

## Synthesis and Aggregation Behaviour of Thermo-Sensitive Copolymer of *N*-Isopropylacrylamide and Sodium Vinylsulphonate

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A series of thermo-sensitive copolymers of poly(*N*-isopropylacrylamide-co-sodium vinyl sulphonate) (PNIPAAm-co-SVS) were synthesized by radical copolymerization of *N*-isopropylacrylamide and sodium vinyl sulphonate in water using 2,2'-azobis (2-methylpropionamide) dihydrochloride (V-50) as the initiator. These copolymers exhibit different lower critical solution temperatures due to their distinct monomer ratios. The salt and pH-tuned phase separation behavior of the copolymers were studied by UV-visible spectrophotometry. The results show that the lower critical solution temperatures (LCST) of the copolymers decreased sharply with the increase of NaCl concentration or the decrease of pH value. Aggregation behaviour of the copolymers in aqueous solution as a function of copolymer composition, added salt and pH value were also studied by dynamic laser light scattering.

**Keywords:** Water soluble copolymer, Thermo-sensitive, Lower critical solution temperature, Aggregation behaviour.

### INTRODUCTION

In recent years, thermo-sensitive copolymers have received much attention for their intelligent response and extensive use in drug delivery system<sup>1-9</sup>, complexant<sup>10,11</sup>, biomaterial<sup>12,13</sup>, textile<sup>14</sup>, antibacterial<sup>15</sup>, etc. These applications were realized through various physical forms such as gels, micelles, core-shell particles and liposomes formed by thermo-sensitive copolymers.

Poly(*N*-isopropylacrylamide) (PNIPAAm), the most common thermo-sensitive polymer, which has been widely investigated for the reversible macromolecular phase transition at about 32 °C known as its lower critical solution temperature (LCST). This thermal reversible phase transition in aqueous solution is a consequence of the macromolecular transition from a hydrophilic to a hydrophobic structure at this temperature. In the last decade, more attention has been paid to copolymers polymerized by *N*-isopropylacrylamide and charged monomers, such as acrylic acid<sup>16-18</sup>, methacrylic acid<sup>19-22</sup>, allylamine<sup>23-24</sup>, ethyleneimine<sup>25</sup>, etc.

In this paper, a series of random copolymers of *N*-isopropylacrylamide (NIPAAm) and sodium vinyl sulphonate were synthesized and characterized. The bovine serum albumins of the copolymers were studied, also, the effect of pH as well as sodium vinyl sulphonate content on LCSTs of the copolymers were investigated. Finally, the hydrodynamic radius distributions of the copolymers were investigated at different conditions.

### EXPERIMENTAL

*N*-isopropylacrylamide bought from Shanghai Wujing Chemical Technology Co., Ltd. was recrystallized in *n*-hexane. Sodium vinyl sulphonate was purchased from Zibo Chemical Reagent Company, refined twice by dissolving it in distilled water, filtered, precipitated with ethanol and finally dried in vacuum at 50 °C. 2,2'-Azobis (2-methylpropionamide) dihydrochloride (V-50) as well as sodium chloride from Tianjin Chemical Reagent Company were chemical pure reagents. Ethanol and methanol were bought from Xilong Chemical Co., Ltd. All the other solvents and reagents were of analytical grade and used without purification. All the solutions were prepared using distilled de-ionized water which has a resistivity of 18.2 μΩ cm.

**Synthesis of poly(*N*-isopropylacrylamide-co-sodium vinyl sulphonate) (PNIPAAm-co-SVS):** A series of random copolymers of *N*-isopropylacrylamide and sodium vinyl sulphonate were prepared by radical random copolymerization of the two monomers in water using V-50 as the initiator. Designed mixture ratio of NIPAAm and sodium vinyl sulphonate were dissolved in de-ionized water and degassed with dry nitrogen for 0.5 h at room temperature. V-50 dissolved in water was then added and the polymerization reaction was

carried out at 55 °C for 10 h. The resultant copolymers were precipitated by methanol and then dried in vacuum at 50 °C for 48 h.

