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SYNTHESIS OF P(N-ISOPROPYL ACRYLAMIDE - HYDROXYPROPYL METHACRYLATE) THERMO RESPONSIVE COPOLYMER FILMs BY INITIATED CHEMICAL VAPOR DEPOSITION METHOD

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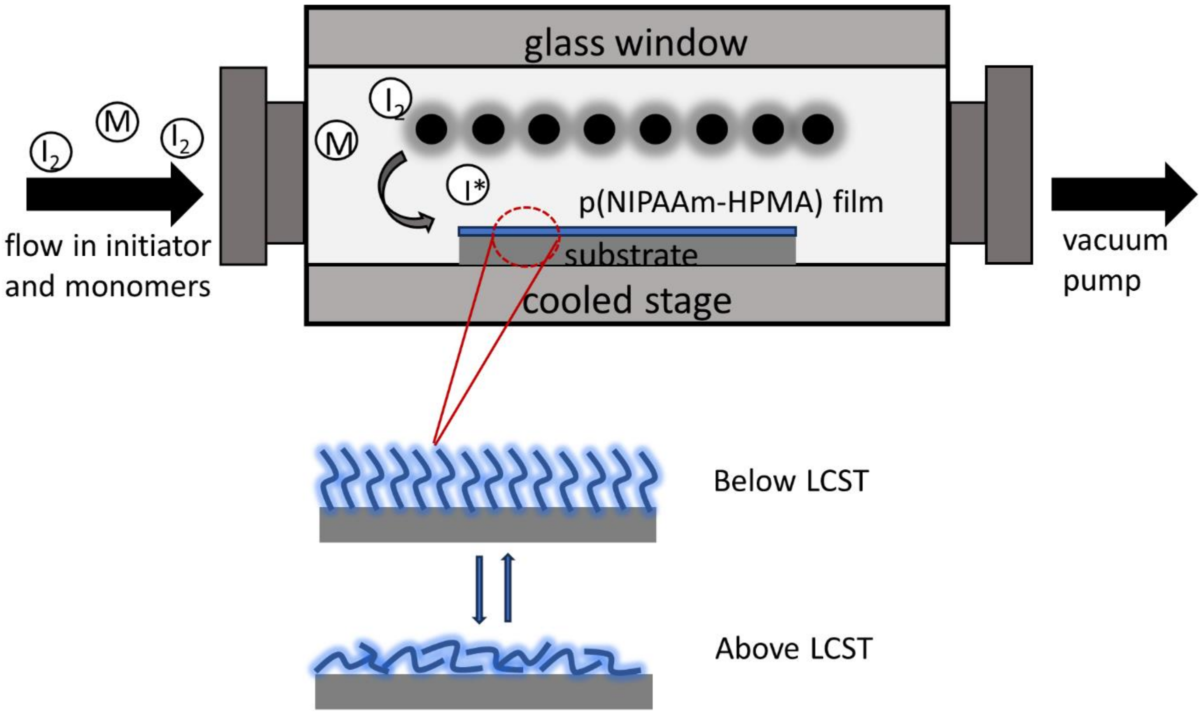
Highlights

- P(NIPAAm-HPMA) thermo-responsive copolymer thin films were synthesised by iCVD method.
- The LCST temperature of the copolymers was determined by temperature-dependent contact angle measurement.
- The LCST range obtained for the copolymers was found to be significantly lower (19-23°) than the value reported in the literature for pNIPAAM (~32°).

Graphical Abstract



Schematic illustration of iCVD p(NIPAAm-HPMA) film synthesis

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ABSTRACT: This study illustrates the deposition of thermo responsive p(N-isopropyl acrylamide-hydroxypropyl methacrylate) p(NIPAAm-HPMA) copolymer thin films by initiated chemical vapor deposition (iCVD) method using tert-butyl peroxide (TBPO) as the initiator. Copolymers were deposited at three different HPMA flow rates and the effects of NIPAAm/HPMA flow rate ratio on the deposition rate, structure and responsive properties of the as-deposited films were investigated. The highest deposition rate of 50 nm/min was observed for the copolymer deposited using lowest NIPAAm/HPMA monomer ratio studied. The deposition rate showed a significant increase with decreasing NIPAAm/HPMA flow ratio. Results of FTIR and XPS spectroscopy analyses revealed a significant preservation of structural retention in iCVD p(NIPAAm-HPMA) thermo-responsive films. Lower critical solution temperatures (LCST) of p(NIPAAm-HPMA) films were determined by carrying out a temperature-dependent contact angle analysis. Accordingly, it was shown that LCST was varied between 19 and 23 ^{o}C, which was observed to be dependent on the NIPAAm/HPMA monomer ratio. That LCST range is considerably below the literature- reported values for pNIPAAM, which makes the as-deposited copolymer suitable for applications that require thermos-responsive properties at lower temperatures.

