

## Preparation of Core-Shell Latex for the Pigmented Ink of Textile Inkjet Printing

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**ABSTRACT:** A core-shell latex comprising poly(butyl acrylate) as core and poly(styrene-methyl methacrylate) as shell was synthesized by emulsion polymerization using allyloxy nonylphenoxy propanol polyoxyethylene ether ammonium sulfonate (ANPS) as emulsifier. Transmission electron microscope, differential scanning calorimeter, and thermogravimetric analyses suggested the prepared latex had a core-shell structure. The particle size of the core-shell latex was about 102.8 nm with a molar ratio of butylacrylate, methyl methacrylate, and styrene at 6 : 2 : 2, a mass ratio of ANPS and monomers, ammonium persulfate and monomers at 15% and 1.0%, respectively. The core-shell latex showed high centrifugal stability and excellent freeze-thaw stability. The clogging nozzle rate of the pigmented ink containing 20 wt % core-shell latex was small, whereas the printed fabrics with this pigmented ink exhibited high rub and washing fastness. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

**KEYWORDS:** preparation; core-shell latex; pigmented ink; inkjet printing; reactive emulsifier

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### INTRODUCTION

Textile inkjet printing has attracted lots of people's attention for high resolution, little pollution, and especially fast response to the frequent shift of cloth fashion. Pigmented ink suitable for all sorts of fabrics becomes the main colorant in this technology.<sup>1,2</sup> However, preparation of the pigmented ink with excellent rub and washing fastness is still a great challenge.<sup>3</sup>

Adding a certain amount of fixation agents to the pigmented ink is an effective method to improve the rub and washing fastness of the printed fabrics. At present, different kinds of fixation agents have been developed, such as polyurethane acrylate oligomers,<sup>4</sup> cured hybrid polymers,<sup>5</sup> emulsion,<sup>6</sup> and so on. Among all of these fixation agents, emulsion becomes the most important one for preparation of the pigmented ink. To improve the handle feeling of the printed fabrics, the microemulsion with high content of soft monomers, which could form a soft film on the printed fabrics, has been also developed.<sup>7</sup> However, many experimental results illustrates that the stability and printing performance of the pigmented ink are destroyed when some traditional latexes are added.<sup>8–15</sup> Unlike the pigment particles, the latex can easily absorb some energy to change its morphology due to its high visco-elasticity. In addition, the latexes with low glass transition temperatures ( $T_g$ ) can easily form a film on the nozzle of the printed

head during the printing, thus leading to poor printing performance. Moreover, although there are lots of researches about the latex preparation, they are mainly applied for the traditional pigment printing,<sup>16–21</sup> and few types of latexes are developed for pigmented ink of the textile inkjet printing.

To get a latex that satisfies the requirement of the pigmented ink for textile inkjet printing, we propose to prepare a core-shell latex comprising poly(butyl acrylate) (PBA) as core and poly(styrene-methyl methacrylate) as shell by emulsion polymerization using a reactive emulsifier [allyloxy nonyl-phenoxy propanol polyoxyethylene ether ammonium sulfonate (ANPS)] in this research, and the synthesized conditions and its properties are also investigated.

### EXPERIMENTAL

#### Materials

Butylacrylate (BA, AR grade), methyl methacrylate (MMA, AR grade), and styrene (St, AR grade) which purchased from Lingfeng Chemical Reagent Co., Shanghai, China, were distilled under reduced pressure before using. Sodium dodecylsulfate (SDS, AR grade), ammonium persulfate (APS, AR grade), *p*-octylpolyethylene glycol phenylether (OP-10, AR grade), and ANPS (Chart 1, AR grade) were commercially available and used as received. Pigment dispersions (magenta, yellow, blue,

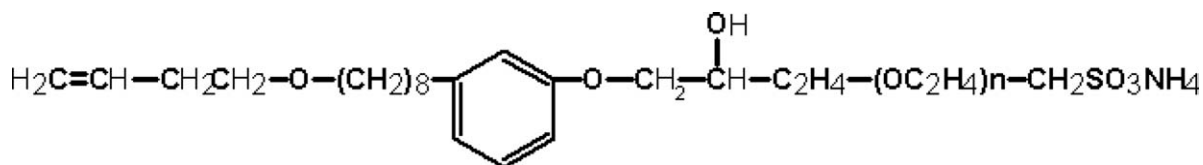


Chart 1. Chemical structure of ANPS.

and black) with 10 wt % solid content were prepared in our lab. All the distilled water was used in the experimental.

