Supplementary Material (ESI) for RSC Advances

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# Visual Detection of Methanol in Alcoholic Beverages Using Alcoholresponsive Poly(*N*-isopropylacrylamide-*co-N*,*N*-dimethylacrylamide) Copolymers as Indicators

**Supplementary Material** 

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## Compositional Analyses of Poly(NIPAM-co-DMAA) Linear Copolymers

The actual molar contents of the hydrophilic monomer DMAA in poly(NIPAM-*co*-DMAA) linear copolymers ( $C_n$ ) are determined by Nuclear Magnetic Resonance Spectrometry (<sup>1</sup>H-NMR). The <sup>1</sup>H-NMR spectra of poly(NIPAM-*co*-DMAA) linear copolymers with different feed DMAA contents are shown in Figure S1. The chemical shift at around 3.9 ppm is the characteristic peak of protons in the isopropyl groups of NIPAM, and the chemical shifts at around 2.9 and 3.2 ppm are the characteristic double peaks of protons in the DMAA. The  $C_n$  is calculated according to Equation (S1)

$$C_{\rm n}(\%) = \frac{M_{\rm DMAA}}{M_{\rm (NIPAM+DMAA)}} \times 100\% = \frac{(I_{\delta 2.9} + I_{\delta 3.2})/6}{I_{\delta 3.9} + (I_{\delta 2.9} + I_{\delta 3.2})/6} \times 100\%$$
(S1)

where,  $C_n$  is the actual molar content of DMAA in the poly(NIPAM-*co*-DMAA) linear copolymers, *M* is the molar weight, and  $I_{2.9}$ ,  $I_{3.2}$  and  $I_{3.9}$  are the integral of characteristic peaks at around 2.9 ppm, 3.2 ppm and 3.9 ppm, respectively. From Equation (S1), the  $C_n$  values of poly(NIPAM-*co*-DMAA) copolymers with feed molar contents of 6.3, 7.4, 9.1, and 10.3 mol% are determined as 6.3, 7.7, 9.5 and 12.4 mol%, respectively.



**Figure S1.** <sup>1</sup>H NMR spectra of poly(NIPAM-*co*-DMAA) copolymers with different molar contents.

## Molecular Weights of Poly(NIPAM-co-DMAA) Linear Copolymers

The molecular weights and polydispersity indices of poly(NIPAM-*co*-DMAA) linear copolymers with various DMAA contents are determined by gel permeation chromatography (GPC, Waters-2410, Waters) using THF as the mobile phase and polystyrene as the standard. The results are shown in Table S1. The Error!<sub>w</sub> range of the copolymer is quite narrow (~5000 g/mol), and polydispersity indices are ranging from 1.38 to 1.84. Since the narrow distribution of molecular weights, the effects of molecular weights of the series of poly(NIPAM-co-DMAA) linear copolymers with various DMAA contents on the LCST values of such copolymers in the alcohol solutions can be neglected.

	Error! <sub>w</sub> (g/mol)	Error! <sub>n</sub> (g/mol)	Polydispersity
PND-6.3	5470	2980	1.84
<b>PND-7.7</b>	5410	2910	1.86
PND-9.5	5000	3410	1.47
PND-12.4	4530	3280	1.38

Table S1 Molecular weights and polydispersity of the poly(NIPAM-co-DMAA) copolymers

## Effects of the Concentration of Poly(NIPAM-co-DMAA) Linear Copolymers on

## **Transmittance Change of Alcohol Solution**

To obtain an optimum concentration range, the effects of the concentrations of PND-12.4 linear copolymers on the optical transmittance change of 30 vol% ethanol solution are investigated (Figure S2). When the copolymer concentration in the range of 0.2~1.5 wt%, the optical transmittance of alcohol solution dramatically decreases from nearly 100 % to 0 % at the temperature around the LCST of P(NIPAM-*co*-DMAA) linear copolymer due to the thermoresponsive conformational transition of copolymer in ethanol solution. However, when the concentration of P(NIPAM-*co*-DMAA) linear copolymer is as low as 0.1 wt%, the transmittance of ethanol solution shows slow change with increasing the temperature and is hard to reach 0% in a narrow temperature range. With the concentration of P(NIPAM-*co*-DMAA) linear copolymer of P(NIPAM-*co*-DMAA) linear copolymer and is hard to reach 0% in a narrow temperature range. With the concentration of P(NIPAM-*co*-DMAA) linear copolymer of P(NIPAM-*co*-DMAA) linear copolymer and is hard to reach 0% in a narrow temperature range. With the concentration of P(NIPAM-*co*-DMAA) linear copolymer of P(NIPAM-*co*-DMAA) linear copolymer increasing from 0.1 to 1.5 wt%, the LCST value in ethanol solution decreases from 31.7 to 17.8 °C.

The basic principle for methanol detection in our study is that the transmittance change of alcohol solution containing P(NIPAM-*co*-DMAA) linear copolymer is large enough to distinguish visually at a certain operation temperature when a certain amount ethanol is replaced by methanol. However, the isothermal transmittance change of alcohol solution is originally from the thermo-responsive conformational transition of P(NIPAM-*co*-DMAA) linear copolymer in alcohol solution with different methanol concentrations. On one hand, if the temperature-dependent transmittance change is slow, the transmittance difference between solutions with/without methanol at a certain operation temperature may not be distinguished visually. Therefore, the copolymer concentration of 0.1 wt% is not optimum concentration to achieve the methanol detection. On the other hand, when the copolymer concentration increases to 1.2 wt%

or above, the solubility of the P(NIPAM-*co*-DMAA) linear copolymer in 30 vol% ethanol solution becomes worse and thus the optical transmittance decreases to  $\sim 80$  %. Therefore, the optimum concentration range of P(NIPAM-*co*-DMAA) linear copolymer is 0.2~0.9 wt%. Considering the large transmittance difference and low amount of copolymer, the copolymer concentration of 0.3 wt% is chosen in the further experiments.



**Figure S2**. Effects of the concentration of poly(NIPAM-*co*-DMAA) linear copolymer on the transmittance change of 30 vol% ethanol solution.