Keywords: *Thermo-responsive, iCVD, LCST, Polymeric Thin Film, Hydrogel*

1. INTRODUCTION

Polymers that respond to stimuli undergo alterations in their properties based on the external conditions. Physical or chemical stimuli like temperature [1], pH [2], electric or magnetic field [3], light intensity [4], and biological molecules [5] induce macroscopic reactions such as swelling/collapse or transformation from solution to gel in stimuli responsive polymer materials. Temperature is the most studied stimulus for stimuli-responsive polymers. Thermo-responsive polymers are structures that show a volume phase transition at a specific temperature [6]. While various temperature-sensitive polymers exist, including shape memory materials [7] and liquid crystal materials, the most commonly utilized types are polymer solutions that respond to liquid-liquid phase transitions triggered by changes in temperature. In this phase transition, a change from a transparent solution to a turbid solution is often observed, resulting from the difference in refractive index after the transition from a low-concentration polymer solution to a high-concentration polymer solution. The temperature where this phase transition occurs upon heating beyond a specific point is termed as LCST, while the temperature marking the onset of the opposite phase behavior is referred to as upper critical solution temperature (UCST) [8]. Polymers that undergo an LCST phase transition in water dissolve in water at low temperatures, and phase separation occurs as the temperature increases. Polymer chains transition from helix to sphere to aggregate at this point.

Poly(N-isopropylacrylamide) (pNIPAAm) stands out as one of the temperature-stable polymers that has been thoroughly investigated [9-11]. The thermal phase transition behavior of pNIPAAm was first reported in 1968 [12]. When pNIPAAM is immersed in an aqueous solution, it undergoes an abrupt shift

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in volume-phase upon reaching temperatures above the lower critical solution temperature (LCST) of approximately 32°C. Below this temperature, hydrogen bonding predominates and the polymer chains are completely saturated with water and swell; above this temperature, hydrophobic interactions predominate and the polymer chains collapse by expelling water. Nevertheless, altering the lower critical solution temperature (LCST) of a thermosensitive hydrogel is achievable through the incorporation of suitable monomer units [13, 14]. Coating solid supports like silicon substrates with thin films of heat-shrinkable polymers enables expansion and contraction exclusively perpendicular to the substrate [15]. This gives rise to a temperature-responsive hydrogel structure with promising applications in sensors, actuators, and smart surfaces within the fields of biotechnology and medicine. [16-21].

Various techniques, whether solution-based or vapor-based, have been suggested for the synthesis of thin films of pNIPAAm. [22-25]. Methods used to produce polymeric thin films can be categorized into two groups.: solution-based or gas-based methods. Solution-based processes such as ATRP, dip coating, sol-gel, and layer-by-layer coating are among the frequently used techniques because they do not require special equipment and are easy to apply [26, 27]. On the other hand, the use of solvents in these processes may damage fragile substrates and the need for steps such as purification and drying may cause losses in terms of energy and cost [28]. Additionally, the porous or three-dimensional nature of the substrate used may make it difficult to obtain a conformal coating. In vapor-based methods such as CVD, the problems caused by solvent-based methods are minimized by eliminating the use of solvents [29-31]. With vapor-based techniques, materials with complex geometries that are difficult to coat with liquid phase methods or delicate surfaces such as paper and textiles can be coated conformally [32, 33]. Different types of CVD are used to obtain polymeric thin films [34-36]. In the iCVD process, alongside the monomer, an initiator species is introduced into the reactor. This initiator readily dissociates into reactive chemical species with minimal energy input, thanks to the presence of weak peroxide bonds, thereby lowering the heat energy needed to initiate the reaction. [37-39]. Thus, undesirable side reactions are prevented and chemical functionality is preserved. Another advantage of the system is that the coatings are applied at low surface temperatures and all-dry vapor environment.

2-hydroxypropyl methacrylate (HPMA) is a hydrogel with high biocompatibility. While HPMA is highly soluble in water, its polymer is not soluble. Copolymers of biocompatible HPMA hydrogels with various vinyl monomers have been used for medical applications [40]. The objective of this study was to deposit p(NIPAAm-HPMA) copolymer films using with iCVD and to investigate the LCST behavior of copolymers. Di-tertbutyl peroxide (TBPO) was used as the initiator. Kinetic studies were conducted to explore the impact of HPMA flow rate on the deposition rate. Higher deposition rates were observed with increasing HPMA flow rate at copolymers compared to the deposition rate of pNIPAAM. The contact angle measurement was used to determine the LCST temperatures of p(NIPAAm-HPMA) films at different substrate temperatures. The LCST range obtained for the copolymers was found to be considerably lower than the value reported in the literature for pNIPAAM. The high deposition rate of uniform p(NIPAAm-HPMA) thin films with the iCVD process and the tunability of the LCST value may lead to new possibilities for the use of this thermo_responsive hydrogel in different applications.

