Produce a Temperature-Sensitivity Film Coated On the Glass Via Photopolymerization

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Abstract:

In this study, a hydroxylated glass was coated by a poly(N-isopropylacrylamide) (pNIPAM) film via photopolymerization reaction. The pNIPAM film grafted on the glass was investigated by ATR-FTIR and XPS. UV-Vis spectrophotometric direct transmittance analysis was used to study the temperature-sensitivity property of the pNIPAM film. All the results indicated that the pNIPAM film, which was grafted on the surface of the glass, has a good adhesive strength and stability, and it has many potential applications due to the property of discoloration with different temperature.

1. INTRODUCTION

It's well known that Poly(N-isopropylacrylamide) (variously abbreviated pNIPAM) is a temperature-responsive polymer that was first synthesized in the 1950s[1]. By copolymerized with other monomers, pNIPAM with its lower critical solution temperature (LCST) around 32-33 ^{o}C has been widely investigated in recent years, such as triggered release, Janus nanoparticles, hybrid microgel, affinity membrane, micro-vesicles, gates of porous membranes, thermo driven microcrawlers and so on.[2-11]

As we know, chemical methods are often used to modify the surface in order to obtain some special properties. Many functional surfaces were designed, such as superhydrophobic surface, catalytic surface, surface of protein-resistant, surface of biological detection, surface of change of superhydrophobicity and superhydrophilicity, patterned surface and smart response surface. Common surface modification methods included surface initiated redox polymerization, atom transfer

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radical polymerization (ATRP), self-assembled monolayer (SAM), plasma-graft pore-filling polymerization and inverse suspension polymerization[1,2]. But the process to obtain membrane or vesicle was complex. Over the past decade, UV irradiation had become a popular technique because of the superiority of efficiency, energy, ecology and low temperature. The process of photopolymerization only needed few minutes even one second to finish the polymerization at ambient.

In this study, a thermo-sensitive polymer film was coated on the surface of glass substrate via photopolymerization process. The pNIPAM reticulate membrane which was successfully grafted on the surface of glass performed a good bonding strength and stability after several times circulation of heating and cooling. All the results show that it could be used to change the light intensity in greenhouses resulting from a change in greenhouse's temperature and also be used as alarm switch on the light or temperature.

2. EXPERIMENTAL
2.1. Materials

N-isopropylacrylamide (NIPAM) was purchased from Tokyo Chemical Industry Co., Ltd. 3-methacryloxypropyltrimethoxysilane (MPS) was obtained from Nanjing Capatue Chemical Co., Ltd. Trimethylolpropane triacrylate (TMPTA) was donated by Sartomer company as a gift. 2-Hydroxy-2-methylpropiophenone (1173) was given by Changzhou Runtec Chemical, Ltd. All other chemical reagents were obtained from Sinopharm Group Chemical Reagent Co. Ltd., China. Toluene was dried and purified according to the common laboratory methods and other reagents were used as received without further purification. The chemical structures of the monomers and the photoinitiator were shown in Scheme 1.
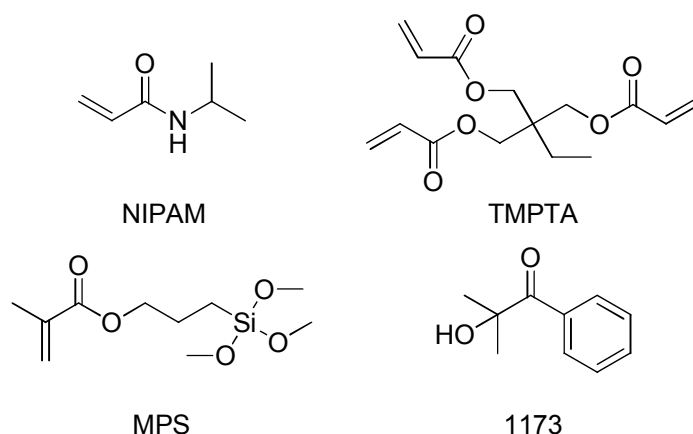
Scheme 1. The chemical structures of the monomers and the photoinitiator.

2.2. Modification of glass slide

The typical process of modification of glass slide was shown in Scheme 2.

Firstly, the glass slide was washed with sodium hydroxide solution in a beaker for 10 min in the ultrasonic cleaner, then following by ethanol and acetone. Each side was subsequently rinsed with distilled water, and dried in the nitrogen atmosphere. The dried glass was immersed into a mixture of 70%(v/v) concentrated sulfuric acid (98% wt. %) and 30%(v/v) hydrogen peroxide solution (30% wt. %), and boiled for 1 h. Then the glass slide was washed with a large amount of distilled water and ethanol, respectively, stored in the distilled water.

