

# A Novel Route for Synthesis of Temperature Responsive Nanoparticles

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**ABSTRACT:** We report the preparation of responsive silica nanoparticles by reaction of epoxy modified silica with stimuli responsive poly (acrylic acid-*N*-isopropylacrylamide) (poly (AA-*co*-NIPAAm)). A series of copolymers of poly (AA-*co*-NIPAAm) were synthesized by a novel route, employing solid state condensation of polyacrylic acid and isopropyl amine in different feed ratios (44 mol %–100 mol % AA). The structure of the copolymers was characterized by FT-IR, <sup>1</sup>H-NMR. The lower critical solution temperature (LCST) was found to vary with the copolymer composition. The pH dependence of the LCST was also observed, and the copolymers exhibited a higher LCST at neutral pH than at acidic pH (4–5). Selected

copolymers were used to prepare responsive core-shell particles. Silica nanoparticles modified using glycidoxypropyl trimethoxy propyl silane were reacted with the responsive copolymer to form responsive core-shell particles. The influence of reaction conditions on the modification of silica particles and reaction with responsive copolymers was investigated. The hydrodynamic behavior of the synthesized thermo responsive nanoparticles was also studied. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 335–344, 2011

**Key words:** thermo responsive; LCST; smart nanostructures; switchable surfaces

## INTRODUCTION

Environmental responsive or stimuli responsive polymers show a change in their behavior according to the external stimuli. The external stimuli for these “Responsive” polymers can be physical, chemical, or biochemical.<sup>1</sup> These stimuli affect the level of system’s energy and thereby alter molecular interactions at the transition point. Consequently, aqueous solutions of these polymers exhibit abrupt changes in their solubility as a function of environmental temperature.<sup>2,3</sup> Poly(*N*-isopropylacrylamide) (PNIPAAm) has most intensively been studied for the reason that in solution, it demonstrates lower critical solution temperature (LCST) close to 32°C.<sup>4</sup> It is also reported that the LCST of PNIPAAm grafted from the surface of solid substrates, crosslinked hydrogels, and block polymers is nearly identical to the LCST of a homopolymer in aqueous solution. Potential for use of these polymers as switchable substrates for temperature-controlled cell harvesting<sup>5</sup> and for control of bacterial biofouling<sup>6</sup> has also been

demonstrated. The PNIPAAm hydrogels provide a negative temperature-responsibility to the drug release, i.e., slow drug release at higher temperature and rapid drug release at lower temperature.<sup>7</sup> These temperature-triggered materials are particularly useful in water-dispersible products/flushable personal care products such as diapers, tampons, feminine pads, pant liners, etc.

PNIPAAm can be synthesized<sup>7–9</sup> via free radical polymerization or controlled radical polymerizations. UV grafting of NIPAAm on polymer substrates<sup>10</sup> and plasma polymerization of NIPAAm on polyethylene<sup>11,12</sup> and polypropylene membranes<sup>13</sup> have also been reported in the literature. It has been widely studied that by copolymerization, the transition temperature of the temperature-responsive polymers, such as PNIPAAm copolymer, can be tuned to suit particular end application.<sup>14–16</sup>

The chemical reaction/grafting of such responsive copolymers on the surface of inorganic nanoparticles can be utilized for variety of applications. Such nanoparticle/polymer (core/shell) hybrids exhibit properties that are combination of both inorganic nanoparticles (optical, electronic, and mechanical) and those of polymers (solubility, film formation, and chemical activity).

The functionalization of nano silica can be achieved by treatment of nanosilica with epoxy/amino silanes.<sup>17,18</sup> Glycidoxypropyl trimethoxy silane (GPMS) has been used to coat colloidal silica

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with covalent bonding and reactive epoxide group remain on the silica surface. By reaction of temperature sensitive copolymer on epoxy modified silica, we speculate that hybrid nanoparticles suitable for modification of surfaces can be obtained. Additionally, these hybrid particles can also impart roughness to the substrate for enhanced performance. Based on the above considerations, we wish to synthesize responsive hybrid nanoparticles with the capability of modifying textile surfaces to create switchable hydrophobicity.

In the present study, we report a novel method to synthesize thermoresponsive copolymers based on NIPAAm, a temperature responsive monomer, and acrylic acid. The transition temperature in the polymers was tuned by altering the ratio of acrylic acid and NIPAAm moieties. The copolymers were prepared by amidation of polyacrylic acid. The main advantage of this technique is that method eliminates the limitations of the reactivity ratios for synthesis of copolymers. Further, the reactive carboxylic acid groups in responsive copolymer have been used for reaction with epoxy functionalized silica to obtain responsive nanoparticles. These responsive nanoparticles may open up large number of new applications for creating responsive surfaces.

## EXPERIMENTAL

### Material

Azo-bis-isobutyronitrile (AIBN) was obtained from SD Fine Chemicals. Acrylic acid (AA, 99 wt %), toluene, dimethyl ether, isopropylamine, and ethanol were purchased from Merck. Hydrophilic fumed silica (AEROSIL 200) and GLYMO-GPMS were procured from Evonik and used as received.

### Synthesis of poly (acrylic acid)

Poly (acrylic acid) (PAA) was synthesized by suspension polymerization in a toluene using AIBN as an initiator. Briefly 240 g of toluene and 60 g of AA were purged with nitrogen and 0.3 wt % of AIBN (with respect to monomer) was added to this. Polymerization was carried out at 65°C under nitrogen atmosphere with continuous stirring for 3 h. After polymerization, the polymer was isolated by precipitation from diethyl ether. The white precipitate of PAA was washed several times with diethyl ether, filtered, and finally dried under vacuum. The yield of polymer PAA was 60%.

