

Supporting Information

Photografted temperature-sensitive poly(*N*-isopropylacrylamide) thin film with a superfast response rate and an interesting transparent-opaque-transparent change in its deswelling process

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Experimental part

UV equipment

The UV system with a shutter assembly and an air cooling fan was supplied by RunWing Co., Ltd. (Shenzhen, China). The input power of the high-pressure mercury UV lamp was 2 kW. Quartz glass was used to isolate UV light. The UVC (254 ± 10 nm) intensity on sample surfaces was 7.3 mW/cm^2 .

Grafting procedure

Photografting was carried out in an 8-cm-diameter Petri dish containing 10.0 mL solution and one PE film floating on the top surface of solution with only one side contacting the solution. The Petri dish was covered with polyethylene foil to prevent the evaporation of the solution. Then the PE film was irradiated with UV light for a desired period. The grafted films were firstly washed with deionized water at ambient temperature for several times, and then subjected to soxhlet extraction with acetone to remove residual monomer and homopolymer. Then the samples were vacuum dried at $40 \text{ }^\circ\text{C}$ for another 24 h.

The extent of grafting (G), in $\mu\text{g/cm}^2$, was expressed as the mass increase per surface area of the sample, and was calculated from Equation (1):

$$G = \frac{m_g - m_0}{S} (\mu\text{g} / \text{cm}^2) \quad (1)$$

where m_g and m_0 are the masses of the PE sample after and before grafting; S is the surface area of PE sample (25 cm^2). The mass was determined using an electronic balance (0.1 mg). Typical relative errors in G of three samples were $\pm 5\%$.

ATR-FTIR characterization

Attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectra were obtained from pristine and grafted thin film samples on an Avatar-380 spectrometer (Nicolet Analytical Instruments, Madison, WI) equipped with a Smart Orbit assessor (Thermo Electron Corporation, Waltham, MA). The number of scans was 32 at a resolution of 4 cm^{-1} . Carbonyl index (CI) was used to study the grafting semi-quantitatively and it was calculated by Equation (1):

$$CI = \frac{A_{C=O}}{A_{C-H}} \quad (1)$$

where $A_{C=O}$ is the absorbance of carbonyl $A_{C=O}$ stretching vibration peak at about 1629 cm^{-1} , which is the characteristic peak of carbonyl group in PNIPAAm, and A_{C-H} is the absorbance of CH_2 scissors vibration at 1460 cm^{-1} , which had no significant change during grafting process and was used as an internal reference to facilitate semi-quantitative analysis. These peaks were auto-baselined before calculating the absorbance. The automatic baseline correction and the calculation of absorbance were treated with the EZ OMNIC 5.2 software accompanying the instrument.

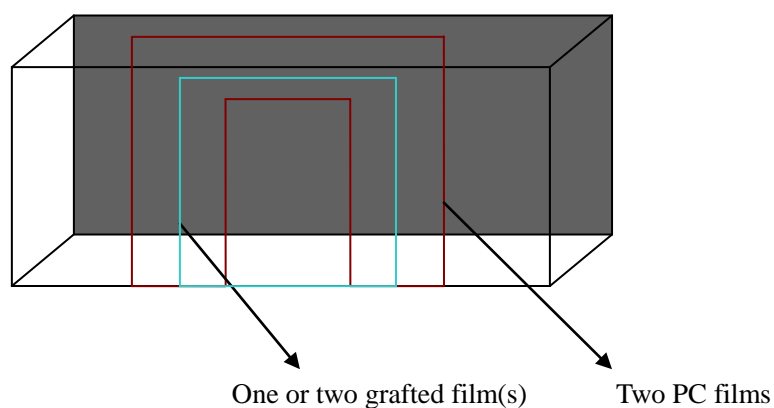


Fig. S1. Schematic apparatus for measuring the grey scale change during deswelling.