2. MATERIAL AND METHODS

2.1 Material

The depositions took place in a specially designed iCVD reactor. Si wafers (University wafer,100, P-type), approximately 4x3 cm^2 in size, were placed in the reactor to perform depositions. Before coating, the Si wafers were cleaned in an acetone and 2-propanol mixture and dried with nitrogen. The synthesis of p(NIPAAm-HPMA) copolymer thin films was carried out using N-isopropyl acrylamide (NIPAAm) (Aldrich, %98), hydroxypropyl methacrylate) (HPMA) (Aldrich, %98) and di-tert-butyl peroxide (TBPO) (Luperox, %97) as monomers and initiator, respectively. The precursors were utilized without undergoing any purification or modifications. The polymerization structures p(NIPAAm-HPMA) are shown in Figure 1.

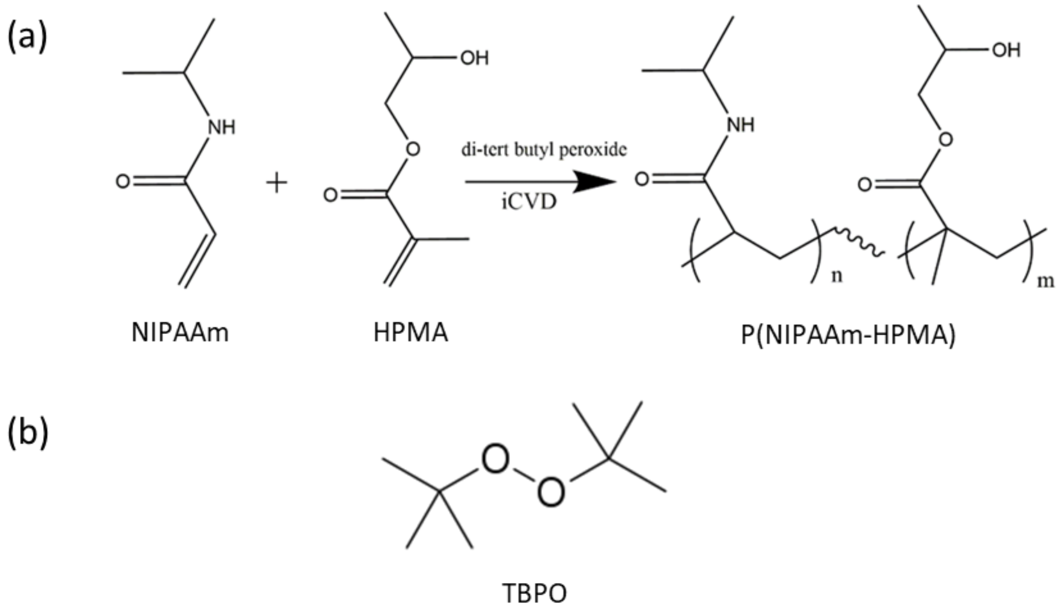

Figure 1. a) The polymerization structure of P(NIPAAm-co-HPMA) films b) the initiator used during the iCVD

2.2 iCVD of P(NIPAAm-HPMA) Copolymer Films

Initiator and monomer vapors were introduced into the chamber via distinct lines. The NIPAAm monomer was heated to 80 °C and supplied to the reactor through a line kept at 95 °C. The HPMA monomer was heated to 60 °C and directed into the reactor through a line held at 95 °C. TBPO was vaporized at room temperature (25 °C). The flow rates of the monomer and initiator were controlled using needle valves. Depositions were made at three different HPMA flow rates and carried out until reaching 200 nm coating thickness. The deposition process included the real-time monitoring of film thickness using a laser interferometer, which was equipped with a 650 nm diode laser source and a laser power meter. The pressure inside the reactor was managed through a downstream pressure controller (MKS), which was fitted with a Baratron vacuum gauge (MKS). A dry vacuum pump (Edwards XDS-10) coupled with a liquid-nitrogen cold trap was employed to attain the vacuum. The substrate was cooled with water from a recirculating chiller (Thermo Neslab). Table 1 shows detailed deposition conditions.

Table 1: Deposition conditions of p(NIPAAm-HPMA) polymeric films

	p(NIPAAm-HPMA)-1	p(NIPAAm-HPMA)-2	p(NIPAAm-HPMA)-3
Initiator Flowrate	1 sccm	1 sccm	1 sccm
NIPAAm Flowrate	0.5 sccm	0.5 sccm	0.5 sccm
HPMA Flowrate	0.21 sccm	0.27 sccm	0.36 sccm
(NIPAAm/HPMA) monomer ratio	2.38	1.85	1.39
Substrate Temperature	30 °C	30 °C	30 °C
Filament Temperature	240 °C	240 °C	240 °C
Reactor Pressure	200 mtorr	200 mtorr	200 mtorr
Deposition rate	9 nm/min	30 nm/min	50 nm/min

To determine the LCST by contact angle measurement, films deposited on Si wafers were placed on a temperature-controlled aluminum plate. The contact angle measurement setup is shown in Figure 2. The temperature of the plate was varied between 5 degrees and 48 degrees at regular intervals. After the temperature of the plate reached the set value, it was allowed to reach thermal equilibrium for at least 20 minutes before contact angle measurements and at least three measurements were taken at each temperature.

