surface can be obtained by coating a surface with poly(N-isopropylacrylamide-*block*-styrene) block copolymer; however, the response lies within the limits of hydrophilicity.

1. Introduction

Responsive polymers based on poly(N-isopropylacrylamide) (PNIPAM) exhibits solubility changes in response to external stimuli such as temperature, pH, ionic strength, osmotic pressure, etc.^{1–7}. The response, in particular, the temperature (T), lies in the architecture of the monomer-isopropylacrylamide, which has a hydrophilic amide linkage and a hydrophobic isopropyl group. Below the lower critical solution temperature (LCST), the amide groups on the PNIPAM chains form hydrogen bonds water and favours polymer-solvent (water) interaction. Above the LCST of PNIPAM, the hydrogen bonding between water and the amide groups is broken; this increases the entropy of the system resulting in favorable polymer-polymer interactions. Thus the juxtaposition of the transition in hydrogen bonding ability below and above the LCST of PNIPAM with other polymers in block copolymer systems will allow for developing surfaces that can exhibit controllable switchable wetting characteristics. The advantage of coating surfaces with block copolymers is, the combination of the different properties of the blocks and the formation of new morphologies that depend on conditions like

T , solvent conditions, chemical composition, nature of the surface, etc. Thus, polymers with switchable wettability (manipulating hydrophilicity and hydrophobicity) will have applications in smart coatings, textiles, sensors, etc. The wetting behavior of a surface can be determined by measuring the water contact angle. Four different surfaces can be recognized based on the incongruous behavior of water on a solid surface. If the water contact angle (θ) made with the surface is $\theta = 10 \leq 90$, then the surface is hydrophilic; if $\theta = 90 \geq 150$, then it is a hydrophobic surface and if $\theta = 0 \leq 10$ and $\theta = 150 \geq 180$, the surfaces are termed superhydrophilic and superhydrophobic respectively⁸.

The choice of selecting monomers that can be coupled to PNIPAM and thus forth forming block copolymers with switchable wettability lies in the polymer architecture. Controlled radical polymerization techniques, such as atom transfer radical polymerization (ATRP), nitroxide-mediated polymerization (NMP), and reversible addition-fragmentation chain transfer (RAFT) has enabled the facile synthesis of a variety of responsive block copolymers^{9–14}. RAFT polymerization is interesting as it yields controlled block copolymers with a predefined and narrow range of molecular weights¹⁰ than conventional free radical

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polymerization conditions and is compatible with a wide range of monomers.

In a previous study, we reported the synthesis of low molecular weight poly(N-isopropylacrylamide)-*b*-polystyrene (PNIPAM₆₇-*b*-PS₂₇)¹⁰. Light scattering studies have shown that micelles are formed in 0.005 wt% in aqueous solutions. We also observed a weak-gel and a sol state below and above the LCST, respectively. Below the LCST (31.6°C) of the polymer, the weak gel state arises from the entanglement of micelles with one another, whereas disentanglement of the micelles above the LCST results in viscoelastic liquid behaviour. In this work, we synthesized poly(N-isopropylacrylamide)-*block*-polystyrene (PNIPAM₁₉₆-*b*-PS₉₀) by RAFT polymerization and fabricated a surface by dip coating on glass substrates. By investigating the wetting characteristics of the PNIPAM₁₉₆-*b*-PS₉₀ thick films as a function of temperature, here we show that the films can serve as switchable wetting surfaces within the limits of hydrophilicity.

2. Experimental Section

2.1. Chemicals

N-isopropylacrylamide (NIPAM, 97%), styrene (99%), 2,2'-azobis(2-methylpropionitrile) (AIBN, 98%), 1,4-dioxane (99.8%) and 2-(dodecylthiocarbonothioylthio)-2-methylpropanoic acid (DDMAT) (98%) were purchased from Sigma Aldrich. NIPAM was recrystallized in n-hexane before use. Styrene was purified before use to remove the stabilizer 4-tert-butylcatechol. All glassware was precleaned and dried before use.