Results and Discussion

ATR-FTIR characterization

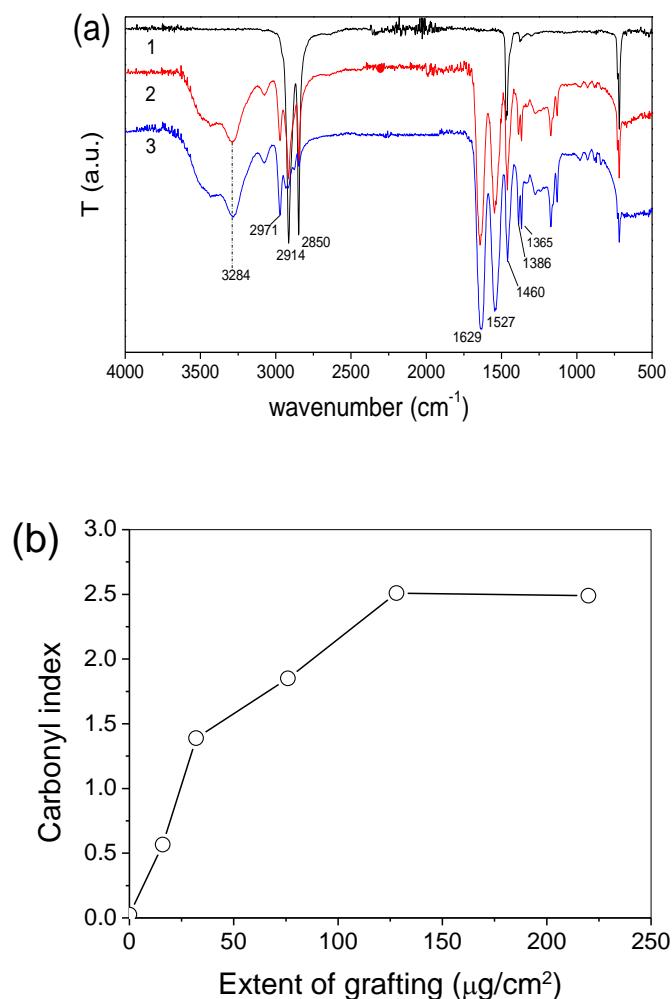


Fig. S2 ATR-FTIR characterizations. (a): ATR-FTIR spectra of pristine PE film (1) and the PE films photographed for 4 min (2) and 8 min (3); (b) Carbonyl index (CI) of PE films with different EOG. Grafting reactions were performed in 1.5 mol/L NIPAAm solution.

ATR-FTIR spectroscopy is a surface-sensitive technique that provides molecular-scale information on surfaces. The pristine PE film and the grafted films were characterized with ATR-FTIR (Fig. 2a). Compared with the spectrum of pristine PE film which has only simple absorption bands attributed to the vibration of C-C and C-H bonds, the spectra of the grafted films show the characteristic absorption peaks of PNIPAAm,^{1,2} *i.e.* an wide strong absorption band in the 3100-3700 cm⁻¹ region with the peak at 3284 cm⁻¹ due to N-H stretching vibration,

an absorption peak located at 2971 cm^{-1} due to the stretching vibration of C-H in CH_3 group, a strong but shifted C=O band at 1629 cm^{-1} due to the stretching vibration of the C=O group which is inter and intra-molecular hydrogen bonded,³ a absorption peak at 1527 cm^{-1} due to N-H in-plane bending vibration and C-N stretching vibration, a peak at 1460 cm^{-1} attributed to CH_2 scissors vibration and CH_3 antisymmetric deformation, and the doublet absorption peak at 1386 cm^{-1} and 1365 cm^{-1} corresponds to the symmetrical bending vibration of isopropyl $-\text{CH}(\text{CH}_3)_2$ group. The ATR-FTIR characterization proves that PNIPAAm chains have been successfully grafted onto the surface of PE film.

The calculated CIs of the grafted samples are shown in Fig. 2b. The CI of the grafted samples increased very quickly with the increase of EOG till about $120\text{ }\mu\text{g}/\text{cm}^2$, and then kept almost constant. The leveling of CI with the EOG appears at a much lower EOG than that found with transmission FTIR,⁴ since the large number of total internal reflections makes ATR-FTIR at least two orders of magnitude more sensitive than transmission infrared spectroscopy.⁵ The leveling off in CI may indicate that the surface of PE film has been fully covered with PNIPAAm chains.