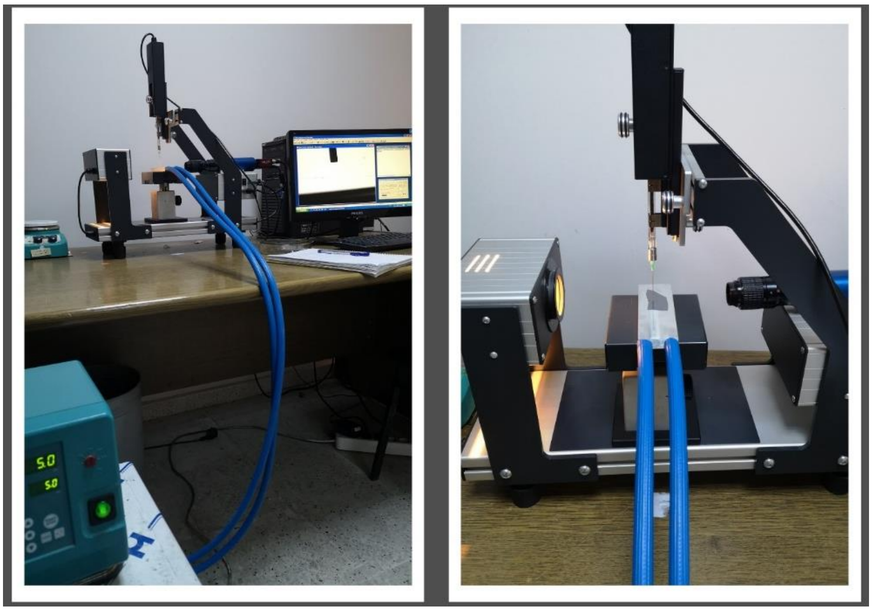

Figure 2. Water contact angle measurement set-up

2.3 Film Characterization

The chemical structure of the deposited films was analyzed using Fourier-transform infrared (FTIR, Bruker, Vertex 70) and X-ray photoelectron (FTIR, Thermoscientific) spectroscopy techniques. FTIR measurements were conducted with a reflectance accessory in the range of 4000–400 cm^{-1}, employing an average resolution of 4 cm^{-1} over 64 scans. A 100 nm-thick aluminum layer was applied to the surfaces of glass substrates for reflectance-FTIR measurements, creating an IR-reflective surface. XPS analysis was carried out using a monochromatized aluminum X-ray source at a measurement take-off angle of 60 degrees. The water contact angles of p(NIPAAm-HPMA) were determined using microliter sessile drop contact angle analysis (Kruss Easy Drop). 5.0 μL of distilled water was used in the experiments. The contact angle measuring device was used to determine the LCST temperatures of p(NIPAAm-HPMA) copolymer films by carrying out the measurements at different tempeatures. The experiment employed an aluminum heating plate as the substrate holder, and temperature control was accomplished by connecting it to a recirculating chiller (Lab. Companion, RW-0525G).

3. RESULTS AND DISCUSSION

Firstly, the effect of changing HPMA flow rate on the deposition rate of p(NIPAAm-HPMA) copolymers was investigated. For the iCVD of pNIPAAm homopolymer, the deposition rate is usually quite low [40]. The deposition rate exhibited a significant increase with the synthesis of pNIPAAm as a copolymer with pHPMA. First, pNIPAAm was coated as a homopolymer and the deposition rate was measured at 4 nm/min. Later, the deposition rate of p(NIPAAm-HPMA)-1 copolymer, where the HPMA flow rate is the lowest, was found to be 8 nm/min. In subsequent experiments, the rates for p(NIPAAm-HPMA)-2 and p(NIPAAm-HPMA)-3 were found as 25 nm/min, and 50 nm/min respectively. Figure 3 shows the change in deposition rates versus monomer HPMA flow rate in the copolymer. Compared to the deposition rate of homopolymer pNIPAAm, it is seen that high deposition rates are achieved with increasing HPMA flow rate in copolymers. The 82 nm/min deposition rate was reported for iCVD of PHPMA homopolymer in literature , which may be the reason for achieving a high deposition rate for the copolymers deposited using this monomer [41].