Secondly, MPS (10 mg) and acetic acid (3 drops) were added in 10 mL toluene. The solution was stirred for 1 min at room temperature, and then the pretreated glass slides were then immersed into the solution for 12 h. After that, the slides were washed with ethanol and dried with nitrogen stream.

Finally, One drop of the mixing solution was added on the MPS-modified slide, then the slide was irradiated by a UV lamp (EXFO OmniCure series 1000) with a light intensity of 50 mW/cm^2. The grafted slide was washed with ethanol, distilled water and dried.
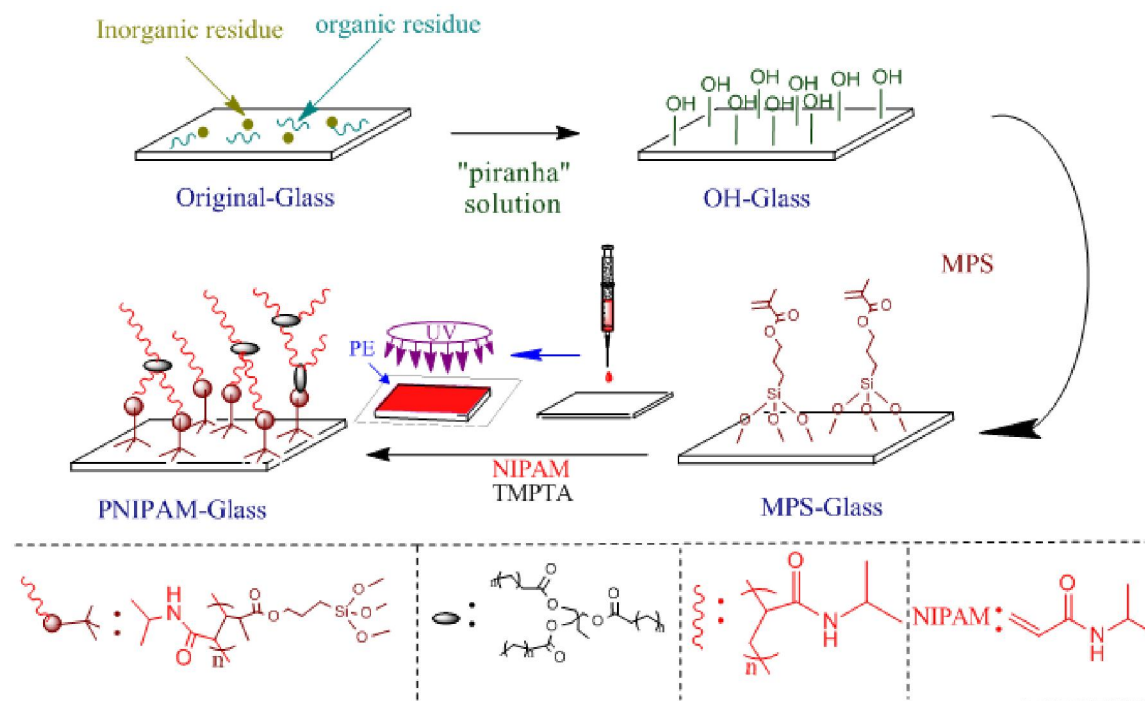
Scheme 2. Schematic illustration of the process of the glass modified.

2.2. Characterization

Attenuated Total Reflection-Fourier Transform Infrared Spectroscopy (ATR-FTIR) spectra was carried out by using Nicolet 6700 instrument (Nicolet Instrument, Thermo

Company, USA) in the range of 4000-600cm^{-1} with a resolution of 4 cm^{-1}. XPS (ESCALAB 250, Thermo Fisher Scientific, USA) was employed to study the chemical composition of the surface before and after grafted with pNIPAM. Hitachi U-3010 UV-vis spectrophotometer (Hitachi High-Technologies Corporation, Tokyo, Japan) was used to investigate the change of transmittance of pNIPAM-Glass in the different temperature condition.