2.2. Synthesis of poly (N-isopropylacrylamide-*block*-styrene) (PNIPAM₁₉₆-*b*-PS₉₀)

PNIPAM-*b*-PS was synthesized as described previously¹⁰. In brief, the macro poly(N-isopropylacrylamide)-chain transfer agent (PNIPAM-CTA) was prepared by dissolving a 325:6:1 ratio of NIPAM, DDMAT, and AIBN in 10 mL of 1,4-dioxane. This solution was degassed by three freeze-pump-thaw cycles and reacted at 70°C for 60 hrs under nitrogen atmosphere. After polymerization, the reaction mixture was cooled to room temperature and precipitated from cold ether and purified thrice by thorough washing using cold water/hexane mixture. Next, the PNIPAM-*b*-PS was synthesized using macro PNIPAM-CTA,

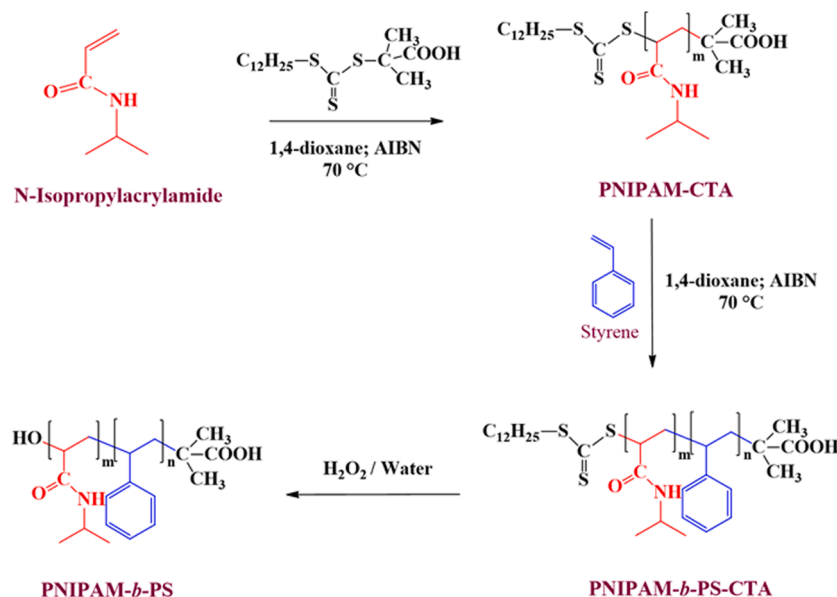
styrene, and AIBN in the ratio 300:7:1, dissolved them in 1, 4-dioxane and polymerized at 70°C for 24 hrs. The trithiocarbonate group (CTA) was removed from the polymer by treating it with hydrogen peroxide for 2 hours and purified thrice by thorough washing using cold water/hexane mixture. The synthesis of the PNIPAM-*b*-PS block copolymer outlined in [scheme 1](#) includes the sequential RAFT synthesis of the PNIPAM-CTA, PNIPAM-*b*-PS-CTA and CTA terminated PNIPAM-*b*-PS block copolymer.

2.3. Film preparations

Clean glass substrates were prepared by soaking them in aqua regia, followed by washing in ultrapure water. Different weight fractions (1, 2, and 5wt/wt%) of the PNIPAM-*b*-PS copolymer were dissolved in water and deposited on the glass substrate by dip-coating. Films were dipped and pulled out with a uniform pulling rate of 10 mm/s, allowing a dry time of two minutes after every dip. After the deposition, the films were dried at 25°C for 12 hours; the dried films were stored under vacuum.

3. Characterization Techniques

The proton nuclear magnetic resonance (¹H NMR) spectra were recorded on a JEOL 400 MHz NMR spectrometer using CDCl₃ as a solvent. The molecular weight of the homopolymer and diblock copolymer and the polydispersity indices were determined from advanced polymer chromatography (APC) (ACQUITY, Waters) using DMF as the eluent at the flow rate 0.5 mLmin⁻¹ and polymethylmethacrylate (PMMA) as the calibration standard. Fourier transform infrared (FTIR) spectra of the polymers were recorded on a Bruker Instrument (USA) using the KBr pellet technique. Thermogravimetric Analysis (TGA) on the PNIPAM-*b*-PS block copolymer was carried out using a TGA/SDTA851e thermogravimetric analyzer (Mettler Toledo, Switzerland). The temperature was varied from 40 to 600°C at a heating rate of 10°C/min. Raman spectroscopy (Renishaw, InVia Reflex confocal Raman Microscope, UK). The spectra were recorded using an excitation wavelength of 512 nm with 1800 mm⁻¹ grating coupled with an optical microscope (Leica, Germany) under ambient conditions. The film thickness was measured using a stylus Profilometer (Dektak XT, Bruker, USA). AFM imaging is carried out with a NTEGRA Prima NT-MDT system (Ireland) at 25°C using the tapping mode. The contact angle variation with temperature was measured by the sessile liquid drop method using a KRÜSS advance



Scheme 1. Sequential RAFT synthesis of PNIPAM-CTA, PNIPAM-*b*-PS-CTA, and CTA terminated PNIPAM-*b*-PS block copolymer.

drop size analyzer (DSA)-100 (Germany) with a temperature-controlled environmental chamber.