### Synthesis of poly (AA-co-NIPAAm)

The copolymers were synthesized by modification of PAA with isopropyl amine. Ten grams of PAA was

**TABLE I**  
**Feed Molar Ratios of AA Units (in Polyacrylic Acid) and Isopropyl Amine Used for Preparing Different Copolymers**

Polymer code	Poly(acrylic acid) : Isopropyl amine (molar ratio)
P 0.44	1 : 0.44
P 0.54	1 : 0.54
P 0.67	1 : 0.67
P 0.8	1 : 0.8
P 1.0	1 : 1

dissolved in 100 mL of ethanol and stirred to make the clear solution. To this solution, an appropriate amount of isopropyl amine was added with stirring. A white precipitate of the intermediate salt was formed and separated and dried in vacuum for 2–3 h at 100°C. A series of salts of different compositions were prepared by varying the feed ratio of AA units to isopropyl amine from 1 : 0.44 to 1 : 1. The obtained salts were subjected to solid state condensation reaction in a three neck round-bottom flask under nitrogen atmosphere at 140°C for 4 h. Copolymers of varying composition were obtained by this solid state condensation of salts. The copolymers were isolated and coded as PX, where X indicates the proportion of isopropyl amine used (Table I).

### Surface modification of nanosilica

Prior to modification, it is necessary to disperse the silica particles to obtain a uniform dispersion. For this, the effect of pretreatment/dispersion conditions—silica concentration, dispersion method (stirring or sonication), temperature, and time on the size of silica particles was investigated (Table II). Based on these results, a suitable dispersion method was arrived at and was followed for all further experiments. In a typical method, 5 g (2 wt %) of nanosilica was added to a mixture of 100 mL of deionized water and 150 mL of ethanol and stirred for 60 min at 25°C. Subsequently, the mixture was sonicated for 60 min at 55°C and the pH was adjusted to pH 2.

For epoxidation of silica, nanoparticles were dispersed using the conditions indicated for sample code SN7 (Table II). Modification was carried out using GPMS as coupling agent. The surface modification of silica was carried out by varying silane to silica ratio,  $R$ , and epoxidation reaction time. The mixture was refluxed for the prescribed duration. The detailed experimental conditions for each sample and the sample codes are listed in Table III. The samples codes include the silane to silica ratio and treatment time. Afterwards, the mixture was cooled and the translucent nanosilica colloidal solution was

**TABLE II**  
The Effect of Dispersion Conditions on the Particle Size of Silica Nanoparticles

Sample code	Solvent	Silica conc. (wt %)	Treatment			Average particle size (nm)
			Method	Time (min)	Temperature (°C)	
SN 1	Ethanol	0.005	Sonication	15	18	871
SN 2	Ethanol	0.005	Sonication	15	35	536
SN 3	Ethanol	0.005	Sonication	15	55	499
SN 4	Ethanol	0.005	Sonication	30	18	397
SN 5	Ethanol	0.1	Sonication	30	18	428
SN 6	Ethanol	0.1	Stirring	30	18	730
SN 7	Ethanol/water	2.0	Stirring	60	18	
			Sonication	60	55	470

centrifuged at 5000 rpm for 15–30 min to isolate the epoxy modified silica particles. The product was collected, washed with acetone, and dried.

### Synthesis of thermo responsive silica nanoparticles

Epoxidised silica nanoparticle sample (MS1.2–3h) was used along with thermoresponsive copolymer (P 0.67/P 0.54) in the ratio of 1 : 10 (0.2 wt % : 2 wt %) in a 50 : 50 ethanol-water mixture. The reaction was investigated by microwave heating as per the reaction conditions detailed in Table IV.

After the reaction, the silica particles were separated from the suspension by centrifugation and then washed several times by centrifuging/resuspension in deionized water. Finally, the obtained nanosilica particles were dried at 80°C for 5 h in vacuum. The dried responsive nanosilica particles, coded as SiO<sub>2</sub>-P 0.54 (treatment temp, time) or SiO<sub>2</sub>-P0.67 (treatment temp, time), were used for characterization. The modification was confirmed from the thermoresponsive behavior of the isolated silica particles after the treatment.

### Characterization

The polyacrylic acid, various copolymers (poly (AA-co-NIPAAm)), nanosilica, and selected samples of epoxy functionalized nano silica and responsive nanosilica were characterized. FT-IR spectra were recorded on a Perkin-Elmer 7 spectrometer as KBr pellet. The <sup>1</sup>H-NMR spectra were recorded with Bruker Spectrospin 300 MHz using tetramethylsilane (TMS) as the internal reference.

Turbidity test was performed to determine the LCST of the copolymers (poly (AA-co-NIPAAm)). The hydrodynamic diameter of modified nanosilica was measured with Laser particle analyzer (Coulter, LS13, 320). Malvern Zetasizer nano-ZS was used to determine the particle size of thermo responsive nanoparticles and epoxidised nanosilica with increasing temperature to study the swelling behav-

ior. Ethanol was used as the flowing liquid in all cases.

Thermogravimetric measurements were performed on TGA Q 500 system from room temperature to 850°C at a heating rate of 20°C min<sup>-1</sup> under nitrogen atmosphere. The thermal degradation behavior of responsive nanosilica was compared with the Aerosil 200.