**Characterization:**  $^1\text{H}$  NMR experiment was performed on Bruker AVANCE400 NMR spectrometer.  $\text{D}_2\text{O}$  was used for field-frequency lock, the observed  $^1\text{H}$  chemical shifts are reported in parts per million (ppm). The FT-IR spectra were carried out on a Tensor 27 spectrometer (Bruker, Switzerland) with samples prepared as KBr pellets. The spectra were acquired in the frequency range  $4,000\text{--}400\text{ cm}^{-1}$ . Elemental analysis (C, N, S and H) was performed on Elementar Vario EL III analyzer (German). TGA experiments were done on a TA instrument SDT Q600 with a heating rate of  $10\text{ }^\circ\text{C/min}$  from 25 to  $600\text{ }^\circ\text{C}$  in a dynamic nitrogen atmosphere (flow rate =  $50\text{ mL min}^{-1}$ ). The optical transmittance of the polymer solution was monitored at  $\lambda = 500\text{ nm}$  by a spectrophotometer (analysis instrument factory of Shanghai, China, UV-752) with constant temperature water bath.

Molecular weight ( $M_w$ ) of the copolymers were characterized by gel permeation chromatography coupled with multi-angle laser light scattering (GPC-MALLS) measurements with a DAWN-HELEOS multiangle laser photometer combined with a 515 HPLC pump (Waters products) equipped with a OHpak SB-803 column ( $8 \times 300\text{ mmL}$ ), a OHpak SB-804 column ( $8 \times 300\text{ mmL}$ ) and a differential refractive index detector (Optilab-REX) at  $25\text{ }^\circ\text{C}$ . The eluent was  $0.1\text{ mol L}^{-1}$  NaCl aqueous solution with a flow rate  $0.5\text{ mL min}^{-1}$ . The refractive index increment ( $\text{dn/dc}$ ) of the copolymer was measured with the differential refractive index detector on the offline mode at  $25\text{ }^\circ\text{C}$ . The  $\text{dn/dc}$  values of P-1, P-2, P-3, P-4, P-5 were 0.1282, 0.1245, 0.1213, 0.1195 and  $0.1181\text{ mL g}^{-1}$ . All the solutions with a copolymer concentration of  $2\text{ mg mL}^{-1}$  were filtered with a  $0.2\text{ }\mu\text{m}$  filter (Millipore). Calibration was with PEG6000 standards. Astra software was utilized for the data acquisition and analysis. The weight-average molecular weight of each fraction was determined by a Debye plot from the light scattering signal and according to the division principle of GPC.

Dynamic light scattering (DLS) was used to measure the sizes and the distribution of hydrodynamic radius ( $R_h$ ) of PNIPAAm-*co*-SVS copolymers at different conditions. Dynamic light scattering measurements were performed on a multiangle laser photometer equipped with a linearly polarized gallium arsenide (GaAs) laser ( $\lambda = 658\text{ nm}$ ; DAWN HELEOS, Wyatt Technology Co. US). All dynamic light scattering were measured at  $25\text{ }^\circ\text{C}$ .

## RESULTS AND DISCUSSION

**Synthesis and characterization of copolymer:** The copolymers synthesized with different ratio of NIPAAm/SVS are shown in Table-1 and are named P-1, P-2, P-3, P-4, P-5. The samples were polymerized under identical condition except for the different masses of *N*-isopropylacrylamide and sodium vinyl sulphonate. According to Table-1, we could find that the yield of the samples decrease with the increase of sodium vinyl sulphonate content. The reason for this phenomenon may be that, sodium vinyl sulphonate is a compound with sulfonic groups in it, that influenced the polymerization process to a certain degree.

TABLE-1  
FEEDING COMPOSITION OF FIVE SAMPLES

Sample	Mass (g) NIPAAm	Mass (g) sodium vinyl sulphonate	Ratio of NIPAAm/SVS	Yield (%)
P-1	1.0127	0.0553	95:5	94.33
P-2	1.0214	0.1037	90:10	95.72
P-3	1.0063	0.1487	85:15	94.79
P-4	1.0323	0.2018	80:20	87.14
P-5	1.0135	0.2554	75:25	77.15

The formation of the copolymers was confirmed by  $^1\text{H}$  NMR analysis and the spectra of P-1 and P-5 copolymer samples are showed in Fig. 1. As is shown, methyl proton ( $\text{CH}_3$ - of isopropyl) of the PNIPAAm contributed to the signal at 1.08 ppm (peak a), methylene proton in polymer backbone appeared at 1.37-1.65 ppm (peak b). Methine proton ( $-\text{CH}-$  of  $-\text{CH}-\text{CO}-$ ) of PNIPAAm in polymer backbone appeared at 1.94-2.06 ppm (peak c), while methine proton ( $-\text{CH}-$  of  $-\text{CHSO}_3-$ ) of sodium vinyl sulphonate in polymer backbone appeared at 3.63 ppm (peak d). The peak at 3.82 ppm consisted of chemical shift of methine proton of isopropyl. The actual mole ratio of NIPAAm/SVS in the copolymer could be calculated *via*  $^1\text{H}$  NMR spectra through compare the area of peak c and peak d.