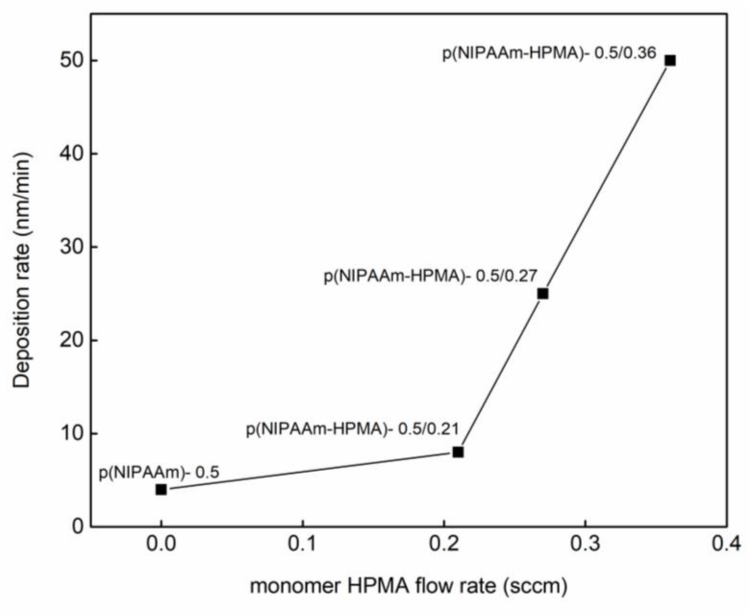

Figure 3: Effect of HPMA flow rate on deposition rate

The FTIR spectra of p(NIPAAm), p(HPMA) and copolymer films are shown in Figure 4. From the FTIR spectra, it can be seen that the characteristic absorption peaks of pNIPAAm and pHPMA appear also in the spectra of p(NIPAAm-HPMA) copolymer films. The peaks at 3280 cm-1 and 1650 cm-1, seen only in pNIPAAm and copolymers, are attributed to secondary amide N-H stretching and primary amide C=O stretching peaks, respectively. The peak at 1730 cm-1 seen in the spectra of pHPMA and copolymers shows the stretching (C=O) peak of carbonyl groups [41, 42]. The N-H bond at 3280 cm-1, the characteristic peak for pNIPAAm, which indicates bonded water molecules within the polymers, became less pronounced with increasing HPMA flow rate. It was also observed that the C-O stretching bond at 1270 cm-1 was more pronounced at copolymer with the increasing HPMA flow rate.

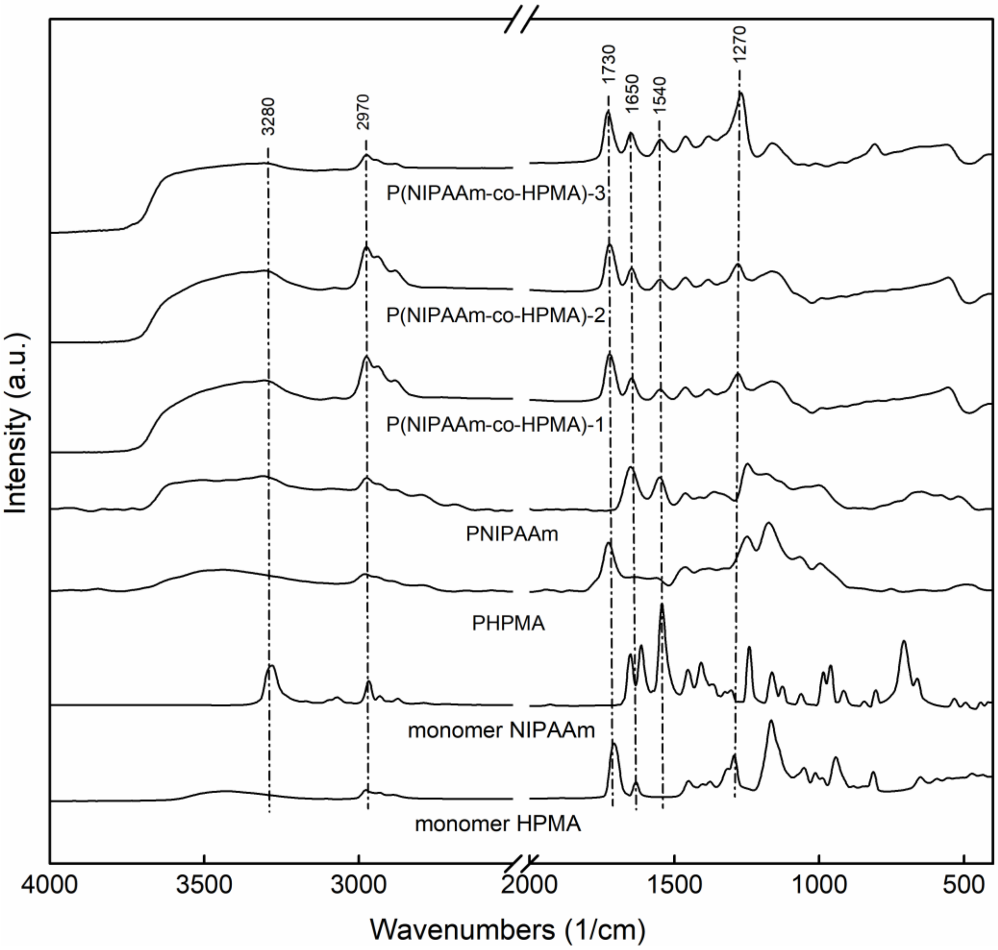

Figure 4: The FTIR spectrum of monomers, pNIPAAm, pHPMA and p(NIPAAm-co-HPMA) films