## RESULTS AND DISCUSSION

### Synthesis and characterization of poly (acrylic acid-*N*-isopropylacrylamide) copolymers

Poly (*N*-isopropylacrylamide), a well studied thermo-responsive polymer, exhibits the transition (LCST) at 32°C. Radical copolymerization of *N*-isopropylacrylamide with hydrophilic comonomers like AA can be used to design copolymers with the transition temperature higher than 32°C. But, the copolymer composition is governed by the relative copolymerization tendencies/reactivity ratios of the two monomers. The comonomer feed causes a change in the composition of the copolymer as one of the monomer preferentially enters the copolymer. Thus, this causes a drift in the comonomer composition towards the less reactive monomer as the degree of conversion increases. In the present study, a novel

**TABLE III**  
Different Silanization Reaction Conditions Used for Modification of Silica Particles

Sample code	Ratio (GPMS/silica)	Treatment time (h)
MS 0.2–3h	0.2	3
MS 0.4–3h	0.4	3
MS 0.6–3h	0.6	3
MS 0.6–6h	0.6	6
MS 0.6–12h	0.6	12
MS 0.8–3h	0.8	3
MS 1.2–3h	1.2	3
MS 10–3h	10	3

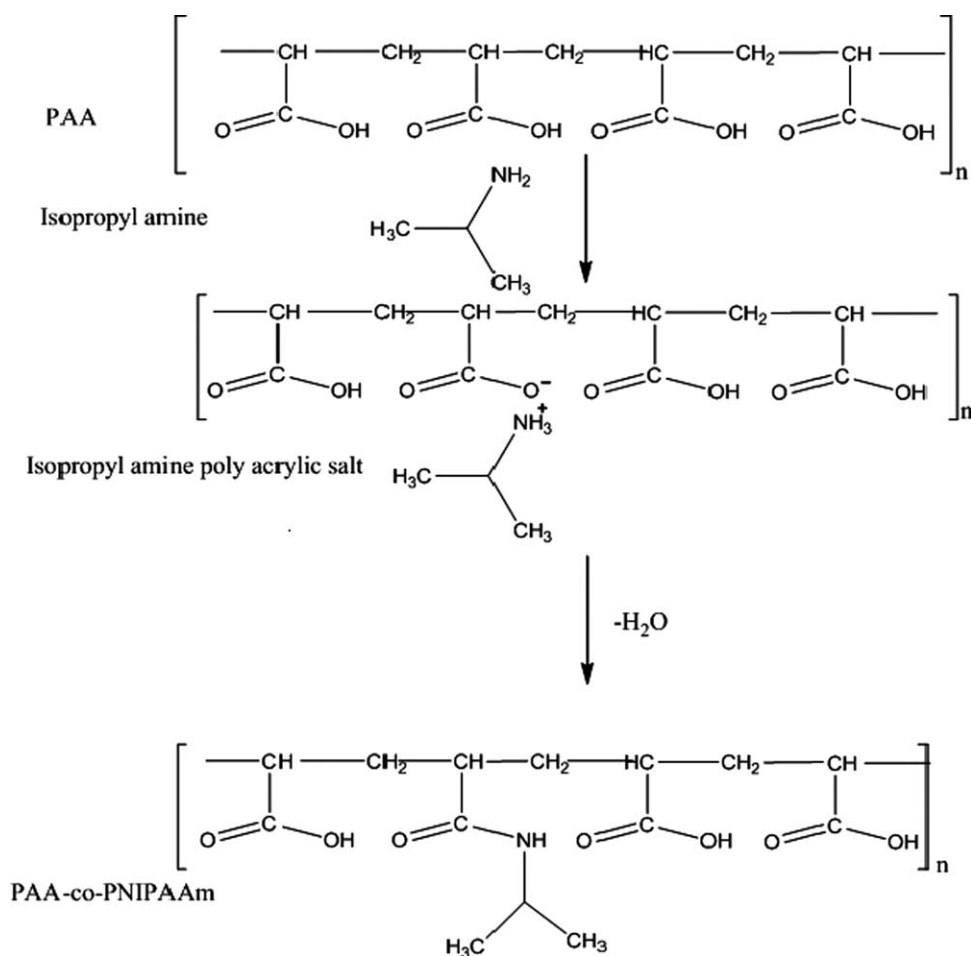
**TABLE IV**  
Effect of Microwave Reaction Conditions on the Formation of Responsive Nanoparticles

Sample code	Copolymer	Temperature (°C)	Time (min)	Response	Gelling
SiO <sub>2</sub> -P0.67 (70,1)	P 0.67	70	1	no	No
SiO <sub>2</sub> -P0.67 (80,1)		80	1	no	No
SiO <sub>2</sub> -P0.67 (90,1)		90	1	yes	No
SiO <sub>2</sub> -P0.54 (70,1)	P 0.54	70	1	no	No
SiO <sub>2</sub> -P0.54 (80,1)		80	1	yes	No
SiO <sub>2</sub> -P0.54 (90,1)		90	1	yes	Yes
SiO <sub>2</sub> -P0.54 (80,1)	P 0.54	80	1	no	No
SiO <sub>2</sub> -P0.54 (80,2)		80	2	yes	No
SiO <sub>2</sub> -P0.54 (80,3)		80	3	no	Yes

synthesis route (as shown in Scheme 1) was followed for the preparation of poly (acrylic acid-*N*-isopropylacrylamide) copolymers starting from poly (acrylic acid). In this approach, the copolymer was obtained by amidation of carboxylic acid groups of PAA with isopropyl amine in definite stoichiometric ratio. As detailed in Table I, a series of responsive copolymers of varying composition of NIPAAm and AA were prepared by varying the proportion of isopropyl amine from 30 to 50 mol % (with respect to

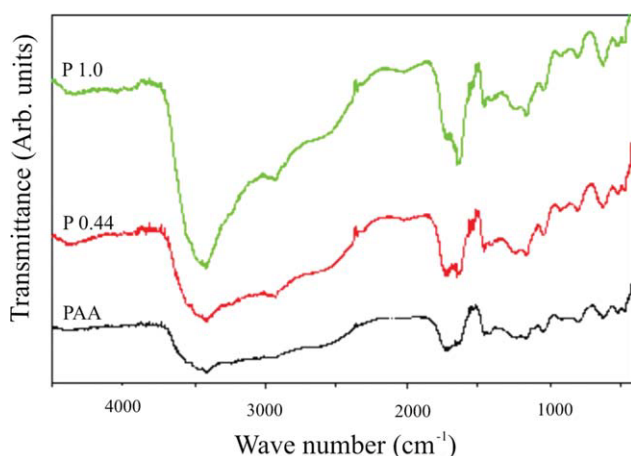
AA moieties). The first step of reaction i.e. the salt formation reaction between the amino groups of isopropyl amine and carboxylic acid groups of PAA was observed to be fast and occurred at room temperature with almost full conversions. The second step of reaction, the solid state condensation (amidation reaction) can occur at high temperature (120–180°C). The synthesis route for the copolymers is shown in Figure 1.

