

Synthesis and Characterization of Novel, Temperature-Sensitive Microgels Based on *N*-Isopropylacrylamide and *tert*-Butyl Acrylate

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ABSTRACT: A series of temperature-sensitive microgels based on *N*-isopropylacrylamide as the main monomer, *tert*-butyl acrylate (tBA) as the comonomer, and *N,N'*-methylene-bis(acrylamide) as the crosslinker were synthesized with a modified surfactant-free emulsion polymerization method. The chemical structure and global shape with an excellent monodispersity of the microgels were confirmed by Fourier transform infrared spectroscopy and scanning electron microscopy, respectively. The temperature-sensitive behavior of the microgels was investigated by dynamic light scattering and ultraviolet-visible spectrophotometric analysis. The results show that the volume phase-transition

temperature of the poly(*N*-isopropylacrylamide-*co-tert*-butyl acrylate) [poly(NIPAM-*co*-tBA)] microgels were tuned over a broad range by the incorporated amount of tBA comonomer and their temperature sensitivity decreased with increasing content of tBA units incorporated into the microgel network. Furthermore, the swelling ratios of the poly(NIPAM-*co*-tBA) microgels were lowered gradually with increasing tBA unit content within the microgel network. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 2962–2967, 2007

Key words: microgels; synthesis

INTRODUCTION

Much attention, in recent years, has been directed at pH-sensitive and temperature-sensitive microgels due to their potential applications in numerous fields, including drug delivery,¹ chemical separation,² and luminescent materials.³ These microgels can be defined as crosslinked, and, stable colloidal particles ranging in diameter from 10 to 1000 nm and can undergo a reversible phase transition in media in response to subtle changes in pH and temperature.⁴

Various methods, including free-radical emulsion copolymerization,^{5,6} surfactant-free emulsion polymerization (SFEP),⁷ reverse emulsion polymerization,⁸ dispersion polymerization,⁹ block copolymerization,¹⁰ and interpenetration networks,^{11,12} have been reported for the preparation of pH-sensitive and temperature-sensitive microgels, among which microgels based on the emulsion copolymerization (with or without surfactant) of *N*-isopropylacrylamide (NIPAM) with a pH-sensitive vinyl monomer such as acrylic acid,^{13–17}

methacrylic acid (MAA),^{18,19} or vinyl acetic acid²⁰ have been extensively studied.

For microgels synthesized by copolymerization methods, however, there are some drawbacks that result from the hydrophilic properties of acrylic acid or MAA. First, the amount of pH-sensitive comonomer greatly affects the volume phase-transition temperature (VPTT) and hydrodynamic diameter (D_H). In addition, the phase-transition temperature of the microgels strongly depends on the degree of ionization of the pendant carboxyl or amine groups. In light of these disadvantages, many researchers have made various attempts. Hoare and Pelton²¹ prepared a series of temperature-sensitive poly(*N*-isopropylacrylamide) (PNIPAM) based microgels containing carboxylic acid functional groups via copolymerization with MAA and acrylamide, which was selectively hydrolyzed under optimized conditions to generate the carboxylic acid functionality.

It is well known that the VPTT of PNIPAM-based microgels can be reduced by copolymerization with hydrophobic monomers.²² Ma et al.²³ synthesized a series of PNIPAM-based temperature-sensitive microgels and selected feebly hydrophobic ethyl methacrylate (EMA) as the comonomer, whose VPTT decreased as the content of EMA increased. Chowdhry et al.²⁴ found that the incorporation of vinyl laurate monomer with strong hydrophobicity had little effect on

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TABLE I
Feed Compositions of Poly(NIPAM-co-tBA) Microgels

Microgel code	NIPAM (mmol)	tBA (mmol)	MBA (mmol)	APS (mmol)	Water (mL)
MG0	12.4	0	0.7	0.45	150
MG16	12.4	1.6	0.7	0.45	150
MG24	12.4	2.4	0.7	0.45	150
MG32	12.4	3.2	0.7	0.45	150
MG48	12.4	4.8	0.7	0.45	150

VPTT of PNIPAM microgels because a core-shell-type structure was formed.

According to the studies mentioned previously, we designed a novel route for the preparation of dual pH-sensitive and temperature-sensitive microgels of PNIPAM with hydrophobic *tert*-butyl acrylate (tBA) as the comonomer by SFEP method, which tends to hydrolyze under acidic or basic condition. The temperature sensitivity of the microgels was examined by dynamic light scattering (DLS) and ultraviolet-visible (UV-vis) spectrophotometric analysis. In addition, the chemical and morphological structures of the microgels were investigated by means of Fourier transform infrared (FTIR) spectroscopy and scanning electron microscopy (SEM).