#### Synthesized of the Latex

Two grams of SDS, 1 g OP-10, 63 g distilled water, 10 g BA, and 1 g APS solution (10 wt %) were put into a four-neck flask and emulsified at 40°C for 30 min. The mixture was heated to 78°C and kept for 10 min. A total of 20 g BA and 2 g APS solution were dropped into the flask. The mixture was kept at 78°C for 1 h, and then cooled down to give the core latex.

Certain amounts of St, MMA, and ANPS were dropped into the core latex and emulsified at 40°C for 1 h. The temperature was raised to 78°C and corresponding amount of APS solution was dropped into the flask. The temperature was kept 78°C for 1 h. The mixture was cooled down to room temperature, and filtered through a membrane (0.5- $\mu\text{m}$  pore size) to give the core-shell latex.

A total of 2.3 g ANPS, 7.8 g MMA, 7.6 g St, and 59 g distilled water were put into a four-neck flask and emulsified at 40°C for 30 min. The mixture was heated to 78°C and then 1.8 g APS solution (10 wt %) was dropped into the flask. The mixture was kept at 78°C for 2 h, and then cooled down and filtered through a membrane (0.5- $\mu\text{m}$  pore size) to give the shell latex.

Two grams of SDS, 1 g OP-10, 6.8 g ANPS, 30 g BA, 7.8 g MMA, 7.6 g St, and 63 g distilled water were put into a four-neck flask and emulsified at 40°C for 30 min. The mixture was heated to 78°C and then 4.54 g APS solution (10 wt %) was dropped into the flask. The mixture was kept at 78°C for 2 h,

and then cooled down and filtered through a membrane (0.5- $\mu\text{m}$  pore size) to give the traditional latex.

#### Formulation of the Pigmented Ink

A weight-based formulation of pigmented ink was given as follows: pigment dispersion 50%, core-shell latex 20%, glycerol 15%, ethylene glycol mono-methyl ether 10%, urea 2%, Tween-80 1.5%, and distilled water 1.5%. The above components were stirring at 300 r/min until a homogeneous dispersion was obtained. After filtered through a 0.5- $\mu\text{m}$  pore filtering sieve, the pigmented inks were prepared and loaded on an inkjet printing machine (Mimaki JV4-180, Piezo-electric inkjet printer, Japan).

#### Characterization

**Dynamic Light Scattering.** The particle size was determined by dynamic light scattering (DLS) method using a Malvern Zetasizer Nano ZS90 instrument at 25°C with a fixed angle of 90 degree. The cumulate analysis was used for analyzing the DLS data of all the samples. Each sample was measured for three times, and the particle size was reported as an average value.

**Transmission Electron Microscope.** The sample was diluted with distilled water until the latex was no longer opaque. One drop of the diluted sample was placed on a copper grid, the excess liquid was removed with a tissue, and the grid was left to dry. The morphology was observed using A Phillips CM12.