It was observed that at a temperature of 120°C, very long reaction time was necessary for



**Figure 1** Synthesis scheme for poly (AA-co-PNIPAAm).





**Figure 2** FTIR spectra PAA and PAA-*co*-PNIPAAm (a) PAA, (b) P0.44, and (c) P1.0. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

completion of reaction, whereas temperatures above 150°C resulted in non uniform reaction and partial degradation/crosslinking of the product. Therefore, the condensation reaction conditions were optimized in the temperature range of 140–145°C. A series of copolymers were successfully synthesized using the salts prepared by varying molar ratios of AA units to isopropyl amine. FTIR, NMR, and phase transition method were used to confirm the structure and thermo responsive behavior of the synthesized copolymers.

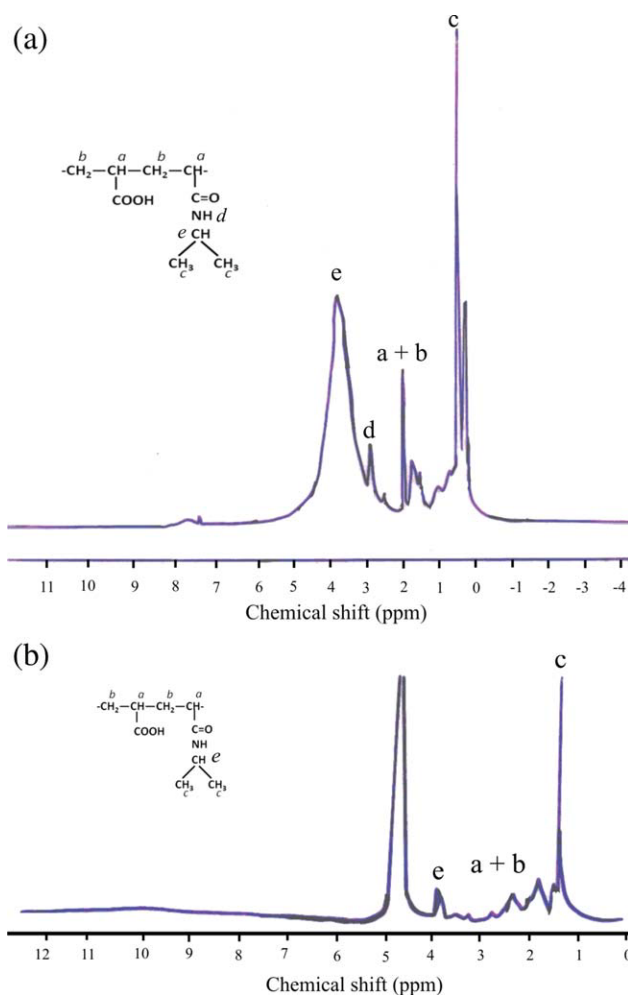
The FTIR spectra of the synthesized PAA and poly (AA-*co*-NIPAAm) were characterized by the typical absorption bands for NIPAAm and carboxylic acid units. The infrared spectrum of PAA had a strong characteristic peak for carbonyl group of carboxylic acid functional groups at 1711  $\text{cm}^{-1}$ . Weaker bands associated with scissoring and bending vibrations of  $-\text{CH}_2-$  were observed at 1445 and 1417  $\text{cm}^{-1}$ , respectively, (Fig. 2). In the spectra of poly (AA-*co*-NIPAAm) copolymers, the intensity of the peak corresponding to the carbonyl stretching of acid groups at 1711  $\text{cm}^{-1}$  was observed to decrease, and additional characteristic stretching vibrations of amide I and amide II at 1640 and 1549  $\text{cm}^{-1}$ , respectively were observed. In the copolymer P1.0, the carboxylic carbonyl stretching peak at 1711  $\text{cm}^{-1}$  appeared as a weak shoulder, indicating almost complete amidation of carboxylic functional groups. The two peaks at 3439  $\text{cm}^{-1}$  and 1161  $\text{cm}^{-1}$  were attributed to the amine group of the copolymer whereas the peak at 2927  $\text{cm}^{-1}$  was assigned to carbon-hydrogen stretching vibration.