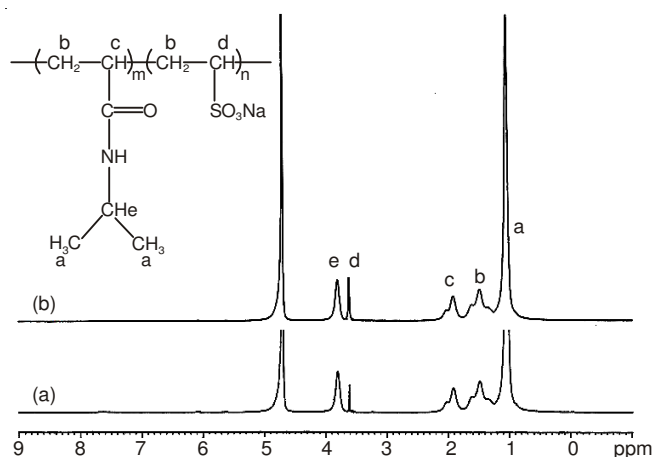


Fig. 1.  $^1\text{H}$  NMR spectra of P-1(a) and P-5(b) samples

Fig. 2 shows the FTIR spectra of the copolymer samples P-1 (a), P-2 (b), P-3 (c), P-4 (d), P-5 (e). The characteristic peaks around  $1064$ ,  $1122$  and  $1187\text{ cm}^{-1}$  were assigned to the absorption band of sulfonic groups of the copolymer samples. By comparison, we could find that the peaks in these samples increased gradually from P-1 to P-5, which indicated the increase of the content of sodium vinyl sulphonate in the copolymer samples.

The compositions of the copolymers were determined by the elemental analysis. The weight percentages of carbon, hydrogen, nitrogen and sulfur from elemental analysis of the samples are presented in Table-1. The actual mole ratio of NIPAAm/SVS in polymer was calculated *via* the weight percentages of nitrogen and sulfur as listed in Table-2. The results indicate that the reactivity ratio of sodium vinyl sulphonate is less than that of NIPAAm in the copolymerization. In addition, the determined copolymer compositions of polymers *via* elemental analysis are in good agreement with the results from  $^1\text{H}$  NMR analysis.

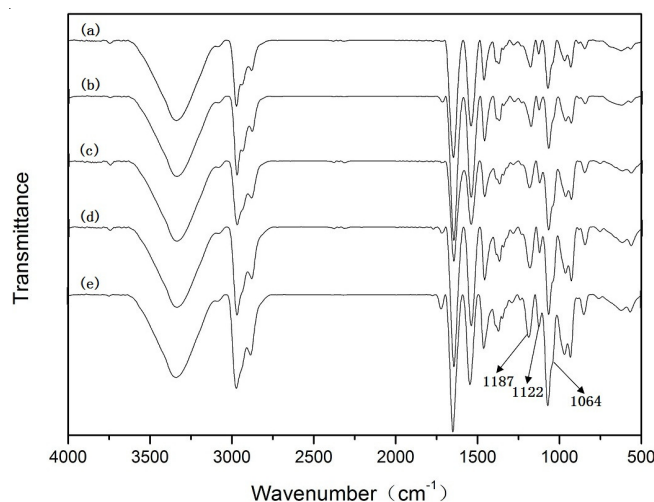


Fig. 2. FT-IR spectra of P-1(a), P-2(b), P-3(c), P-4(d) and P-5(e) samples

The molecular weight (Mw) and polydispersity indices (Mw/Mn) data of the copolymer samples P-1 (a), P-2 (b), P-3 (c), P-4 (d), P-5 (e) were obtained *via* GPC-MALLS. The eluent solution containing 0.1 mol L<sup>-1</sup> NaCl allowed sufficient screening of charges on PNIPAAm-*co*-SVS copolymers for GPC-MALLS analysis. The molecular weights of the copolymers got from GPC-MALLS analysis were shown in Table 2. The Mw values of the copolymers ranged from  $6.307 \times 10^4$  to  $1.539 \times 10^6$  g mol<sup>-1</sup>, while the Mw/Mn values of the copolymers ranged from 1.456 to 1.896. The Mw of the copolymers decreased gradually with the increase of the percentage of sodium vinyl sulphonate in the copolymers.