References

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Table S1. Elemental composition of the grafted surfaces.

EOG ($\mu\text{g}/\text{cm}^2$)	Elements % of thin films						
	C	C _{1s,a}	C _{1s,b}	C _{1s,c}	N	O	C/N
17	76.69	47.94	16.25	12.50	12.03	11.28	6.37
110	76.59	48.48	15.70	12.41	12.14	11.27	6.31

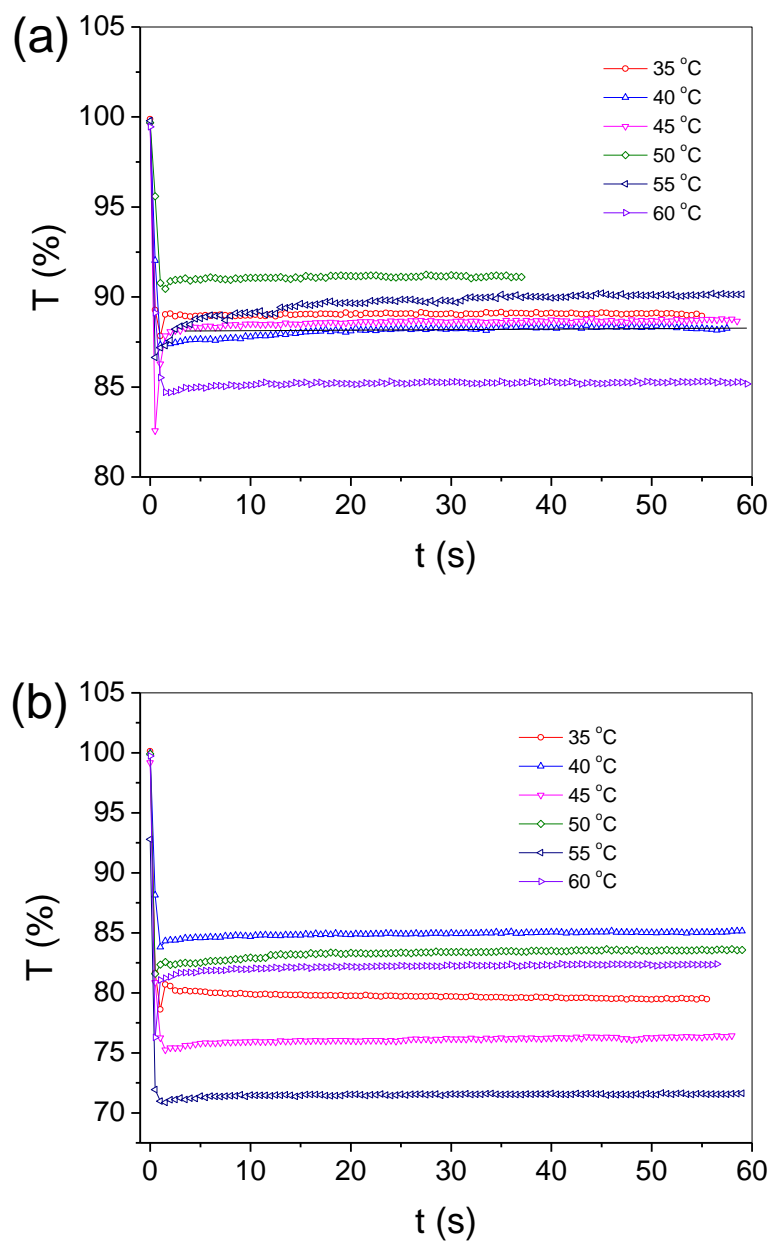


Fig. S3. Transparency change in the deswelling process of PNIPAAm layer photografted in 2 mol/L NIPAAm solution for 6 min (a) and 8 min (b).



Fig. S4. Photos showing the transparency change in the deswelling process of grafted PNIPAAm at 50 °C. The sample used was photografted in 2 mol/L NIPAAm solution for 10 min.