$^1\text{H}$ -NMR of the copolymer samples was carried out using  $\text{D}_2\text{O}$  and DMSO as solvents. The assignments of  $^1\text{H}$ -NMR resonance signal are based on the literature.<sup>19,20</sup> Solvent signal position at 4.8 ppm in

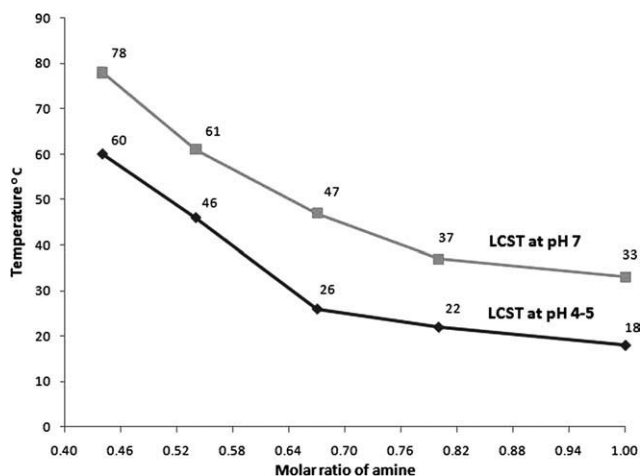
$\text{D}_2\text{O}$  and 2.5 in DMSO has been used to rescale the  $^1\text{H}$  chemical shift of polymers. From Figure 3, the characteristic peaks in the spectra of copolymer can be assigned as (1) 6H,  $\text{CH}_3$  two methyl group of NIPAAm unit at  $\delta$  0.9–1.3 ppm (2) 2H,  $\text{CH}_2$  and 1H, CH of backbone NIPAm unit at  $\delta$  1.2–2.24 ppm (3) 1H, NH  $\delta$  3.2 ppm, and (4) 1H, CH in isopropyl group of NIPAAm unit at  $\delta$  4.0 ppm.

### Transition behavior of poly (AA-*co*-NIPAAm) copolymers in solution

Figure 4 shows the LCST of copolymers prepared with varying ratio of isopropyl amine (at pH 4–5 and pH 7). The phase transition behavior of linear copolymers was found to be quite sensitive, reversible, and reproducible to thermal stimuli. The copolymers exhibit a change in their LCST with change in isopropyl amine feed ratio (change in composition). With increase in amine ratio in the feed from 0.44 to



**Figure 3**  $^1\text{H}$ -NMR spectra of PAA-*co*-PNIPAAm copolymer in (a)  $\text{D}_2\text{O}$  and (b) DMSO. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 4** Dependence of LCST on the mole ratio of amine used for synthesis.

1.0, the LCST of the copolymers decreased from 60 to 18°C and 78 to 33°C in acidic and neutral conditions, respectively. This is because with increase in the amine ratio the conversion of carboxyl groups into acrylamide groups increases. Thus, the copolymer has a higher proportion of amide containing moieties (NIPAAm) compared with the carboxyl groups, which is also confirmed by the FTIR spectra of these copolymers. This increases the hydrophobic content of the copolymer and causes a decrease in the transition temperature (LCST). The LCST can be tailored in the range of 78–33°C.

Secondly, it was found that with the change in pH of the solution the LCST also changes. On changing the solution pH from acidic to neutral, the LCST increases.

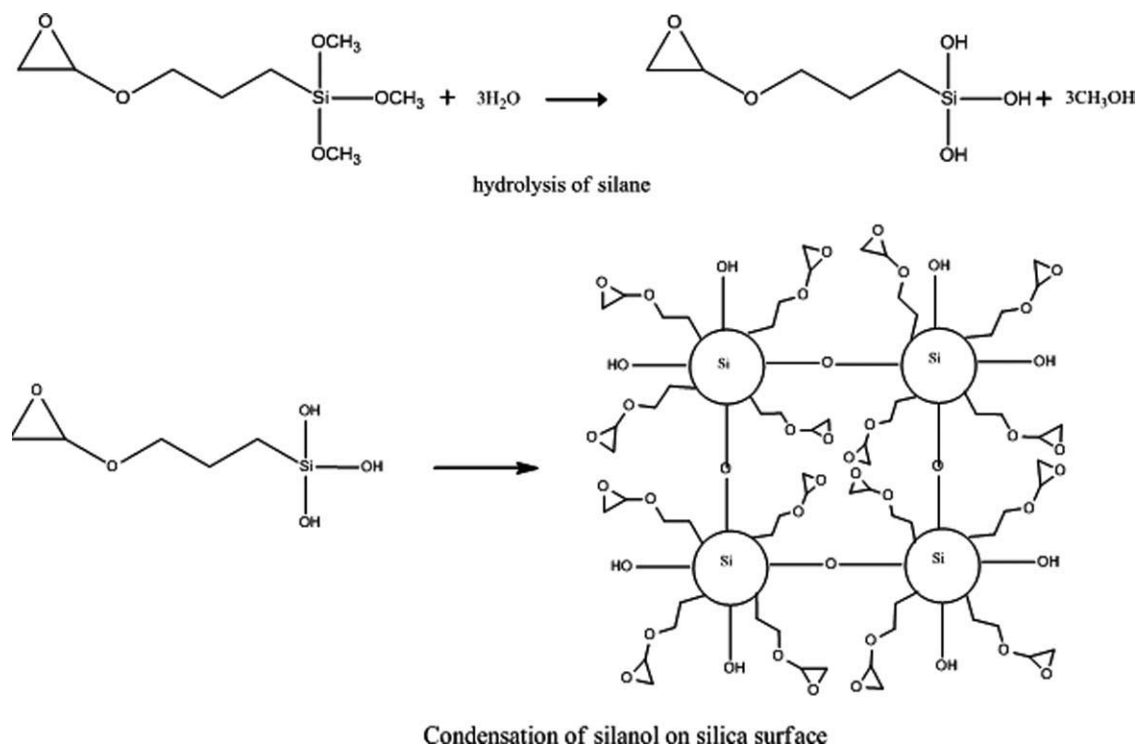
Both the AA and NIPAm components are in their most hydrophilic state at a high pH and low temperature. The loosely coiled conformation of the poly (AA-co-NIPAAm) chains and intermolecular hydrogen bonding with water molecules lead to a higher LCST. At a low pH and high temperature, the PAA chain will become uncharged. Both the AA and NIPAAm components are at their most hydrophobic level. The compact and collapsed conformation of the poly (AA-co-NIPAAm) chains, which is induced by intramolecular hydrogen bonding between C=O, N-H, and the acrylic acid groups in the copolymer chains, leads to a lower LCST. In the other conditions i.e., both pH and temperature either higher or lower, the LCST is decided by the competition of the intermolecular and intramolecular hydrogen bonding.