4. Results and Discussion

PNIPAM-CTA and PNIPAM-*b*-PS were synthesized by RAFT polymerization technique using DDMAT as the RAFT agent and AIBN as the initiator. Figure 1a shows the ^1H NMR spectrum of PNIPAM-CTA and PNIPAM-*b*-PS recorded under the same instrumental conditions. The chemical shifts of the RAFT terminal of PNIPAM-CTA occur at 0.99-1.30 (*m*, 3H, $-\text{CH}_3$), 1.39-2.25 (*m*, $-\text{CH}(\text{CH}_3)_2$ and $-\text{CH}_2-\text{CH}-$ on the polymer's main chain), 3.1-3.77 ($-\text{CH}_2\text{S}$), 3.96 (*s*, $-\text{NHCH}(\text{CH}_3)_2$); whereas for the PNIPAM-*b*-PS block copolymer in addition to the above chemical shifts, shifts at 0.9-3.5 (*m*, $-\text{CH}(\text{CH}_3)_2$ and $-\text{CH}_2-\text{CH}-$ on the polymer's main chain), 3.97 (*s*, $-\text{NHCH}(\text{CH}_3)_2$), 6.07-7.1 (*m*, C_6H_5 of styrene) were detected. From the FTIR spectrum (Fig. 1b), the formation of PNIPAM-CTA is confirmed by the peaks at 1070-1246 cm^{-1} (stretching vibration of C=S and C-S-C-), the peak at 1640 cm^{-1} shows the secondary amide C=O of the acid group (COOH) and the CH_3 asymmetric stretching vibration bands appear at 2970 cm^{-1} . The peaks at 3292 cm^{-1} correspond to the secondary amide N-H stretching cm^{-1} . The peaks identified at 615-879 cm^{-1} (aromatic C-H bending), 1500-1700 cm^{-1} (aromatic C=C bending), CH_2 asymmetric and symmetric tension at 2875-2976 cm^{-1} , and the peaks at 3076 cm^{-1} (C-H aromatic tension) confirms the formation of PNIPAM-*b*-PS. The molecular weight of the PNIPAM-CTA and PNIPAM-*b*-PS obtained from APC analysis was found to be 22.5 KDa and 31.9 KDa, respectively. The details of the molecular weight and related calculations are shown in table 1, and the APC curves are given in Fig.S1. The theoretical molecular weight, $M_{n(\text{theory})}$, is calculated using equation (1).

$$M_{n(\text{theory})} = \frac{[\text{M}]_0}{[\text{CTA}]_0} \times M_{\text{mono}} \times \text{conversion} + M_{\text{CTA}} \quad (1)$$

where $[\text{M}]_0$ and $[\text{CTA}]_0$ are the initial concentration of the monomer and CTA, M_{mono} , and M_{CTA} are the molecular weight of the monomer and CTA, respectively. The degree of polymerization calculated based on the molecular weights indicates about 196 PNIPAM and 90 PS blocks. The PNIPAM-*b*-PS is thus referred to as PNIPAM₁₉₆-*b*-PS₉₀ in this paper.