3 Results and Discussions

3.1 ATR-FTIR spectroscopy

Figure 1 was shown that OH-Glass treated by "piranha" solution had no significant peaks, which could be indicated that most of the organic compounds on the glass surface had been removed. After the OH-Glass treated by MPS solution, the MPS-Glass exhibited the characteristic methyl peaks at 2952.37 and 2924.87 cm^{-1}, C=O peak at 1718.02 cm^{-1} and C=C stretching peak at 1634.44 cm^{-1}. All these results were confirmed the presence of MPS on the MPS-Glass. After grafting pNIPAM onto the MPS-Glass, the amide peak (N-H and C-N) at 1535 cm^{-1} and (C=O) at 1640 cm^{-1} were indicated that pNIPAM had been successfully grafted on the glass substrates by the method of photopolymerization.
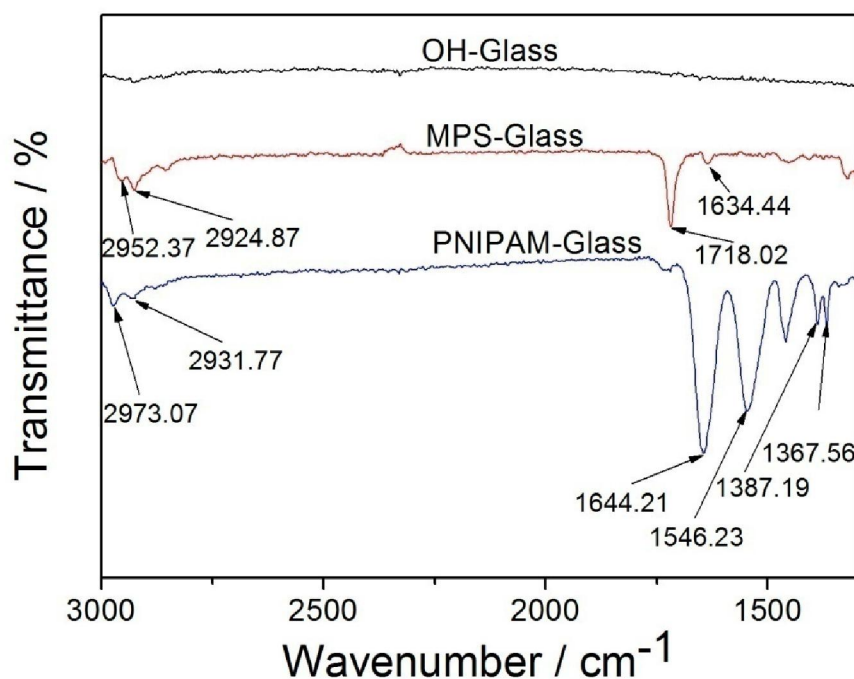

Figure 1. ATR-FTIR spectra of OH-Glass, MPS-Glass and pNIPAM-Glass.

3.2 **X-ray photoelectron spectroscope**

The XPS spectra of glass slides before and after modification of MPS and pNIPAM were shown in Figure 2.
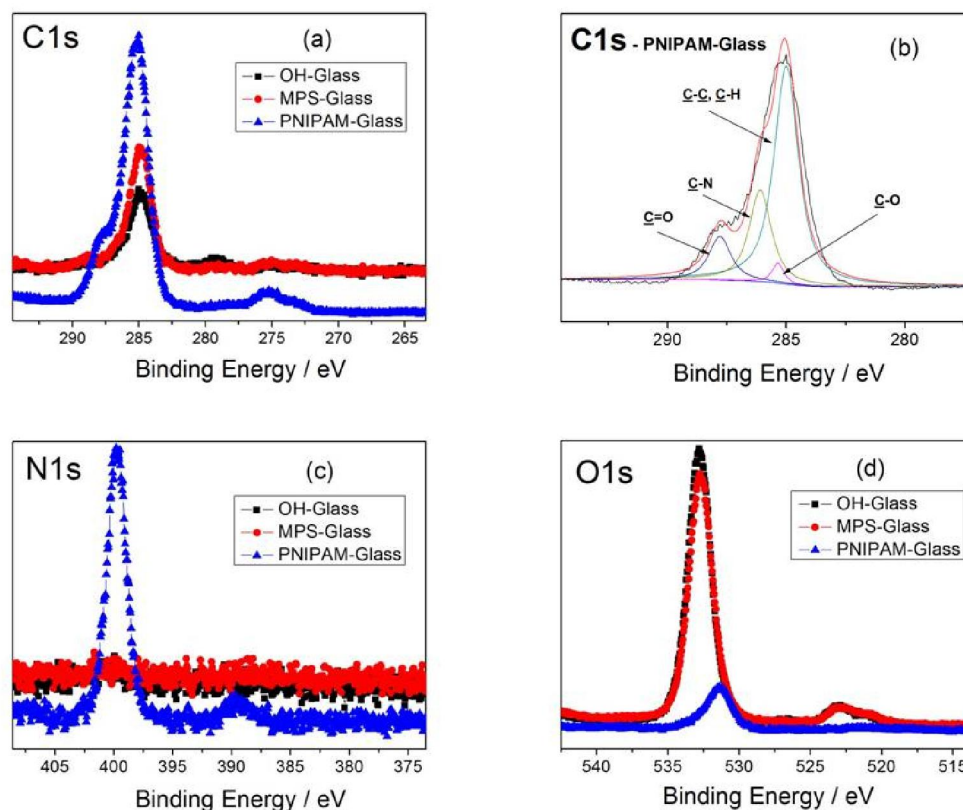

Figure 2. XPS spectra of the surface: OH-Glass, MPS-Glass and pNIPAM-Glass.