EXPERIMENTAL

Materials

Before polymerization, NIPAM (95%, Tokyo Kasei Kogyo Co., Tokyo, Japan) and tBA (98%, Tokyo Kasei Kogyo Co., Tokyo, Japan) were purified by recrystallization from a mixture of toluene and hexane (60 : 40 v/v) and distilled under reduced pressure to remove inhibitor. *N,N'*-methylene-bis(acrylamide) (MBA; 95%, Aldrich, USA) and ammonium persulfate (APS; analytical grade, Shanghai Chemical Reagent Co., Shanghai, China) were recrystallized from methanol and ethanol solvents, respectively. All water used in the synthesis and characterization of the microgels was Millipore Milli-Q grade.

Synthesis of NIPAM-co-tBA microgels

Poly(*N*-isopropylacrylamide-co-*tert*-butyl acrylate) [poly(NIPAM-co-tBA)] microgels were synthesized by surfactant-free radical emulsion polymerization. A fixed molar ratio of NIPAM and MBA was dissolved in 150 mL of deionized water until it turned transparent, and then, different amounts of tBA were injected immediately into the mixture with a micropipette. The reaction was operated in a four-necked, round-bottom flask equipped with a condenser (a fap funnel), a thermometer, and a nitrogen inlet under continuous stirring with a corn rotor and nitrogen stream to eliminate oxygen. After the solution was heated to 70°C for

30 min, APS (dissolved in 10 mL of water) was added to initiate the polymerization. The color of solution turned sky blue from transparent until it reached an ultimate ivory white. The reaction proceeded for 6 h at a constant temperature. Then, the microgel suspension was cooled for 12 h under continuous stirring and a nitrogen stream. The crude microgel was cleaned via repetitive centrifugation and was then decanted and redispersed in deionized water. The feed compositions of these microgels are listed in Table I.

Characterization of the poly(NIPAM-co-tBA) microgels

FTIR spectroscopy

Before the measurement, the purified latex microgel particles were dried at room temperature in a vacuum oven and ground into a powder. The chemical structure was analyzed with an FTIR spectrometer (Nicolet Instruments Co., NEXUS-670, Madison, WI) with a KBr tablet containing microgel powders.

SEM

We prepared the SEM sample by dropping a tiny microgel latex onto a cover glass and allowing it to dry. To observe the morphology of the latex microgel particles, SEM observation was performed on the gold-sputtered specimens with a JSM-5600LV instrument (Jeol, Tokyo, Japan).

DLS

D_H and size distribution of the microgel particles at different temperatures ranging from 5 to 50°C were determined by DLS (Mastersizer 2000, Malvern Instruments Ltd., Worcestershire, UK) at a scattering angle of 90° and were collected on a Malvern digital correlator. The scattered light of a polarized argon laser beam with a wavelength of 532 nm was used. The temperature of the dispersions was maintained by a Peltier thermocouple stage, and the samples were equilibrated at each temperature for a minimum of 20 min to arrive at swelling/deswelling equilibrium in water before data collection. Data were analyzed with the Malvern software provided by the manufacturer. D_H under each temperature was the mean D_H of three measurements.

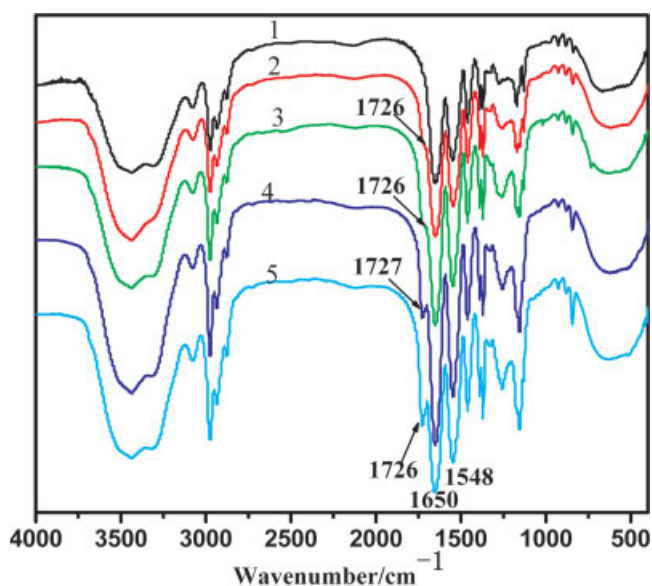


Figure 1 FTIR spectra of the poly(NIPAM-*co*-tBA) microgels: (1) MG0, (2) MG16, (3) MG24, (4) MG32, and (5) MG48. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