The bonding characteristics of PNIPAM-CTA and PNIPAM₁₉₆-*b*-PS₉₀

Table 1

Molecular weight of PNIPAM-CTA and PNIPAM₁₉₆-*b*-PS₉₀

Polymers	$[\text{M}]_0:[\text{CTA}]_0$ [I] ₀	Time (h)	Conv. (%)	M_n^1 (kg mol) M_n theory	M_n APC	De
PNIPAM-CTA	325:6:1	24	92.5	24.3	22.5	1.02
PNIPAM ₁₉₆ - <i>b</i> - PS ₉₀	300:100:1	24	62.0	51.4	31.9	1.05

De (M_w/M_n) determined by APC analysis. (M_w -weight average molecular weight; M_n -number average molecular weight).

were investigated by Raman spectroscopy and is shown in Fig. 2. The strong bands at $\sim 2950 \text{ cm}^{-1}$ and $\sim 2890 \text{ cm}^{-1}$ are assigned to the symmetric and asymmetric CH_2 valence vibrations, respectively. The sharp peak at $\sim 1012 \text{ cm}^{-1}$ is assigned to the aromatic ring and C-H

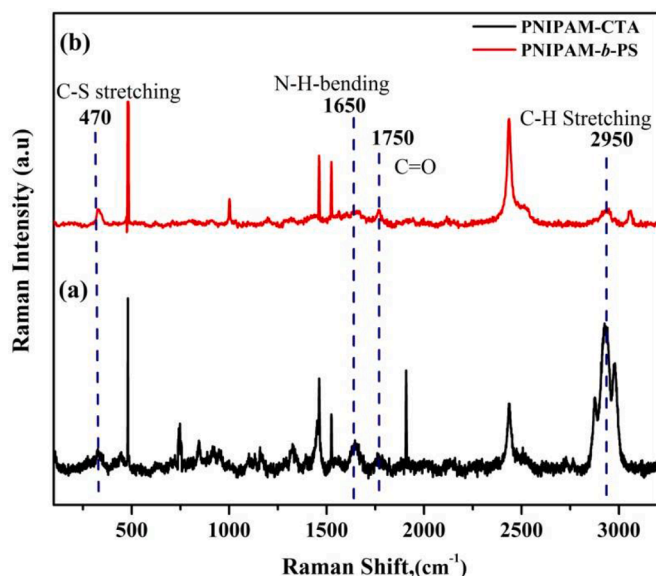


Figure 2. Raman spectra of PNIPAM-CTA and PNIPAM₁₉₆-*b*-PS₉₀ diblock copolymer

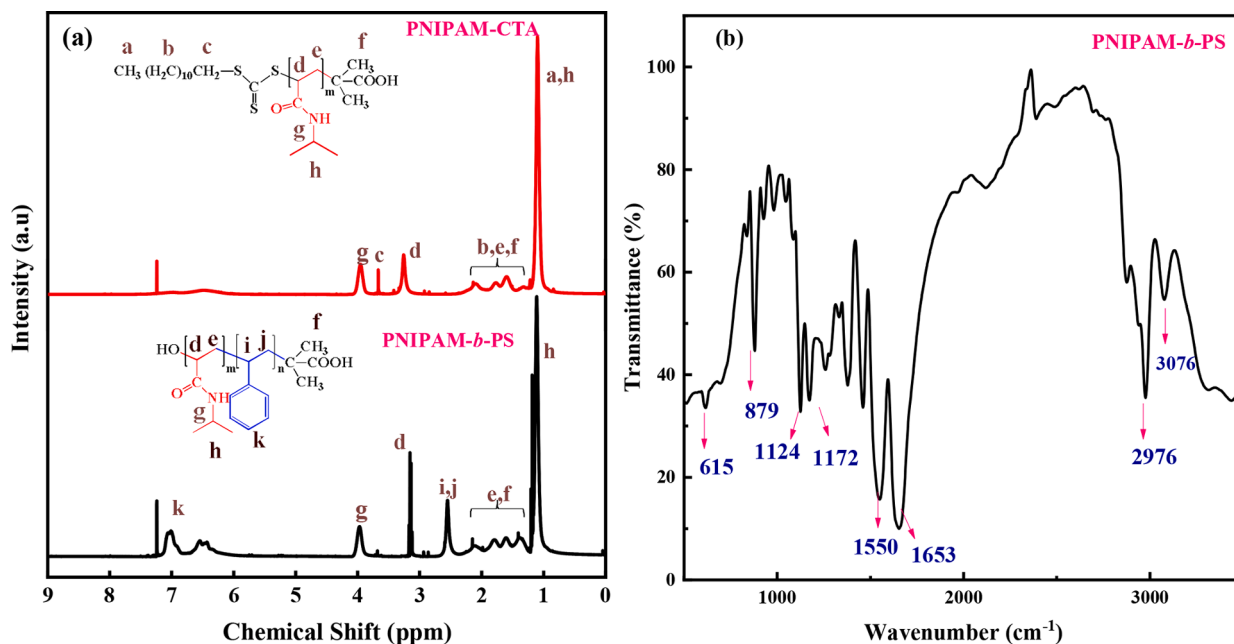


Figure 1. (a) ^1H NMR spectrum of PNIPAM-CTA and PNIPAM₁₉₆-*b*-PS₉₀, (b) FTIR spectrum of the PNIPAM₁₉₆-*b*-PS₉₀ diblock copolymer.