XPS analysis was performed for a detailed investigation of the composition of p(NIPAAm-HPMA) copolymer films. Figure 5 shows the XPS survey scan and high-resolution C1s spectra of the films. According to the survey scan results, C1s, O1s and N1s peaks were observed in all copolymer spectra, as expected from the chemical structures of HPMA ($C_7H_{12}O_3$) and NIPAAm ($C_6H_{11}NO$) monomers. The elemental compositions of the films are given in Table 2. Looking at the atomic percentage results given in Table 2, it was observed that the percentage of nitrogen in the structure decreased while the percentage of oxygen increased in parallel with the increase in the HPMA flow rate in the copolymer. A more comprehensive chemical analysis of p(NIPAAm-HPMA) polymer films was conducted through the examination of the high-resolution C1s spectrum. The C1s spectrum can be analyzed by fitting it with five primary peak components corresponding to -CH3, -CH2 -C, -CH2-N,-O-CH2-, and -O-C* C=O*, respectively [43]. Table 3 shows the binding energy values seen in the high-resolution C1s spectra of the films. In the copolymer film sample (fig 4c), the intensity of the C=O peak increases with increasing HPMA flow rate, indicating a higher incorporation of carbonyl groups into the structure. This observation is consistent with expectations, given the higher concentration of carbonyl groups inherent in the structure of the HPMA monomer. Consistent with the findings from XPS and FTIR analyses, it can be inferred that the iCVD technique allows for the production of conventionally polymerized p(NIPAAm-HPMA) copolymer thin films that closely resemble the structural characteristics of the initial monomers.