UV-vis spectrophotometric analysis

The temperature dependence of the conformational transitions of the microgel dispersions was determined turbidimetrically (at 500 nm) against ultraclear water with a PerkinElmer (Boston, MA) Landa 35 UV-vis spectrophotometer equipped with two storage loops for the purpose of cooling. The undiluted dispersions were heated from 15 to 50°C at a heating rate of 1°C/min. The temperature in the sample cell was monitored with a platform thermocouple and was kept constant for 2 min.

Swelling (or deswelling) ratio (α)

α is defined as the volume ratio before and after phase transition, which can be calculated with the following equation:

$$\alpha = \frac{V_{\text{Swollen}}}{V_{\text{Shrunken}}} = \left(\frac{D_{H,5^\circ\text{C}}}{D_{H,50^\circ\text{C}}} \right)^3 \quad (1)$$

Here, α was determined by the ratio of the particle size measured by DLS at 5°C to that at 50°C. V_{Swollen} and V_{Shrunken} were the volume of microgel particles in the swollen and shrunken states, respectively.

RESULTS AND DISCUSSION

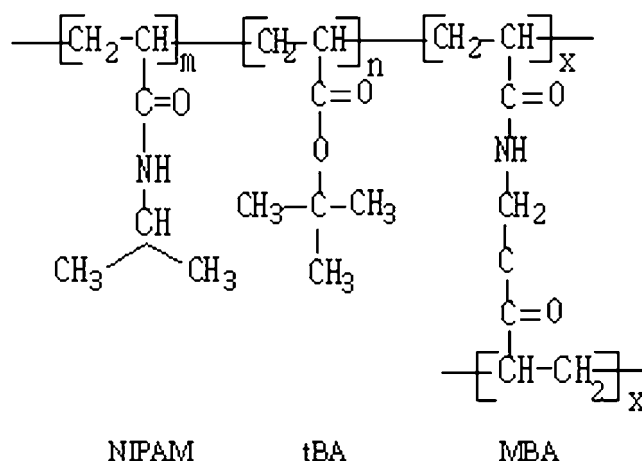
Forming mechanism of the poly(NIPAM-*co*-tBA) microgels

The new-type temperature-sensitive microgel was prepared by copolymerization of the hydrophilic NIPAM

monomer, hydrophobic tBA monomer, and MBA crosslinking agent through the SFEP method. A drop of tBA was injected into the NIPAM and MBA mixture solution with continuous stirring to form the aqueous dispersion. Despite the insolubility of the tBA monomer in water, it was miscible with the aqueous solution of NIPAM and tBA because the hydrophilic amide and hydrophobic isopropyl segments among the NIPAM molecule chain could enhance the solubilization of tBA. Accordingly, a small quantity of micelles was congregated by numerous molecules. Generally speaking, the reactive activity of an acrylamide monomer is higher than that of acrylate. The polymerization between aqueous NIPAM and MBA was initiated first, and the free-radical chains of poly[*N*-isopropylacrylamide-*co*-*N,N'*-methylene-bis(acrylamide)] [poly(NIPAM-*co*-MBA)] oligomers were formed because the polymerization was conducted at 70°C, above the lower critical solution temperature of PNIPAM. The growing poly(NIPAM-*co*-MBA) chains underwent a coil-to-globule transition to form primary particles; this was similar to the nucleation period in the SFEP system. Next, the tBA solubilized by NIPAM was gradually transferred to the interior of primary particles, followed by a chain propagation reaction with NIPAM and MBA among the particles until the colloidal microgel particles were formed ultimately. Furthermore, because sulfate groups decomposed by the persulfate initiator was located on the surfaces of microgel particles, the microgel particles were colloidal stabilized by electrostatic repulsion.