#### Surface modification and characterization of nanosilica

It is known that silica particles can be used along with other coatings to create surface roughness. If

the silica nanoparticles are modified with reactive groups such that it reacts to the organic surfaces as well as with functional/responsive polymers, then such a hybrid materials can be used for surface modification. It is expected that by using such a combination in two-step process or using polymer/silica hybrid structures in one-step process, durable textile finishes with surface roughness can be achieved. To synthesize polymer/silica hybrid structures from silica particles, it is first necessary to synthesize modified/epoxy functionalized silica particles of uniform size from silica nanodispersion. Several factors are expected to influence the silica surface treatment, including the type of coupling agent, concentration of coupling agent, treatment time, and method of predispersion.

First, the effect of various dispersion conditions (as shown in Table II) on the size of silica particles was studied and it was found that the sonication of 0.005 wt % of silica at 18°C (RT) for 15 min resulted in average particle size of 871 nm (SN1). An increase in the dispersion media temperature to 35 and 55°C was found to reduce the particle size to 536 and 499 nm, respectively, (SN 2 and SN 3). Increased time of sonication (30 min) at room temperature was observed to have a greater effect in reducing the average size than the higher temperature (SN3 and SN4). Increase in the silica concentration from 0.005 to 0.1 wt % caused a marginal difference in the average particle size. Also, the mechanical stirring instead of sonication was not effective in reducing the particle aggregates. The sonication of 0.005 wt % of silica for 30 min at 18°C average particle size was 397 nm, but on increasing the concentration of silica to 0.1% and keeping the other conditions (temperature and time) same, a slightly higher average particle size of 428 nm was observed. Interestingly, mechanical stirring under the same dispersion conditions was observed to result in a significantly higher average particle size (730 nm). In another set of experiment (S7), the effect of higher concentration of silica particles in a medium of increased polarity (water : ethanol mixture) and combination of both mechanical stirring and sonication on the dispersion behavior was examined. It is known that fine particles dispersed in the polar medium acquire surface charges because of ionization or dissociation of surface groups or adsorption of ions onto the surface.<sup>21</sup> Hence, they are expected to remain suspended in the dispersion for a long period of time because of the electrostatic repulsion between the charged surfaces. Even with increased silica particle concentration (2 wt %), very stable dispersion with average particle size of 470 was obtained. Based on these results, the dispersion conditions of sample SN7 were selected as optimal conditions for pretreatment/predispersion.



**Figure 5** Schematic illustration of epoxy modification of silica nanoparticles.

For the chemical reaction of nanoparticles to a polymer or substrate, it must have appropriate reactive groups on its surface. For this, functional silane coupling agents with epoxy functional groups, e.g., GPMS can be used for surface modification of silica nanoparticles.

GPMS contains three hydrolysable methoxy groups and an epoxy-functional propyl chain. Under the acidic reaction conditions, the attachment of GPMS onto the surface of silica particles is obtained by condensation reaction between OH groups present on the oxide surface and silanol groups formed by hydrolysis of GPMS. The modification reaction was studied by varying silane to silica weight ratio (from 0.2 to 10) and reaction time (from 3 to 12 h).

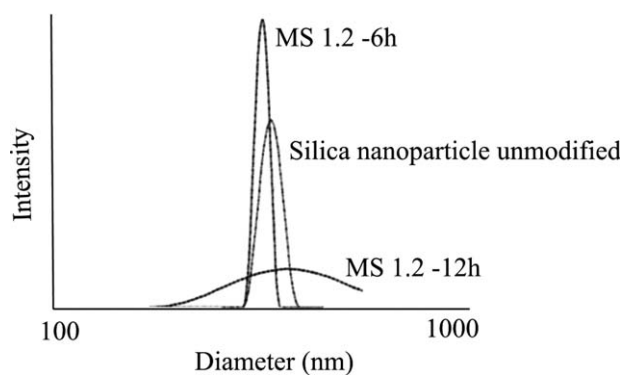
The condensation reaction was monitored/identified by means of simultaneous disappearance (or reduction in intensity) of bands assigned to functional groups of silanes e.g., methoxy, as well as silanol groups on silica nanoparticles. FTIR was used for qualitative analysis of silanol content on particle surface for different GPMS:SiO<sub>2</sub> weight ratios (ratio) and varying reaction times. In the FTIR spectrum, absorption bands at 1104 cm<sup>-1</sup> and 806 cm<sup>-1</sup> were attributed to Si—O—Si asymmetric and symmetric stretching vibration respectively. In addition a band at 477 cm<sup>-1</sup> was observed corresponding to rocking vibration of Si—O—Si. In the FTIR spectrum of modified silica, the C—H stretching vibration corresponding to epoxy group and alkyl chain were observed at 2962 and 2932 cm<sup>-1</sup>, respectively. A typical

breathing vibration of epoxy ring was assigned at 1262 cm<sup>-1</sup> along with C—O—C vibration at 1196 cm<sup>-1</sup>. The band at 1400 cm<sup>-1</sup> was assigned to CH<sub>2</sub> bending and the broad band around 3450 cm<sup>-1</sup> indicated the presence of Si—OH. However, the intensity of absorption peak at 3450 cm<sup>-1</sup> related to the presence of silanol groups was observed to be lower in the treated silica than that in the untreated silica (Aerosil 200).