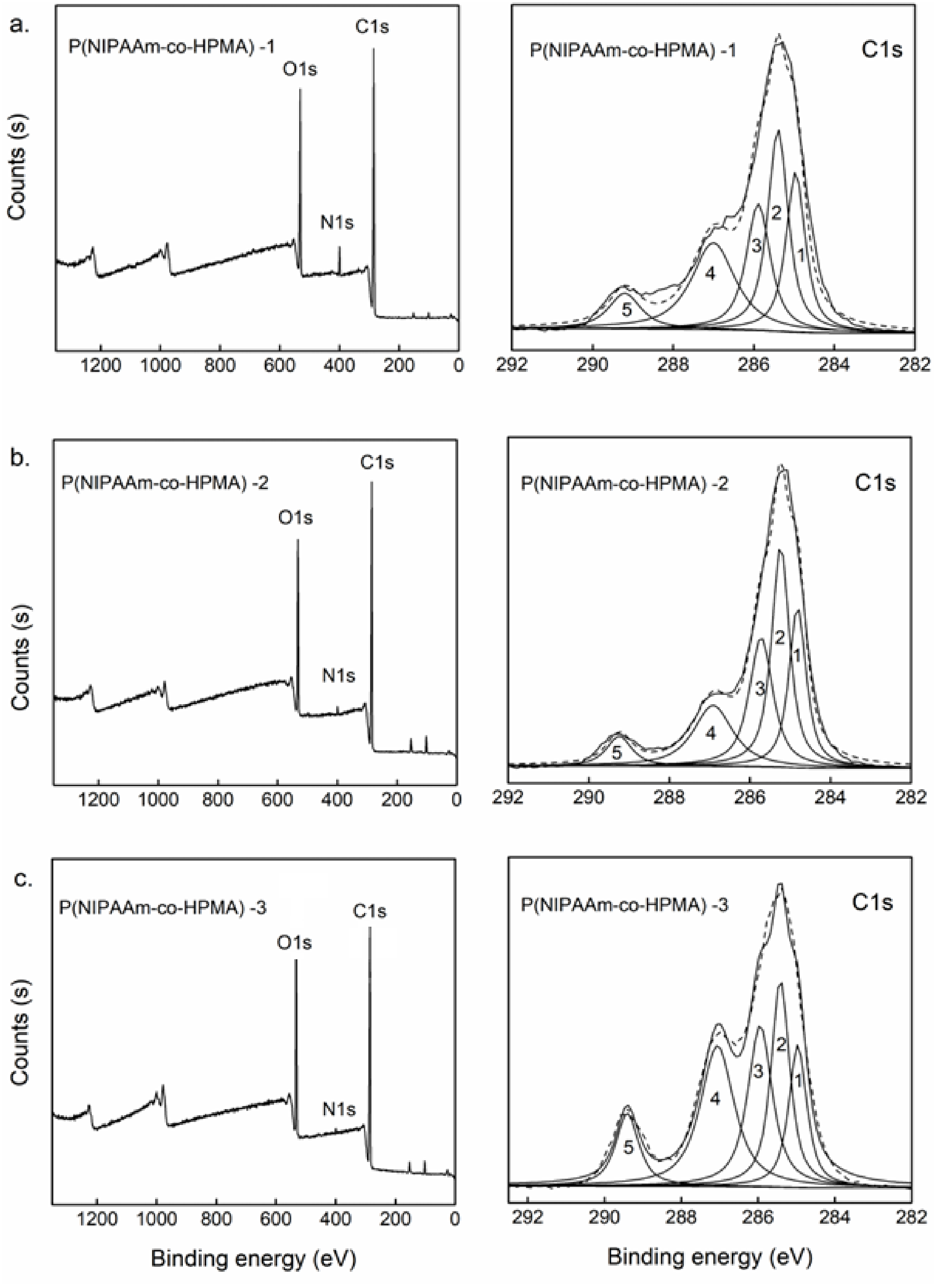

Figure 5: XPS survey scan and high-resolution C1s spectrum of the p(NIPAAm-HPMA) films a) p(NIPAAm-HPMA)-1 b) p(NIPAAm-HPMA)-2 c) p(NIPAAm-HPMA)-3

Table 2: Elemental composition of p(NIPAM-HPMA) films

	Carbon (%)	**Oxygen (%)**	**Nitrogene (%)**
p(NIPAAm-HPMA)-1	73.02	22.00	4.98
p(NIPAAm-HPMA)-2	71.54	24.08	4.38
p(NIPAAm-HPMA)-3	66.78	30.09	3.13

Table 3: High-resolution XPS scan data of the p(NIPAAm-HPMA) films

				iCVD films	**reference [43]**
	Core level	**Peak**	**Origin**	**Binding energy (eV)**	**Binding energy (eV)**
p(NIPAAm-HPMA)-1	C 1s	1	$-C^*H_3$, $-C^*H_2-C$	284.96	285.00
		2	$-C^*H_2-N$	285.40	285.75
		3	$-O-C^*H_2-$	286.00	286.50
		4	$-O-C^*$	287.03	287.00
		5	$C=O^*$	289.10	289.15
p(NIPAAm-HPMA)-2	C 1s	1	$-C^*H_3$, $-C^*H_2-C$	284.82	285.00
		2	$-C^*H_2-N$	285.24	285.75
		3	$-O-C^*H_2-$	285.95	286.50
		4	$-O-C^*$	286.91	287.00
		5	$C=O^*$	289.24	289.15
p(NIPAAm-HPMA)-3	C 1s	1	$-C^*H_3$, $-C^*H_2-C$	284.97	285.00
		2	$-C^*H_2-N$	285.42	285.75
		3	$-O-C^*H_2-$	286.30	286.50
		4	$-O-C^*$	287.06	287.00
		5	$C=O^*$	289.21	289.15

The LCST value of iCVD copolymer films deposited with different HPMA flow rates was investigated using contact angle measurements. The literature research concluded that the temperature should be changed in a wide range to determine the contact angle and the LCST value. For each coated surface, first heating and then cooling measurements were done and the obtained results are given in Figure 6.