Figs. 3 and 4 showed the TGA and DTGA curves of five PNIPAAm-*co*-SVS samples with different sodium vinyl sulphonate ratios which were measured under nitrogen atmosphere. The samples show only one major mass loss step in the temperature range of 400 to 450 °C. The reason to explain this may be that the side chain of the sodium vinylsulphonate link is very short and the monomer ratio of sodium vinyl sulphonate is low, there is no obvious weight loss peak of them in the Fig. 3. But as the increase of the sodium vinyl sulphonate monomer ratios, the decomposition temperature of the copolymers decrease gradually, this might result from the decrease of the molecular weight. It indicates the thermal stability of copolymers increase with molecular weight.

**Aggregation of temperature-induced reversible copolymer:** In order to explore the influence of external stimuli on LCST or cloud point of the copolymers, the light transmittance of the copolymer solutions at different temperatures in different pH values, salt concentrations and NIPAAm/SVS ratios were measured. This thermal reversible phase transition in aqueous

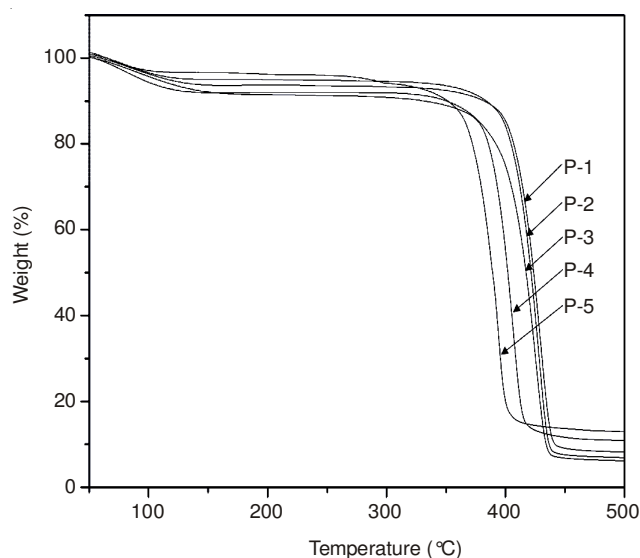


Fig. 3. TGA curves of PNIPAAm-*co*-SVS samples, P-1, P-2, P-3, P-4 and P-5 refer to the copolymers given in Table-1

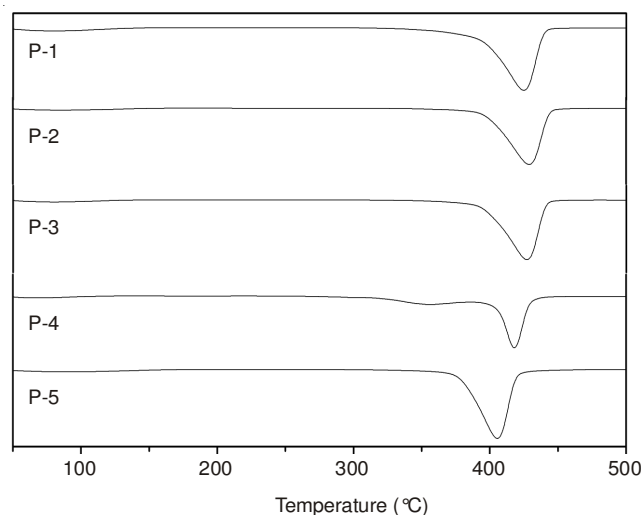


Fig. 4. DTG curves of PNIPAAm-*co*-SVS samples, P-1, P-2, P-3, P-4 and P-5 refer to the copolymers given in Table-1

aqueous solutions is a consequence of the macromolecular transition from a hydrophilic to a hydrophobic structure at this temperature. Since the dissolution and aggregation of the copolymers are completely reversible in a temperature increase and decrease circle, here we just consider the temperature increase process only.