In Figure 2a, the C1s spectra was showed that OH-Glass had only one weak peak which was attributed to the interference of some unavoidable pollutant on glass substrate in the analysis. Due to the presence of MPS, the C1s signal intensity (285.0 eV) of MPS-Glass was enhanced while pNIPAM-Glass (285.0 eV) had significantly enhanced after pNIPAM was grafted on the MPS-Glass. There were four peaks in the C1s spectrum (Figure 2b) of pNIPAM-Glass. The corresponding binding energies were 285.0 eV (C atom in C-C and C-H bond), 285.4 eV (C atom in C-O bond of TMPTA), 286.1 eV (C atom in C-N of pNIPAM chains) and 287.8 eV (C atom in C=O), respectively. For the N1s spectra (Figure 2c), there was almost no N1s signal for OH-Glass and MPS-Glass. Due to the presence of N-H of pNIPAM chains, N1s peak (N-H, at 399.2 eV) of pNIPAM-Glass was obvious. For the O1s spectra (Figure 2d), both the OH-Glass and the MPS-Glass had a same peak with bonding energy of 532.619 eV (O atom in O-Si bond). However, the pNIPAM-Glass had another peak

with bonding energy of 532.538 eV which was attributed to C=O bond of pNIPAM chains.

As the affection of TMPTA, the C1s and N1s ratio of the surface of pNIPAM-Glass was 6.84 to 1 which was slightly higher than that of NIPAM ($C_6H_{11}NO$). The increase in the C1s and N1s ratio and the decrease of the O1s and Si2p ratio indicated that pNIPAM was successfully grafted on the surface of MPS-Glass via photopolymerization.

3.3 Thermo-sensitive investigation

As we known, pNIPAM is a temperature-responsive polymer. With the increasing temperature, pNIPAM-Glass changed from transparent to opaque (heating process in Figure 3b) while pNIPAM-Glass became transparent from opaque (cooling process in Figure 3a) with the decreasing temperature. The competition between intermolecular and intramolecular hydrogen bonding below and above the lower critical solution temperature (LCST)[26] resulted in the change of pNIPAM-Glass. When the temperature was higher than the LCST of pNIPAM, intramolecular hydrogen bonding between C=O and N-H groups in the pNIPAM chains resulted in a compact and collapsed conformation of pNIPAM chains, which made it difficult for the hydrophilic C=O and N-H groups to interact with water molecules. Thus, the film exhibited opaque at high temperature. When the temperature was lower than the LCST of pNIPAM, the predominantly intermolecular hydrogen bonds between the pNIPAM chains and water molecules led to the swollen of pNIPAM chains and resulted in the transparence of pNIPAM-Glass.
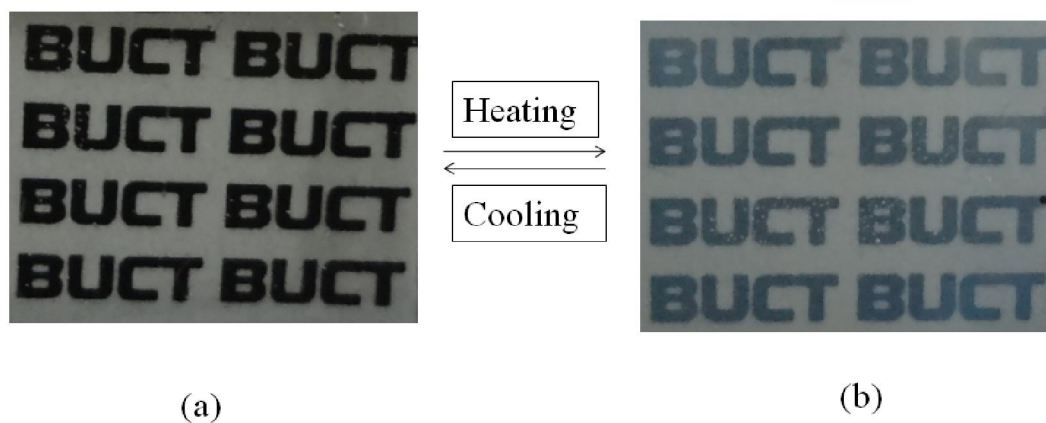

(a)   (b)

Figure 3. pNIPAM-Glass at the temperature of (a) 25 ℃, (b) 40 ℃, under water environment.