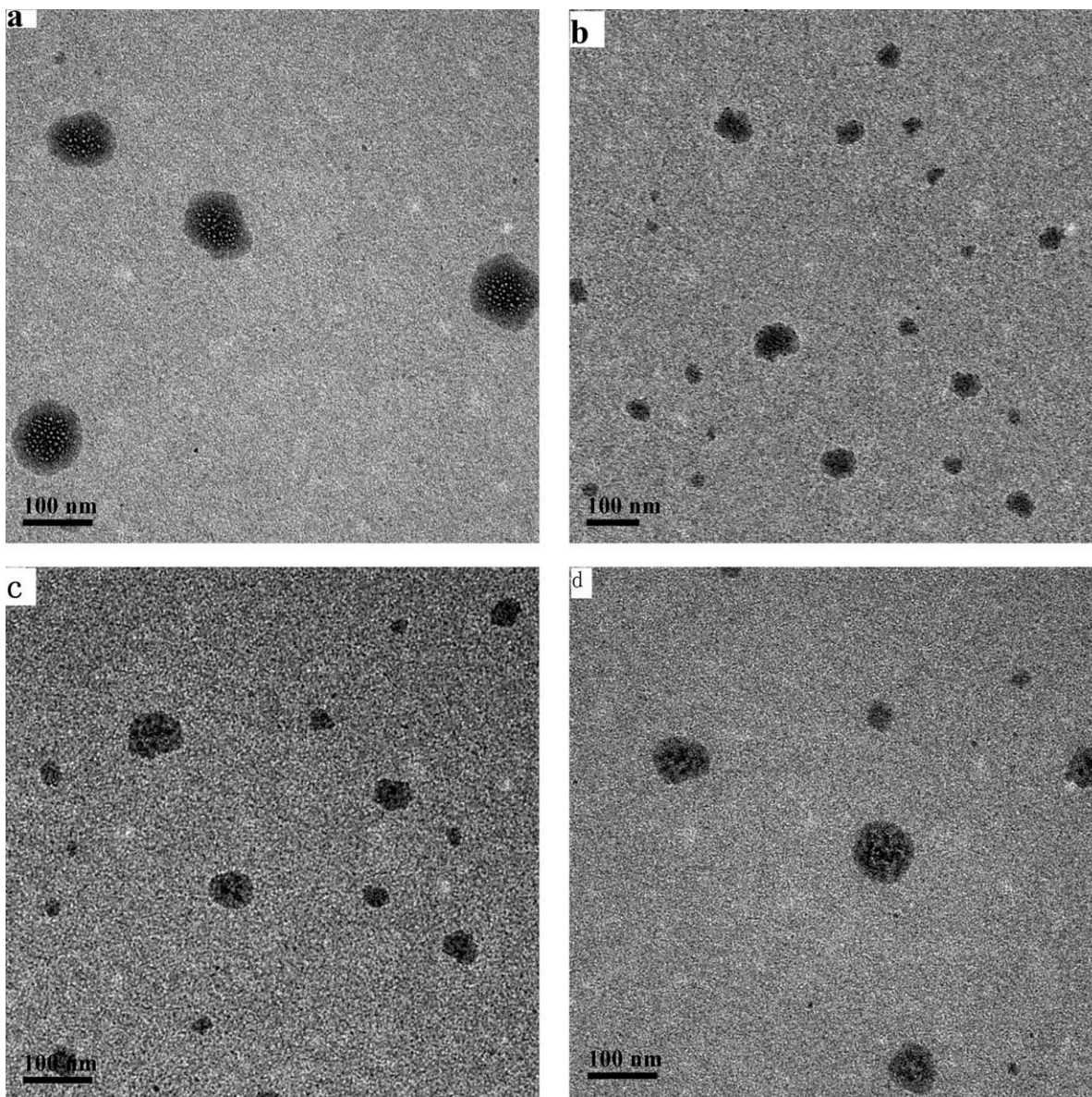
**Differential Scanning Calorimeter Analysis.** Differential scanning calorimeter (DSC) curves were recorded on a Perkin-Elmer Pyris 1 DSC in  $\text{N}_2$  with the scanning rate of 10°C/min. The sample subjected twice heating from -50°C to 140°C.

Table I. Properties of Core-Shell Latex Prepared Under Different Conditions

Runs	Molar ratio of BA : MMA : St	Mass ratio of ANPS to Styrene (%)	Mass ratio of APS to Styrene (%)	$D_n$ (nm) <sup>a</sup>	$S_T$ (%)	Washing fastness (level)	Softness of printed fabrics (by touch)
1	4 : 3 : 3	15	1.0	115.3	4.7	3	Hard
2	5 : 2.5 : 2.5	15	1.0	109.5	3.5	4	Hard
3	6 : 2 : 2	15	1.0	102.8	3.1	4	Soft
4	7 : 1.5 : 1.5	15	1.0	95.1	3.2	3-4	Soft
5 <sup>b</sup>	6 : 2 : 2	5	1.0	280.1	-	-	-
6	6 : 2 : 2	10	1.0	120.9	5.7	4	Soft
7	6 : 2 : 2	20	1.0	100.7	2.8	3	Soft
8 <sup>b</sup>	6 : 2 : 2	15	0.1	Coagulation	-	-	-
9	6 : 2 : 2	15	0.6	228.6	14.3	3-4	Soft
10	6 : 2 : 2	15	1.5	107.6	3.7	3-4	Soft

<sup>a</sup>Note: The maximum standard deviation was about 1.6.