P-4 sample was used to investigate how lower critical solution temperature (LCST) of the copolymer varies with pH values. Fig. 5a shows the visible light transmittance of

TABLE-2  
ELEMENTAL ANALYSIS AND MOLECULAR WEIGHT OF THE FIVE COPOLYMER SAMPLES

Sample	Elemental analysis				Ratio of NIPAAm/SVS in copolymer		Molecular weight		
	C (wt.%)	H (wt.%)	N (wt.%)	S (wt.%)	Determined <i>via</i> elemental analysis	Determined <i>via</i> <sup>1</sup> H NMR	Mw	Mn	Mw/Mn
P-1	55.64	9.343	10.310	1.032	95.8:4.2	95.7:4.3	$1.539 \times 10^6$	$8.260 \times 10^5$	1.863
P-2	53.80	8.936	9.857	1.998	91.9:8.1	92.1:7.9	$2.354 \times 10^5$	$1.617 \times 10^5$	1.456
P-3	50.73	8.315	9.468	2.832	88.7:11.3	88.8:11.2	$1.910 \times 10^5$	$1.179 \times 10^5$	1.620
P-4	47.98	7.847	9.125	3.825	94.4:15.6	84.2:15.8	$1.523 \times 10^5$	$9.207 \times 10^4$	1.654
P-5	45.67	7.356	8.8836	4.618	81.2:18.8	81.3:18.7	$6.307 \times 10^4$	$3.327 \times 10^4$	1.896

PNIPAAm-*co*-SVS solution at different temperatures and different pH values at 500 nm. According to the figure given, we could find that the light transmittance have a sharp decrease at a certain temperature at all these five pH values. In other words, the copolymer sample have different LCSTs at different pH values. Also, from Fig. 5a, we could obtain that, LCST of the copolymer is 34 °C at pH 2, while 39 °C at pH 11, which increase gradually from pH 2 to pH 11, as shown in Fig. 5b. The copolymer has a pH-dependent LCST since sodium vinyl sulphonate is a polyelectrolyte, whose charge density is readily tuned by pH value variation.

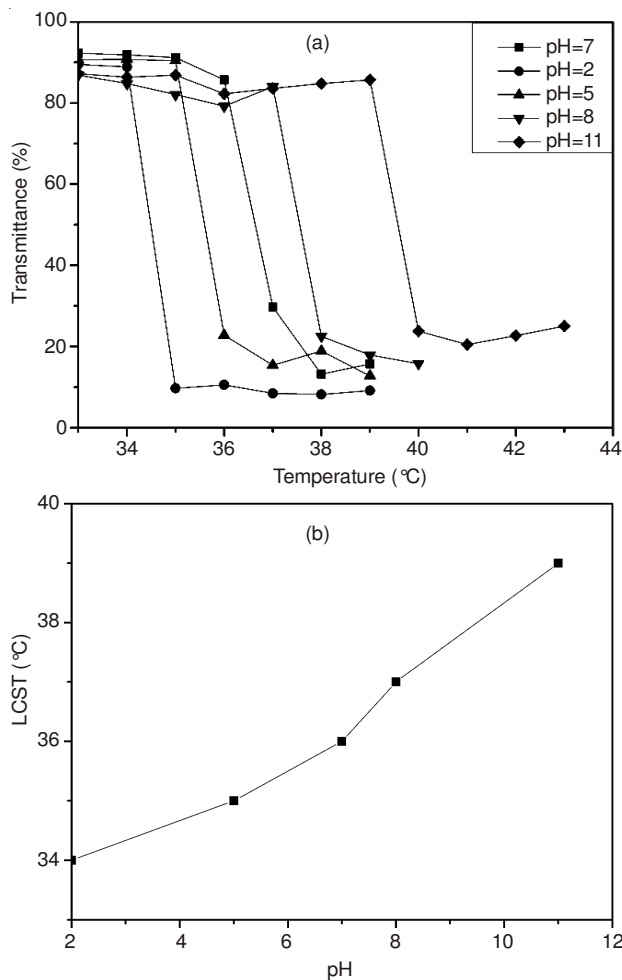


Fig. 5. (a) Visible light transmittance of PNIPAAm-*co*-SVS (P-4) solution at different pH values at 500 nm, (b) LCST ascend slowly as a function of pH value

Further experiments were done to detect the salt concentrations affect on LCST of the copolymer. P-4 sample was also used. The results were displayed in Fig. 6. The concentration of the NaCl solutions varies from 0 to 1 mol L<sup>-1</sup>. As can be seen from the Fig. 6a, the copolymer sample at different salt concentrations have different LCSTs, when there was no NaCl, LCST of the copolymer solution is 36 °C, which is a little higher than that of PNIPAAm homopolymer. LCST decreased to 22 °C when the concentration of NaCl increased to 1 mol L<sup>-1</sup>. From Fig. 6b, we could find that, LCST of the copolymer solution decrease gradually from 36 to 22 °C with the concentration of NaCl increase from 0 to 1 mol L<sup>-1</sup>. The