breathing mode. The intense bands at 1447 cm^{-1} (C=C=O), 1650 cm^{-1} (N-H, bending), and 1720 cm^{-1} (C=O, stretching) confirms the presence of the amide group in both the polymers. It is interesting to note here that the N-H stretching vibration band has overlapped with the O-H stretching bands; this is because both the bands fall under the same range of stretching frequencies. The spectrum also evidenced the presence of aromatic polystyrene at 1645 cm^{-1} , which emanates from the C=C (ring) bonding in styrene.

The Raman spectra of PNIPAM-CTA shows additional vibration modes at $\sim 389\text{ cm}^{-1}$ (C-S symmetric), 470 cm^{-1} (C-S stretching) for the dithioester functional group in the polymer. However, we see an absence/weak intensity for the above Raman lines for the PNIPAM₁₉₆-b-PS₉₀ polymer. This indicates that the polymer has no CTA group left after treating it with hydrogen peroxide. The shift in the frequency of the characteristic bands connected with the amide groups can thus help to elucidate the change in their physical structure. Interestingly, a slight frequency shift corresponding to the amide functional group (1650 cm^{-1} N-H-bending, 1720 cm^{-1} C=O) of the PNIPAM₁₉₆-b-PS₉₀ towards lower wave number suggested that the molecule can be influenced by the water molecules (H-O-H) on the surface. It is reported that amide vibrational modes may strongly influence the intermolecular interactions between the amide bond and surface H/O bonding of water. It is suggested that the hydrogen bonds also selectively affect the conformational changes of the amide group as the relative intensities of PNIPAM₁₉₆-b-PS₉₀ polymer dominated over PNIPAM-CTA. The observation has a good agreement with Dybal *et al.*¹⁵; they suggested that hydrogen bonding affects the more extended CO-H-N bond, which shifts the stretching frequency to the lower region. As the Raman experiments were carried out under an ambient atmosphere ($\sim 21^\circ\text{C}$, 48% humidity), the water molecules present as moisture can interact with the active amide functional group in the PNIPAM film. It is reported that nearly 65% of the amide groups can maintain hydrogen bonding with atmospheric water¹⁶. Therefore, the relative Raman intensities of the PNIPAM-b-PS dominated over PNIPAM-CTA due to the weak intermolecular interactions between the amide groups and water molecules in the dip-coated film.

The thermal stability of the block copolymer was evaluated by TG and DTG studies. The TG and DTG curves obtained by the thermal degradation of the PNIPAM₁₉₆-b-PS₉₀ polymer are shown in Figure 3. The decomposition curve of the PNIPAM₁₉₆-b-PS₉₀ exhibits a multistep decomposition mechanism. The first step occurs with a mass loss of approximately 11% in the temperature range of 25 to 200°C . The second and third steps were observed in the temperature range between 325°C to 525°C , with a mass loss of 84%. Charlene *et al.*¹⁷ reported that the PNIPAM decomposed in a single step in the range of 325°C to 450°C .

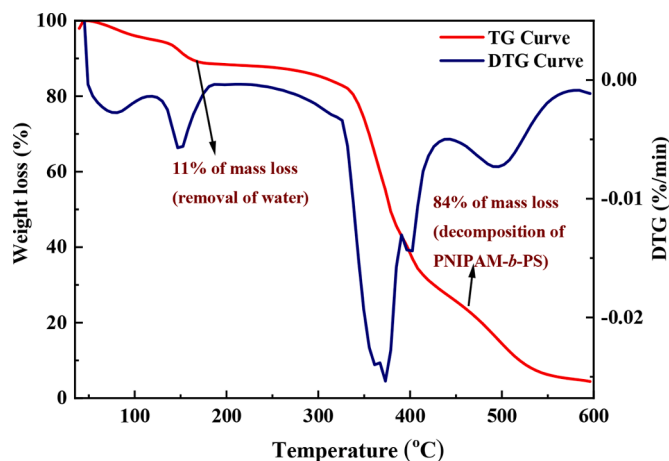


Figure 3. TG-DTG curves obtained by the thermal degradation of PNIPAM₁₉₆-b-PS₉₀ block copolymer.