<sup>b</sup>Note: The corresponding samples could not be used as binder for its large particle size.



**Figure 1.** Transmission electron microscope images of (a) core-shell latex, (b) core latex, (c) shell latex, and (d) traditional latex.

**Thermogravimetric Analyses (TGA).** The prepared latexes were analyzed for their thermal behavior using a Perkin-Elmer Diamond TG/DTA thermal analysis instrument. The samples were heated from 25°C to 650°C at a heating rate of 10°C/min under air atmosphere.

**Freeze-Thaw Stability ( $S_T$ ).** The sample was sealed and stored at  $-5^\circ\text{C}$  for 24 h, and then put into an oven at  $60^\circ\text{C}$  for another 24 h. The particle size was measured using DLS method, and  $S_T$  was evaluated using the change rate of particle size, which was calculated as eq. (1),

$$S_T = \frac{|d_T - d_0|}{d_0} \times 100\% \quad (1)$$

where  $d_0$  is the particle size of the original latex and  $d_T$  is particle size after treatment.

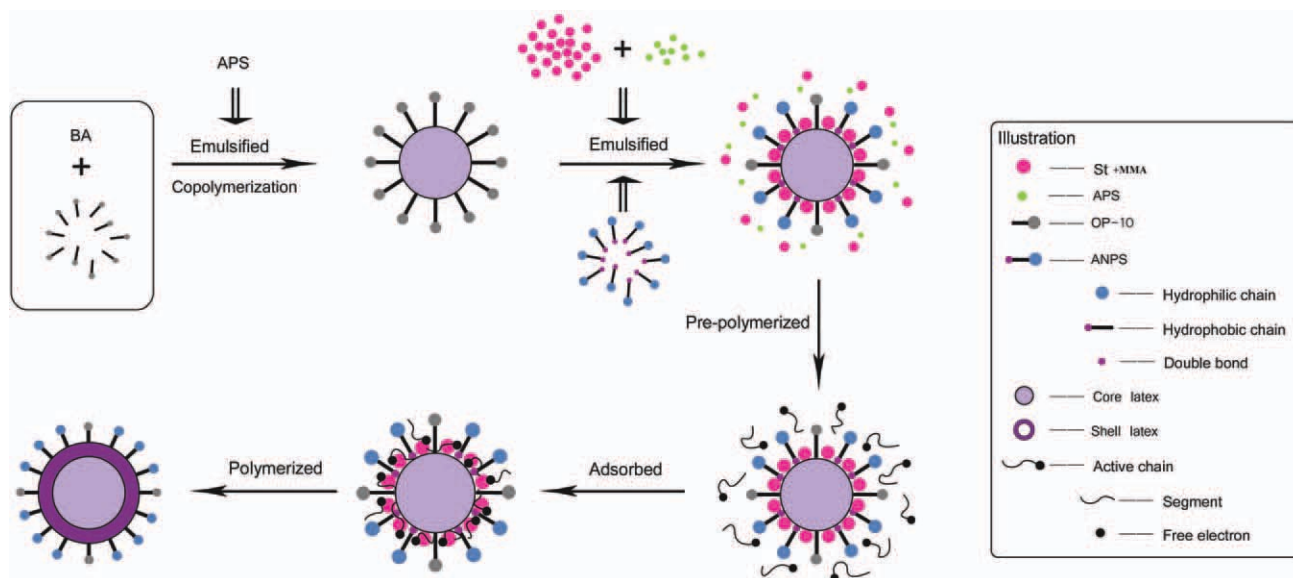
**Centrifugal Stability ( $S_C$ ).** The sample was centrifuged at 3000 r/min for 30 min. The particle size was measured using DLS method, and  $S_C$  was evaluated using the change rate of particle size, which was calculated as eq. (2),

$$S_C = \left(1 - \frac{|d_c - d_0|}{d_0}\right) \times 100\% \quad (2)$$

where  $d_0$  is the particle size of the original latex and  $d_c$  is the particle size of the upper latex.