NaCl in the present system acts undoubtedly as "salt out effect". The effect can be regarded as a result of a decrease of hydrogen bonding among water and the hydrophilic chains and increase of hydrogen bonding among the hydrophilic chains<sup>26</sup>. Besides, the charge repulsion among the sodium vinyl sulphonate segments may also be effectively screened by addition of electrolytes to yield a more coiled molecular conformation. Consequently, the copolymer exhibit a stronger tendency to associate, thus to decreasing their LCSTs.

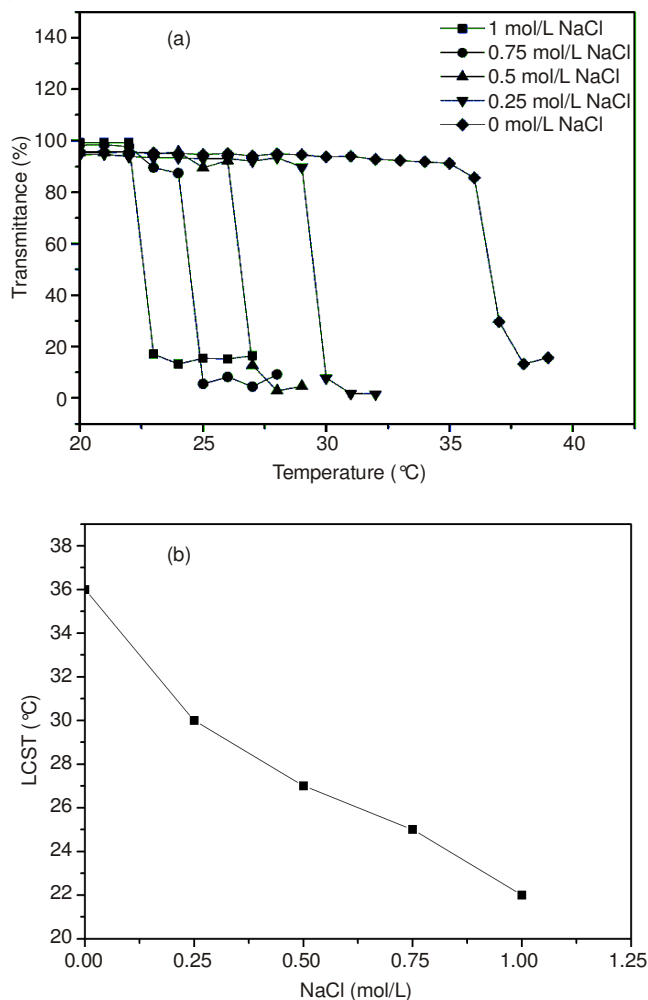


Fig. 6. (a) Visible light transmittance of PNIPAAm-*co*-SVS solution at different NaCl concentrations at 500 nm, (b) LCST reduction as a function of NaCl concentration

LCST of P-1, P-2, P-3, P-4 and P-5 sample, who are different in NIPAAm/SVS ratios were also measured by a visible spectrophotometer at 500 nm, the results were showed in Fig. 7. According to the Fig. 7, we could find that copolymers with different NIPAAm/SVS ratios have different LCSTs, LCST of the PNIPAAm-*co*-SVS copolymer rise gradually from 33 to 37 °C with the increase of sodium vinyl sulphonate ratio. The reason is that, with the increase of the ratio of sodium vinyl sulphonate segments, the charge density of the polymer chains increase, the polymer chains become more stretch for the electrostatic repulsion among polymer chain segments.

**Dynamic laser light scattering:** The aggregation behaviour of PNIPAAm-*co*-sodium vinyl sulphonate copolymer of different compositions in the dilute regime was studied by