$^\circ\text{C}$. In our study, the decomposition follows multistep, and this confirms the presence of styrene molecule in the main chain of the polymer.

Next, we prepared polymer films by dip-coating on precleaned glass substrates; the concentration of the polymer used for dip-coating is 1, 2, and 5 wt/wt%, respectively. The average thickness of the films was measured using a stylus profilometer. Here, the thickness of the film is taken as the difference in height between the uncoated surface and the coated surface. The thickness variation of the PNIPAM₁₉₆-b-PS₉₀ block copolymer film with dipping is shown in Figure 4. Visual as well as surface profiling inspection of the film showed that the 1 wt/wt% polymer had an uneven distribution of the polymer, and the 2 wt/wt% sample had an even thickness throughout the scanned regions of the sample. The 5 wt/wt% films had an uneven distribution of film thickness, and this we assume could be due to the non-uniform drying of the sample as the viscosity of the sample was high compared to the 2 wt/wt% sample.

The surface morphology of the 1, 2, and 5wt% block copolymer film surface was investigated by AFM and is shown in Figure 5. Though we did not observe any phase segregation, the 1 and 5 wt% films had a non-uniform surface (Fig. 5a, c) with a surface roughness $0.30\text{ nm} \pm 0.25\text{ nm}$ and $1.63\text{ nm} \pm 0.51\text{ nm}$ respectively. The image (Fig. 5b) of the 2 wt% films with 10 dips shows a uniformly coated homogeneous surface with a good coating coverage and with no evidence of phase segregation of the PNIPAM and PS blocks. The surface roughness of the 2 wt% films is found to be $0.41\text{ nm} \pm 0.02\text{ nm}$. After ensuring the homogeneity, the thermoresponsive PNIPAM₁₉₆-b-PS₉₀ surface coating is assessed by the water contact angle (CA) measurement using the sessile drop method (Fig 6). Multi-layered dip-coating will increase the uniformity and thickness of deposited films. The investigated films were obtained by 10 dips and are used for the contact angle studies. If the thickness of the films is less, we observed that the water droplet quickly penetrates the film, and even after attaining equilibrium swelling, the water contact angle measured was not a reliable value. In the case of films with 7–8 μm thickness, the films retained the water droplet, and the measured contact angle was almost the same, even in different regions of the film.

Equilibrium condition is achieved by immersing the films in water for 2 hours. The contact angle measurements were performed by placing 100 μL of water on the films and the films were monitored for their swelling. Ten independent measurements were made by placing the water droplet on the film surface, and the average contact angle values are provided. The contact angles for the 1, 2, and 5wt% measured at various temperatures are given below (Fig 6). The contact angle measured for the 2 and 5wt% samples were similar; however, the 1wt% had a significant error of $\pm 8^\circ$. This we assume could be because of the

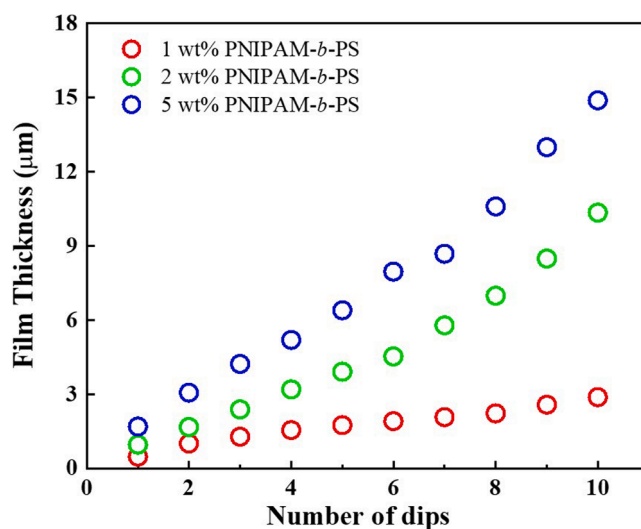


Figure 4. Film thickness change with the number of dipping for the PNIPAM₁₉₆-b-PS₉₀ at different polymer concentrations.