At low silane concentration (GPMS/Silica ratio 0.2), the epoxy content of the modified silica was not sufficient, whereas, at very high silane concentration (GPMS/Silica ratio 10), condensation reactions of highly reactive hydrolyzed silane molecules were observed to be dominant. Therefore, GPMS/silica ratio of 1.2 was chosen for modification of silica. As depicted in Figure 5, a functional siloxane shell is formed around the silica nanoparticles, which can be subsequently utilized for further crosslinking reactions.

The hydrodynamic diameter of the epoxy functionalized silica was studied to arrive at appropriate dispersion conditions (i.e., treatment time). In acidic dispersion media, the average particle size of Aerosil 200 was observed to be ~ 488 nm. As shown in Figure 6, at  $R = 1.2$ , treatment time of 6 h resulted in modified silica nanoparticles of lower average size (472 nm) and narrow dispersity, compared with 12-h treatment time.

The surface modification of nanosilica was also characterized by TGA (Fig. 7). In spite of very



**Figure 6** Average particle diameters of modified silica nanoparticles with varying treatment time.

thorough drying (at 110°C for 6 h), the thermogram of Aerosil 200 exhibited weight loss of  $\sim 1.5$  wt % mainly because of absorbed moisture. The epoxy modified silica exhibited two weight loss peaks, first corresponding to  $\sim 11$  wt % before 300°C and second  $\sim 26$  wt % from 300 to 800°C. The first weight loss may be ascribed to physically absorbed water on the surface (due to large surface area of nanoparticles) and the chemically bonded water as well as residual organics, typically ethanol, from the sol-gel process of the nano silica modification. The debonding and degradation of chemically attached silane functional group on the surface of modified nanosilica were responsible for the continuous weight loss observed from 300°C onwards.

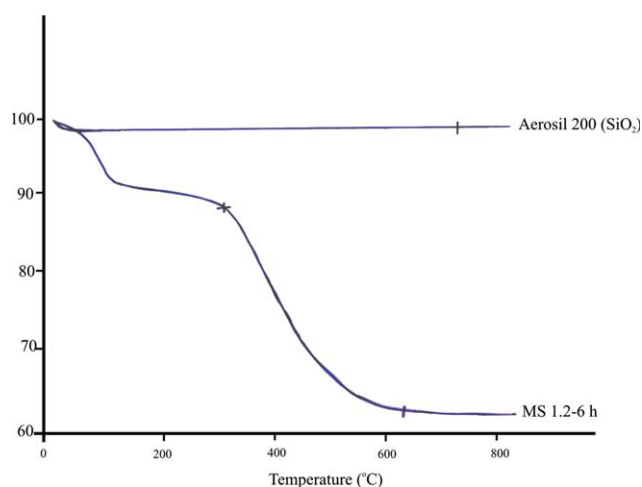
### Synthesis and characterization of thermoresponsive silica nanoparticles

The reaction of epoxy functionalized silica particles prepared using  $R = 1.2$  (GPMS/Silica ratio) and treatment time of 6 h was studied with responsive copolymer P 0.54 and P 0.67. It is expected that the reaction of responsive copolymer on silica nanoparticles would result in responsive hybrid particles; hence the attachment of the copolymer on the nanosilica core can be evidenced by responsive nature of the modified silica nanoparticles. As indicated in Table IV, the samples modified by microwave treatment at 70°C and 80°C for 1 min did not show any response to temperature of the environment. However, treatment at 90°C for 1 min resulted in responsive silica particles. Further, it was observed that under the same reaction conditions, the sample modified with copolymer P 0.54 exhibited gelling, probably because of the crosslinking of acid functional groups. This may be because of the presence of more number of carboxyl groups in the copolymer P 0.54 compared with P 0.67. To limit this crosslinking, the reaction with copolymer P 0.54 was investigated at lower temperature (80°C) and the

effect of varying reaction time was studied. Interestingly, the treatment for 2 min resulted in responsive hybrid silica particles, whereas the treatment for 3 min was sufficient to initiate crosslinking. Therefore, it is pertinent from the above study that optimal reaction conditions for the synthesis of different copolymer silica combination are different. Figure 8 illustrates the attachment of epoxy functionalized silica particles with responsive copolymer.

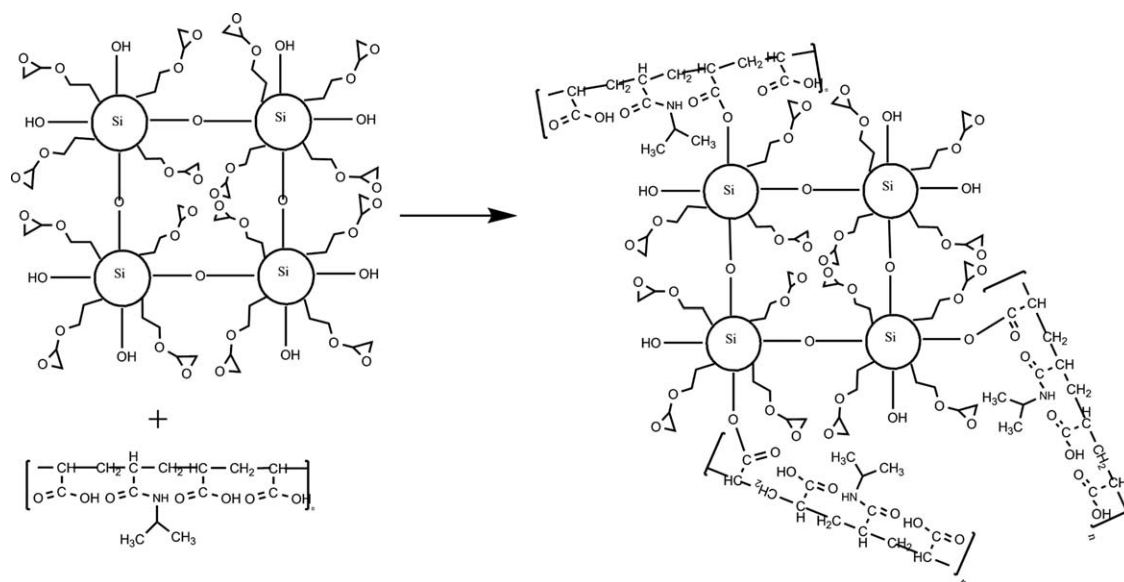
Figure 9 shows the FTIR of the responsive hybrid nanoparticles prepared using copolymer P 0.54 by microwave treatment at 80°C for 2 min. In addition to the Si—O—Si peak at 1106  $\text{cm}^{-1}$ , the FTIR spectrum, exhibited additional characteristic bands for amide I at 1621  $\text{cm}^{-1}$ , C—H stretching vibration at 2925 and N—H stretching vibration at 3419  $\text{cm}^{-1}$ . This further confirms the chemical attachment of responsive copolymer to the silica.