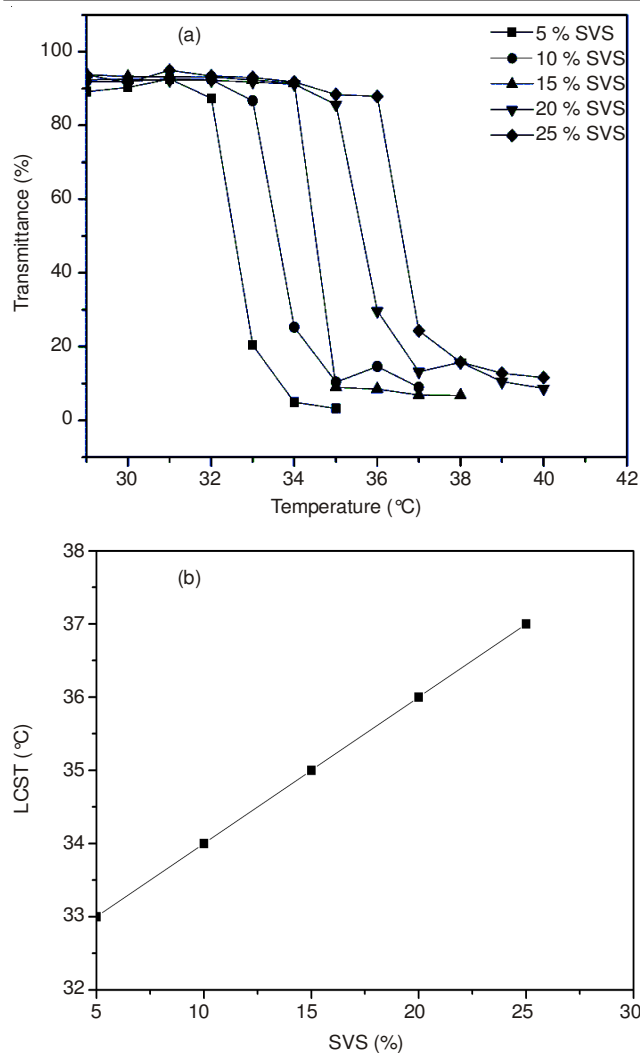


Fig. 7. (a) Visible light transmittance of PNIPAAm-co-SVS solution at different ratio of NIPAAm/SVS at 500 nm, (b) LCST ascend as a function of NIPAAm/SVS ratio

DLS measurement. Fig. 8 shows the average  $R_h$  of five different copolymers in aqueous solution. All the solutions used here were with a concentration of  $2 \text{ g L}^{-1}$ . We could find that the  $R_h$  of the copolymers increase gradually with the increase of the sodium vinyl sulphonate content in the copolymers. The reason to explain this phenomenon may be that with the increase of the sodium vinyl sulphonate segments in the copolymer chains, hydrophilic force of the copolymer chains increase, thus lead to an increase in water-solubility.

In order to investigate the supermolecular structures of PNIPAAm-co-SVS at different solution pH values, dynamic laser light scattering was used to measure the hydrodynamic radius in their aqueous solution. All the measurements were conducted at  $25^\circ\text{C}$ , which is lower than LCST of the copolymer in the pH range of 2–11. The distribution of hydrodynamic radius of copolymer P-4 at different pH values obtained by DLS was shown in Fig. 9. From the results shown, we could find that the  $R_h$  of the copolymer decreased gradually in response to an increase in pH. Due to the existence of the sodium vinyl sulphonate chain links in the polymer chains, the charge density of the copolymer is readily tuned by pH variation. The charge density is a decisive factor to modulate

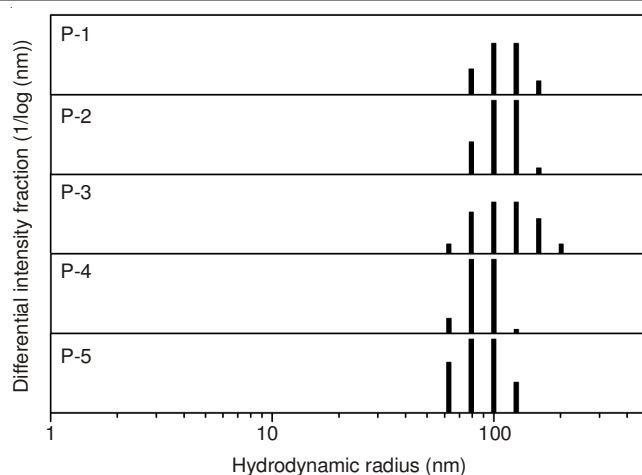


Fig. 8. Hydrodynamic radius distributions of the copolymers at  $25^\circ\text{C}$ , P-1, P-2, P-3, P-4 and P-5 refer to the copolymers given in Table-1

the extent of repulsion between polymer links. This could be responsible for a larger  $R_h$  at lower pH and a smaller  $R_h$  one at higher pH.