FTIR analysis

The FTIR spectra of poly(NIPAM-*co*-tBA) microgels shown in Figure 1 presents typical bands of PNIPAM (3290–3300 cm^{-1} for N–H stretching; 2973, 2934, and 2876 cm^{-1} for C–H stretching; $\sim 1650 \text{ cm}^{-1}$ for the amide I band assigned to C=O stretching; $\sim 1547 \text{ cm}^{-1}$



Scheme 1 Schematic illustration of the molecular skeleton of the prepared microgels.

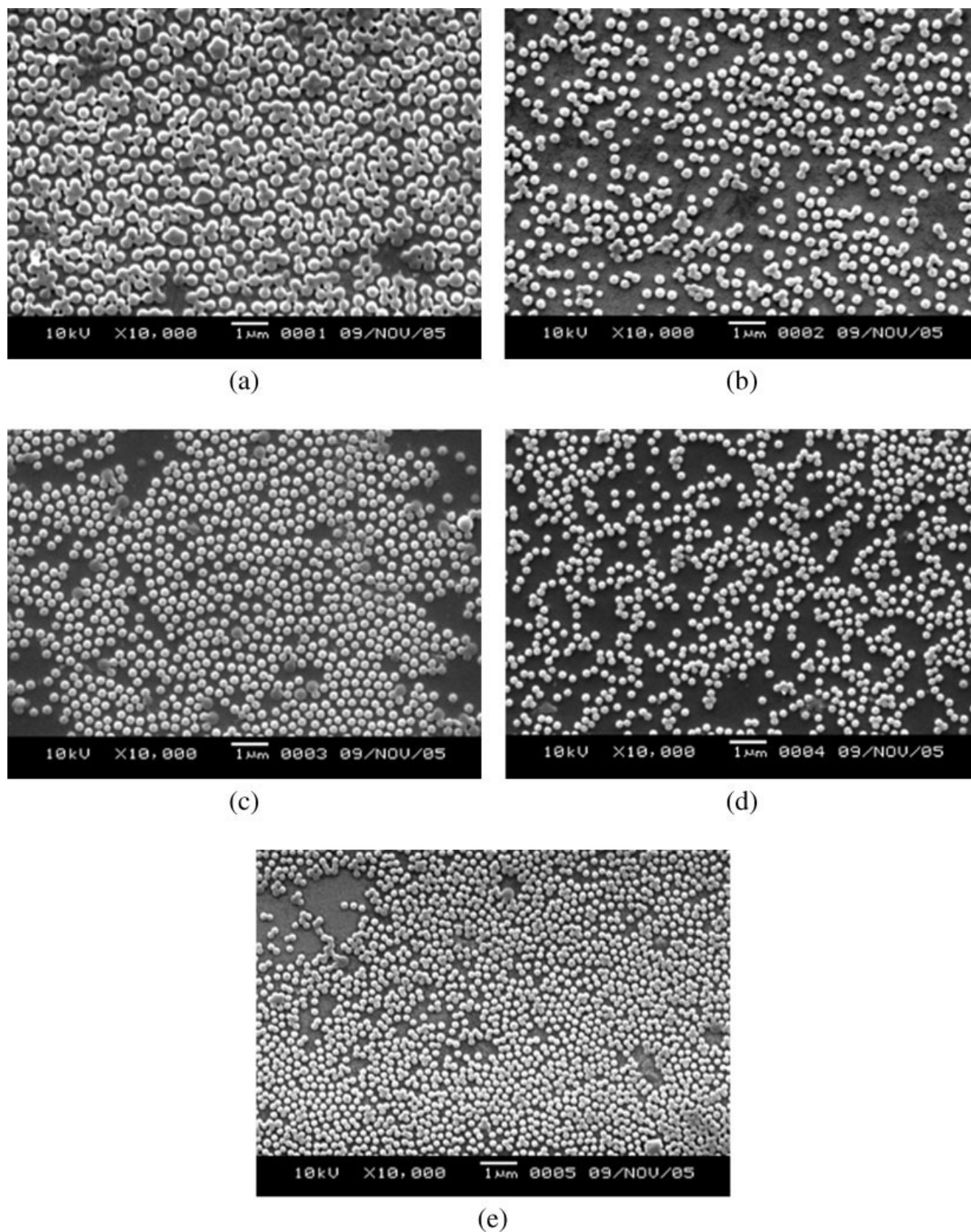


Figure 2 SEM micrographs of the poly(NIPAM-co-tBA) microgels: (a) MG0, (b) MG16, (c) MG24, (d) MG32, and (e) MG48.