We further measured the hydrodynamic diameter/volume of the hybrid particles ( $\text{SiO}_2$ -P0.67 (90,1)) at various temperatures increasing from 25 to 60°C and also in the reverse order (decreasing order). As shown in Figure 10, an increase in temperature of the environment (solution) led to considerable decrease in the hydrodynamic diameter, which was measured by particle size analyzer. The hydrodynamic diameter did not change significantly with the temperature increasing from 25 to 35°C. But from 35 to 55°C, the diameter decreased from 2366 to 1146 nm. This decrease in hydrodynamic diameter corresponds to nearly eight times of decrease in the volume of hybrid silica particles. The polymer chains hydrate and stay in extended structure when the solution temperature is below the transition temperature, giving rise to hydrophilic structure and swelling of shell. In contrast, the polymer chains form intramolecular hydrogen bonds and dehydrate when



**Figure 7** TGA of Aerosil 200 and modified silica nanoparticle.

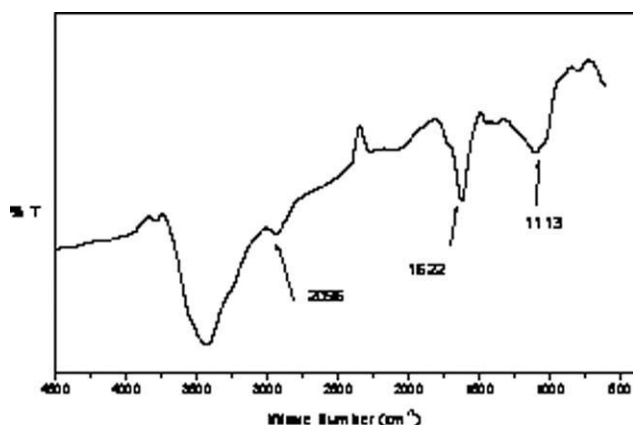




**Figure 8** Schematic illustration of attachment of responsive copolymer on epoxy modified silica nanoparticles.

solution temperature is increased above transition temperature, resulting in compact/shrunk hydrophobic structures.

Interestingly, the copolymer, originally with a LCST of 47°C resulted in hybrid particles of lower LCST (42°C–43°C), indicating a decrease in hydrophilicity of the hybrid particles. These smart hybrid particles can be used to create responsive surfaces that exhibit reversible wettability response to temperature. These surfaces with tunable hydrophobicity may find applications in controlled drug release, molecular filtering, microflow regulation, etc. We expect that these pH and thermo responsive nanoparticles may find application in textiles to create switchable surfaces that exhibit reversible wettability. Further studies addressing in this direction are now underway.



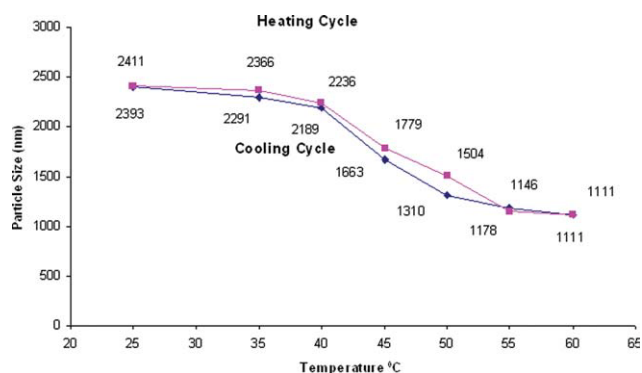
**Figure 9** FTIR spectrum thermo responsive silica nanoparticles.

## CONCLUSIONS

A series of dual responsive (temperature and pH) linear copolymers of AA and NIPAAm were successfully synthesized by solid state condensation of PAA with isopropyl amine. The copolymers exhibited sharp LCST in the range of 33°C–78°C.

FTIR, <sup>1</sup>H-NMR and LCST test confirmed the architecture of copolymer. Further, some selected copolymers were reacted with epoxy functionalized nano-silica to prepare smart nanostructures.

Nanosilica was modified successfully by sonication and condensation with GPMS at  $R = 1.2$  and treatment time of 6 h. Modified silica particles of average size 472 nm were used for synthesis of responsive silica particles. The condensation of epoxy modified silica was successfully carried out by a facile approach via microwave treatment with



**Figure 10** Change in particle size of thermo responsive silica particles (SiO<sub>2</sub>-P0.67 (90, 1)) with temperature. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

responsive copolymer (P0.54 and P0.67). The hydrodynamic diameter of the synthesized responsive hybrid particles (SiO<sub>2</sub>-P0.67 (90,1)) showed a reversible change in the diameter from 2366 to 1146 nm with change in temperature. The coupling of nanoparticles with stimuli responsive polymers is expected to be a promising approach for the development of smart responsive surfaces that exhibit reversible wettability.

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