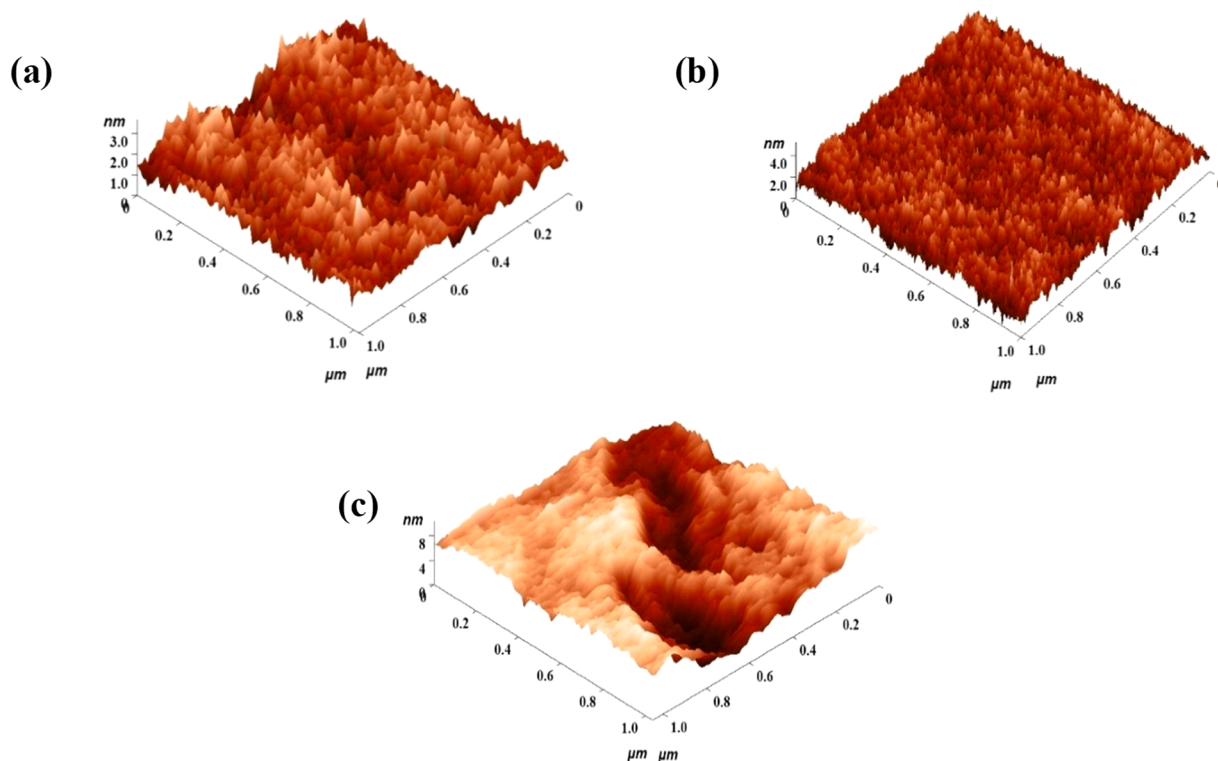


Figure 5. 3D AFM images of the PNIPAM₁₉₆-*b*-PS₉₀ block copolymer films recorded in tapping mode at 25 °C for the 1, 2, and 5wt% films which were dipped 10 times.

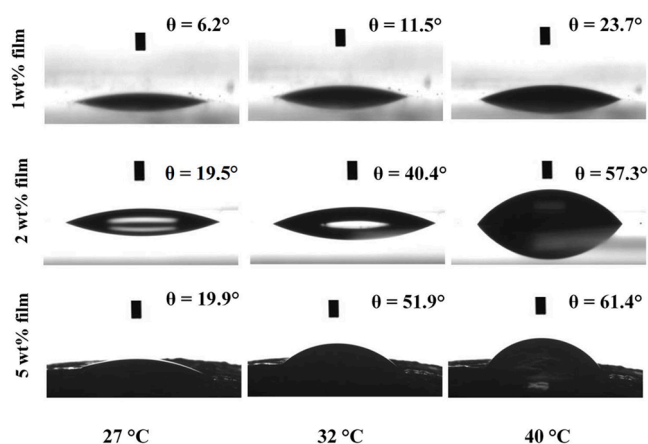


Figure 6. Equilibrium water contact angle of the 1, 2, and 5wt% PNIPAM₁₉₆-*b*-PS₉₀ films as a function of temperature.