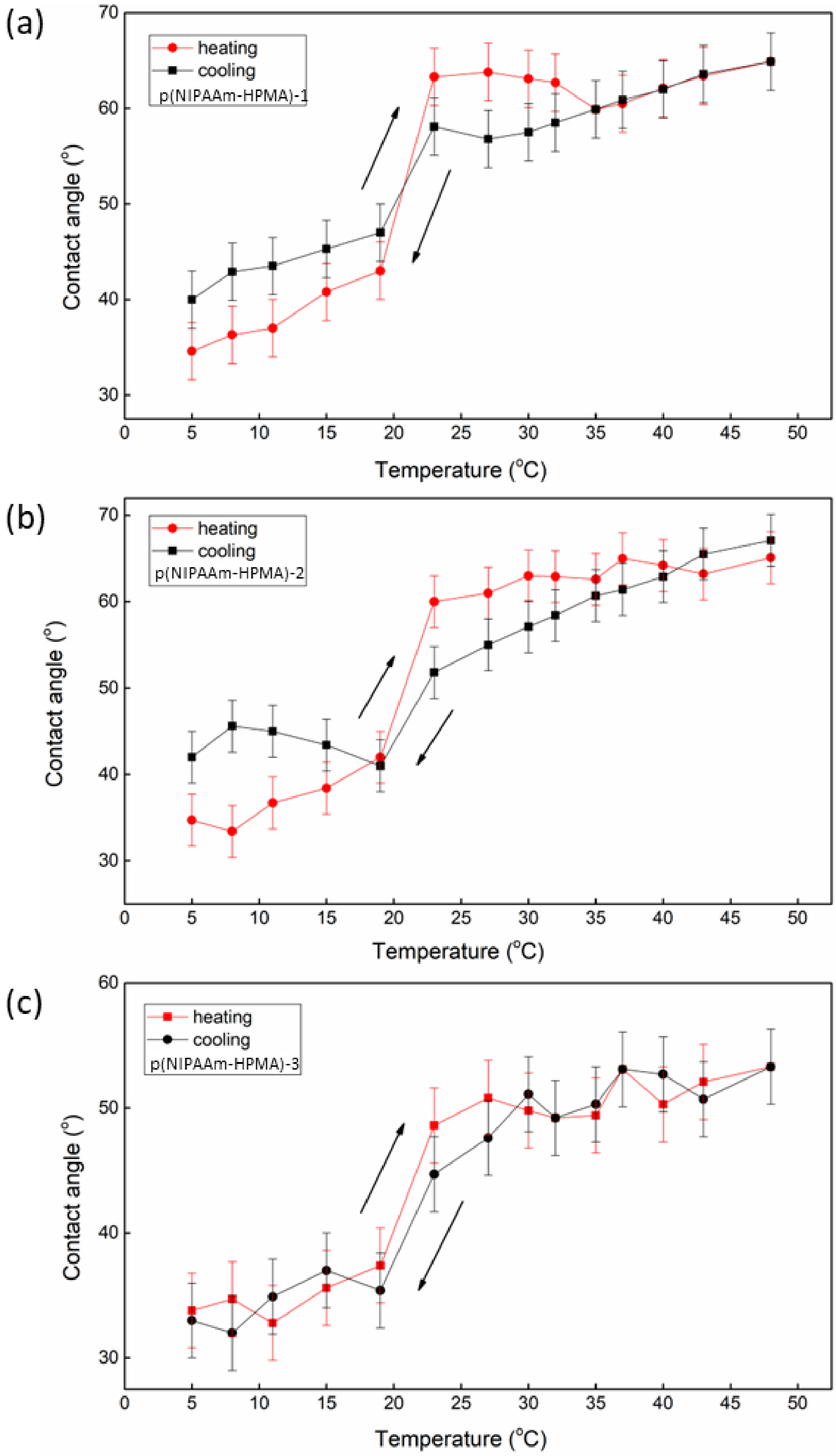

Figure 6: Effect of change in substrate temperature on water contact angle values in p(NIPAAm-HPMA) copolymer films a) p(NIPAAm-HPMA)-1 b) p(NIPAAm-HPMA)-2 c) p(NIPAAm-HPMA)-3

Based on the results, it was observed that the LCST values for the p(NIPAAm-HPMA) films varied within the range of 19 to 23 degrees. Notably, this range is considerably lower than the LCST value of pNIPAAm alone, which is 32 degrees [44]. It is established that the copolymerization of NIPAAm with a comonomer exhibiting greater hydrophobicity leads to a reduction in the LCST, whereas copolymerization with a more hydrophilic comonomer results in an increase in the LCST [9, 45, 46]. The decline in LCST observed in this context can be anticipated, given the relatively heightened hydrophobicity of HPMA, which incorporates a methyl group. A contact angle alteration of around 30° corresponding to the thermo responsive transition between hydrophilicity and hydrophobicity was observed on the flat substrate modified with p(NIPAAm-HPMA) film; this aligns with the conclusions found in the literatüre [47]. This effect is clarified by the interplay between intermolecular and intramolecular hydrogen bonds below and above the LCST, which is approximately 32°C.

4. CONCLUSIONS

P(NIPAAm-HPMA) thermo-responsive hydrogel thin films were deposited by iCVD method on Si wafer surfaces. The effect of NIPAAm/HPMA flow rate on the deposition rate, structure and responsive properties of the as-deposited p(NIPAAm-HPMA) copolymers were revealed. The highest deposition rate of 50 nm/min was observed for the copolymer deposited using lowest NIPAAm/HPMA monomer ratio studied. The deposition rate showed a significant increase with decreasing NIPAAm/HPMA flow ratio. Results of the FTIR and XPS analyzes showed that the iCVD technique was able to tune the composition of the copolymers easily by just changing the monomer flow ratios. The LCST values of p(NIPAAm-HPMA) copolymer films on Si wafer surfaces, which were determined by monitoring the temperature dependence of the water contact angle values on temperature, was shown to vary between 19 and 23 ^{o}C. The LCST, as expected, was observed to be dependent on the NIPAAm/HPMA monomer ratio. That LCST range is considerably below the literature- reported values for pNIPAAM, which makes the as-deposited copolymer suitable for applications that require thermos-responsive properties at lower temperatures.

Declaration of Ethical Standards

The authors declare that all ethical guidelines including authorship, citation, data reporting, and publishing original research are followed.

Declaration of Competing Interest

The authors declare that there is no conflict of interest.

Acknowledgements

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Data Availability

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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