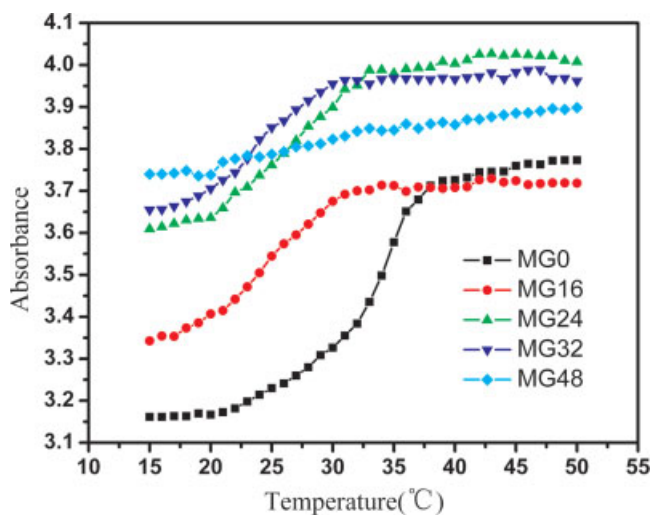


Figure 3 Curves of the absorbency variation of the poly(NIPAM-*co*-tBA) microgel dispersions versus temperature. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

for the amide II band assigned to N—H in-plane bending vibrations; and $\sim 1273\text{ cm}^{-1}$ for the amide III band assigned to the C—N stretching characterization peak). Furthermore, the iso-intensity double peak formed by symmetrical bending vibrations and the coupling split originating from bimethyl of isopropyl group was found at 1388 and 1368 cm^{-1} . By comparing the spectra of samples with each other, we found that ester carboxyl group (C=O) stretching peak appeared at 1726 cm^{-1} , and the peak intensity increased with the addition of tBA. As a result, we concluded that the molecular structure of the microgels prepared was schematically illustrated as shown in Scheme 1.

Morphology of the poly(NIPAM-*co*-tBA) microgels

To observe the morphology of the prepared microgels, SEM was used to investigate the shapes and dispersities of the microgel particles. Figure 2 shows the SEM micrographs of the purified poly(NIPAM-*co*-MBA) microgel particles, from which it was clear that they exhibited a spherical shape and favorable monodispersity; this indicated that the nucleation of particles followed the mechanism mentioned previously and there was no secondary nucleation because of the short nucleation period. Moreover, the average diameter of particles decreased with increasing content of tBA.

Turbidimetric analysis

Figure 3 is the plot of the turbidity (absorbance) of the poly(NIPAM-*co*-tBA) microgels as a function of temperature. The turbidity of the microgels increased with temperature and content of tBA. The turbidity of the microgels was largely dominated by the amount of water contained within the interstitial region, as

this indicated the difference in the refractive indices between the microgel–water macrocomplex and the bulk water. As the temperature increased up to a certain point, the water contained in the microgels was expelled from the microgels due to the disruption of hydrogen bonding between water and the hydrophilic amide groups and the hydrophobic association interactions between isopropyl groups, which led to an increase in the refractive difference between the solvent(water) and microgels. Figure 3 also shows that the temperature range in which the turbidity changed rapidly shifted to a lower temperature as the incorporation of tBA increased. These results were consistent with the DLS results.

Phase-transition behavior of the poly(NIPAM-*co*-tBA) microgels

DLS is a efficient method for determining the phase-transition behavior of temperature-sensitive microgels, from which the plot of D_H of microgel spheres as a function of temperature or VPTT could be obtained. Figure 4 presents D_H of the poly(NIPAM-*co*-tBA) microgels as a function of tBA content and temperature. Clearly, for all of the poly(NIPAM-*co*-tBA) microgels, D_H decreased sharply as the temperature reached a certain range; this indicated that the poly(NIPAM-*co*-tBA) microgels were temperature sensitive. In general, the VPTT of the microgels could be defined as the temperature corresponding to the inflexion point of the plots of D_H versus temperature. The VPTTs determined for the MG0, MG16, MG24, MG32, and MG48 samples were 33, 28, 25, 22, and 18°C , respectively. The phenomenon that the VPTT determined by DLS decreased with increasing tBA