uneven film thickness, where the water dropped on the surface could easily move through the pores of the film. The 2 and 5 wt/wt% films had an average thickness of 10 and 14 μm , and it was observed that at this film thickness, the contact angle measured is free of any influence from the substrate. Below LCST, the water contact angle is found to be 19.5° at 27 °C; whereas above the LCST, the CA increased to about 57° at 40 °C. Unlike the sudden and sharp transition observed across the LCST, we instead observed only a gradual increase in the water CA from 27 to 40 °C. For the 5wt% films, the CA was $\sim 20^\circ$ at 27 °C; whereas above the LCST, the CA increased to about 61° at 40 °C.

In temperature, and pH-sensitive poly(*N*-isopropylacrylamide)-*block*-poly(4-vinylpyridine) (PNIPAM-*b*-P4VP) block copolymer, micelles with PNIPAM corona and a P4VP core was formed when the temperature was lower than the LCST and pH was above 4.7¹⁸. In the

case of poly(*N*-isopropylacrylamide)-*b*-poly(acrylic acid) (PNIPAM-*b*-PAA), at pH < 4.5 and at $T < \text{LCST}$, the PAA chains in the micelles forms the core, and PNIPAM forms the corona. However, at pH > 4.5 and at $T > \text{LCST}$, the PNIPAM chains turn hydrophobic and forms the core, whereas the PAA chains form the corona¹⁹. In a previous study, we reported that poly(*N*-isopropylacrylamide-*b*-styrene) (PNIPAM₆₇-*b*-PS₂₇) diblock copolymer could form micelles beyond a critical concentration¹⁰. The critical micelle concentration was 0.005 wt/wt%, and the hydrodynamic diameter of the micelles was $85.2 \pm 5.66 \text{ nm}$ at 25 °C. In the block copolymer micelles, if the PNIPAM chains lie in the corona, then an inclement possibility of these chains to form hydrogen bonds with the surrounding solvent molecules arises and exhibit swelling changes with change in the solvent temperature.

Here, we present evidence that the PNIPAM chains form the corona in the PNIPAM₁₉₆-*b*-PS₉₀ micelles below and above the LCST. A hydrophobic angle is expected if the polystyrene chains are in the corona. Nevertheless, we observed only a hydrophilic contact angle even above the LCST of the PNIPAM polymer. Though the monomer NIPAM has an isopropyl group, it tends to concentrate near air and other hydrophobic phases; however, the PNIPAM polymer all together presents only hydrophilic domains to water²⁰. In the micelles below the LCST, the PNIPAM chains can associate with the water molecules forming hydrogen bonds. Though increasing the temperature beyond the LCST lowers the chain association of PNIPAM to the water molecules due to compaction; still, the PNIPAM moiety stays hydrophilic, as evidenced by the hydrophilic contact angle of 57° at 40 °C (Fig 6). The PNIPAM₁₉₆-*b*-PS₉₀ coatings thus present a temperature tunable hydrophilic surface.

5. Conclusion

In summary, the PNIPAM₁₉₆-*b*-PS₉₀ block copolymer was synthesized by RAFT polymerization and characterized it for the structure, molecular weight, and wetting nature. We developed a polymer film from PNIPAM₁₉₆-*b*-PS₉₀ block copolymer via dip coating on glass

substrates and studied the film's wetting behaviour as a function of temperature and achieved tunable and controlled wettability. The water contact angles of the block copolymer films measured as a function of temperature from 27°C to 40°C showed only hydrophilic contact angles. The films used in this study offer a stable and peel-free surface even after wetting. Our studies present evidence for the core-corona nature of the micelles formed by the PNIPAM₁₉₆-b-PS₉₀ block copolymer with the PNIPAM chains forming the corona and the PS chains staying in the core.

Credit author statement

SPS and BJ conceived the study and designed the experiments. SPS and SC synthesized the polymer and carried out FTIR and NMR studies. SPS, BJ and TSS carried out the contact angle studies. The manuscript is cowritten by BJ and SPS with inputs from all other co-authors.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at [doi:10.1016/j.surfin.2020.100800](https://doi.org/10.1016/j.surfin.2020.100800).

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