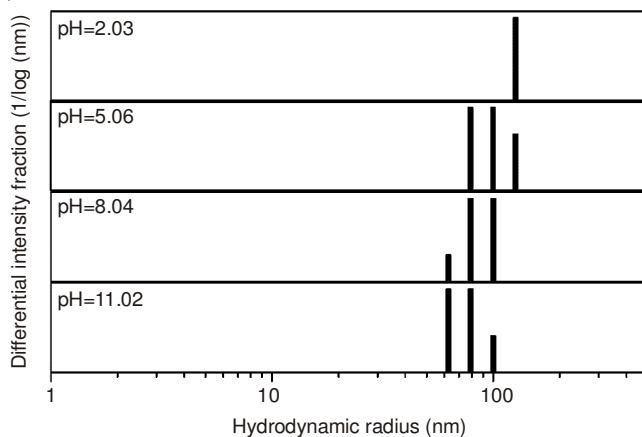


Fig. 9. Hydrodynamic radius distributions of P-4 at different pH

The effect of different concentrations of NaCl on the average hydrodynamic radius of PNIPAAm-co-SVS copolymer is shown in Fig. 10. The experiments were conducted at  $25^\circ\text{C}$  with sample P-4 whose concentration is  $2 \text{ g L}^{-1}$ . As is shown in the Fig. 10, the concentration of NaCl plays an important role in controlling the size of aggregates. When the concentration of the NaCl solutions were  $0.5 \text{ mol L}^{-1}$  and  $0.75 \text{ mol L}^{-1}$ , the  $R_h$  of the copolymers was considerably higher than that of 0 and  $0.25 \text{ mol L}^{-1}$ . This phenomenon attributed to the breakup of the intrachain association and the enhancement of the interchain association due to the increase of ionic strength and intermolecular interactions. From Fig. 10, we could find that when the concentration of NaCl in the aqueous solution is  $0.75 \text{ mol L}^{-1}$ , LCST of the copolymer is about  $25^\circ\text{C}$ , which is approximately the same as the ambient temperature, for the copolymer chains, before reaching the phase transition temperature, water gradually becomes a poor solvent, so that individual ionomer chains undergo an intrachain collapse and at the phase transition temperature, the intrachain collapse and the interchain aggregation are expected to occur simultaneously<sup>27</sup>.

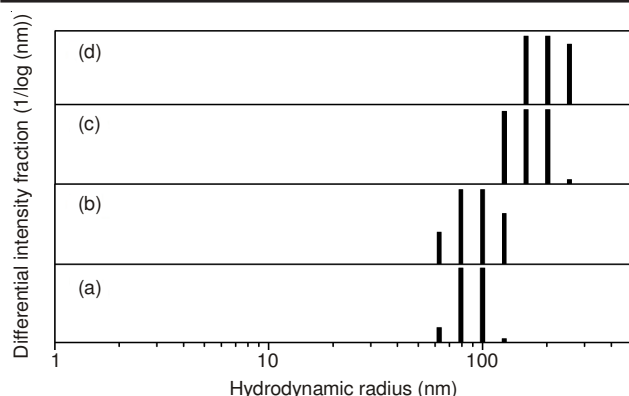


Fig. 10. NaCl concentration dependence of average hydrodynamic radius distribution of P-2 sample with concentration of 2 g L<sup>-1</sup> at 25 °C, (a) cNaCl = 0, (b) cNaCl = 0.25 mol L<sup>-1</sup>, (c) cNaCl = 0.5 mol L<sup>-1</sup>, (d) cNaCl = 0.75 mol L<sup>-1</sup>

## Conclusion

Thermo-sensitive PNIPAAm-*co*-SVS copolymers were successfully prepared by free radical polymerization. The molecular structure and properties of the copolymer were determined *via* <sup>1</sup>H NMR, FT-IR spectroscopy, elemental analysis and TGA. A temperature increase and decrease cycle could cause completely reversible copolymer aggregation above LCST and copolymer dissolution below LCST. The LCSTs of the copolymers can be significantly altered by changes in pH value, salt concentration of the aqueous environment and copolymer composition. Finally, the *R<sub>h</sub>* distributions of the PNIPAAm-*co*-SVS copolymers at different NaCl concentrations, pH values and monomer compositions were achieved by DLS measurements. The results showed that the *R<sub>h</sub>* distributions of the copolymer were affected by all the three factors in the aqueous solution.

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