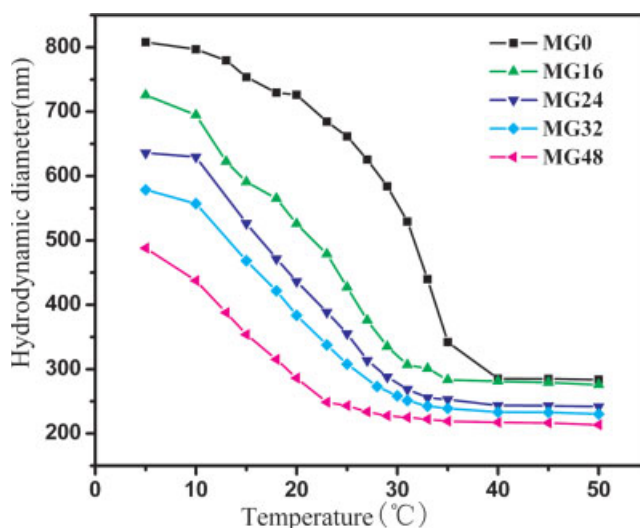


Figure 4 Plots of D_H versus temperature for the poly(NIPAM-*co*-tBA) microgels with various tBA contents. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

content suggested that the microgels copolymerized by tBA and NIPAM had a random sequence structure in character. It also indicated that the distribution of tBA units inside microgels were even and not a core-shell structure. In addition, due to the strong hydrophobicity of tBA units introduced in the poly(NIPAM-co-tBA) molecule chains, the original hydrophilic-hydrophobic balance of the PNIPAM molecule chains was disturbed, which weakened the role of hydrogen bonding between water and poly(NIPAM-co-tBA). Hence, the required energy breaking the hydrogen bonding became less, and then, the poly(-NIPAM-co-tBA) microgels underwent the phase transition at a lower temperature. The higher the tBA content was, the stronger the hydrophobicity of the poly(NIPAM-co-tBA) molecule chains and the lower VPTT responding to microgels were.

In comparison with the literature,²³ the effect on the decrease in VPTT of the microgels for tBA was more remarkable than EMA because the former had a stronger hydrophobicity than the latter. Figure 4 also shows that with increasing tBA content, both the range of phase-transition temperature and the particle diameters of the poly(NIPAM-co-tBA) microgels tended to be wider and smaller, respectively; this suggested that the temperature sensitivity of the microgels gradually fell. The reason for this was that the introduction of too many tBA units in the PNIPAM molecular chains lowered the temperature-sensitivity of PNIPAM microgel and poly(tBA) was not temperature-sensitive.

α

The values of D_H and α are listed in the last column of Table II, in which it is shown that the tBA contents had a stronger effect on α of the microgels at 5°C than they did at 50°C. Below VPTT, the hydrophobicity inside the microgels became stronger due to the past replacement of the hydrophilic NIPAM segments with hydrophobic tBA. Furthermore, hydrophobic interactions among shrunk molecular chains were strengthened due to the enhancement in the hydrophobicity of the polymer chains. Therefore, at lower temperatures, the D_H values of microgels gradually decreased with increasing tBA constituent. Above VPTT of the microgels, in view of the existing hydrophobicity of NIPAM itself, the hydrophobic tBA had little effect on the hydrophilic-hydrophobic balance between the hydrophilic and hydrophobic groups within the poly(NIPAM-co-tBA) polymer chains. When the amount of NIPAM and MBA were kept constant and the amount of tBA was changed, the particle diameter of the poly(NIPAM-co-tBA) microgels in the collapsed condition had little effect. According to the analysis mentioned previously, the reason that α of the poly(NIPAM-co-tBA) microgels had a downward trend was associated with the higher incorporation of tBA.

TABLE II
 α of Poly(NIPAM-co-tBA) Microgels with Various tBA Contents

Microgel code	$D_{H,5^\circ\text{C}}$ (nm)	$D_{H,50^\circ\text{C}}$ (nm)	α
MG0	808	284	23.03
MG16	726	276	18.20
MG24	636	242	18.15
MG32	589	230	16.79
MG48	488	213	12.03

CONCLUSIONS

A novel series of PNIPAM-based microgels modified by tBA as the hydrophobic comonomer were prepared by a modified SFEP method. The microgel particles took on a global shape and excellent monodispersity with the addition of the tBA constituent. The turbidity of the microgels increased with temperature and tBA dosage. In addition, VPTT of the PNIPAM microgels was adjusted successfully through the incorporation of different amount of tBA. The higher the tBA content was, the lower VPTT and α responding to the microgels were, whereas the range of the volume phase transition was broadened.

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