The process of transparency change was reversible with temperature. The presence

of covalent bonds between glass and pNIPAM chains and the reticular structure of pNIPAM membrane increased the adhesive strength of pNIPAM and glass, even after twenty times of heating and cooling process the pNIPAM still on the glass.

Due to the transparency change of pNIPAM-Glass, the UV-vis transmittance of pNIPAM-Glass changed with the varying temperature. The temperature-dependent transmittance was shown in Figure 4.
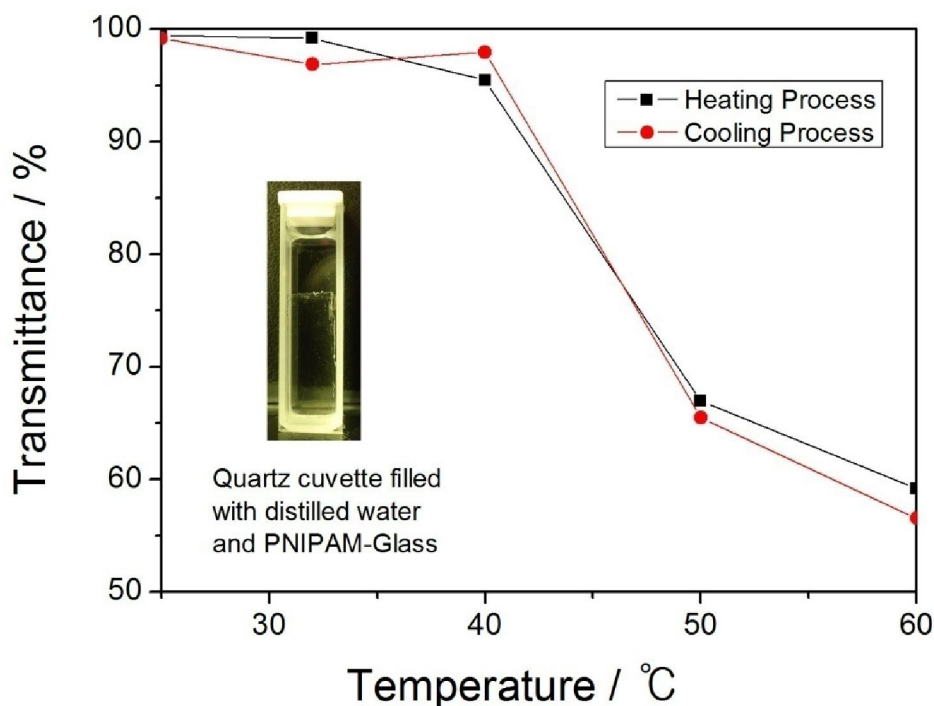

Figure 4. Temperature dependent of UV-vis transmittance at 500 nm obtained for pNIPAM-Glass: heating and cooling process in water.

In the heating process, there was only a slightly variation of transmittance from 25 $^{\circ}$C to 40 $^{\circ}$C. However, when the temperature was over 40 $^{\circ}$C, transmittance showed an obvious change. 40 $^{\circ}$C was the LCST which was attributed the existence of TMPTA. NIPAM and TMPTA formed a reticular membrane through photopolymerization. The reticular structure limited the mobility of the pNIPAM chains. Water molecules needed more energy to escape from the reticular membrane, which resulted in the high LCST value compared with pNIPAM alone.

In the cooling process, when the temperature dropped from 60 $^{\circ}$C to 25 $^{\circ}$C, the transmittance was recovered near 100% as the beginning of heating process. Near 40 $^{\circ}$C the transmittance performed a significant change. Both the heating process and cooling process indicated that the pNIPAM membrane on the glass had good thermal

reversibility and stability.

4 CONCLUSIONS

This study described an effective chemical method for surface modification of glass substrate. pNIPAM was fixed on the surface of glass by covalent bonds, which enhanced the bonding strength between polymer and the surface of glass substrate. It had been observed that the LCST of pNIPAM had increased because of the presence of TMPTA and the pNIPAM-Glass had a good thermal reversibility with the change of temperature. Due to the change of transparency with different temperature, pNIPAM membrane grafted on the surface of glass substrate had potential applications, such as temperature control switch device and greenhouses.

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