**Apparent Viscosity ( $\eta$ ).**  $\eta$  was measured using a spindle-type viscometer (Brookfield DV-III, Middleboro, Massachusetts, America) at  $25^\circ\text{C}$ .

**Surface Tension ( $\sigma$ ).**  $\sigma$  was measured using a ring method in Drop Shape Analysis System DSA100.



**Figure 2.** The synthesized process of core-shell latex with reactive emulsifier. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

**Printing Performance of the Pigmented Ink.** The printing performance of the inks was tested on Mimaki JV4-160. The clogging nozzle rate ( $B$ ) was calculated according to eq. (3),

$$B = \frac{C_1}{S} \times 100\% \quad (3)$$

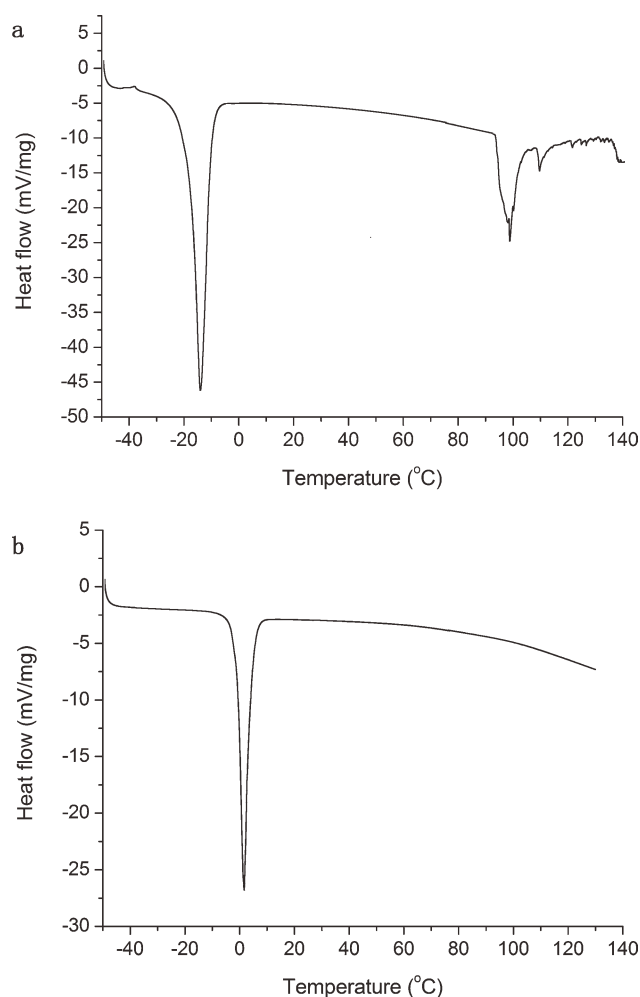
where  $C_1$  is the amount of clogged nozzle and  $S$  is the sum of the nozzle on the print head. The cotton fabrics (24 cm × 24 cm) were printed by Mimaki JV4-180.

**Color Performance of the Printed Fabrics.**  $K/S$  value were measured by colorimeter (Xrite-8400, America) under illuminant D65 using the 10° standard observer. The rub and washing fastness were tested according to AATCC standard 8-2001, 61.

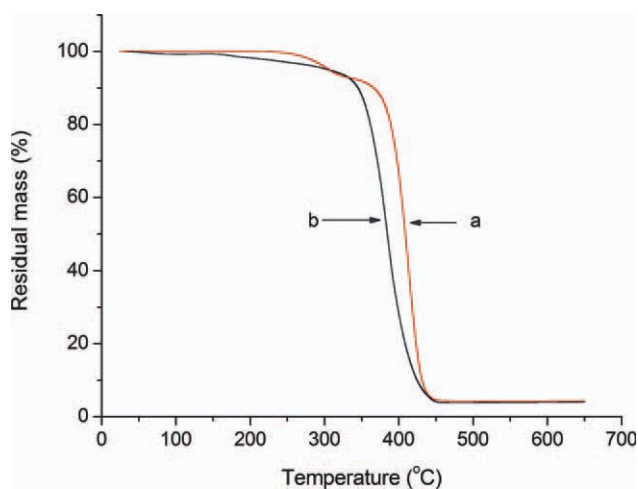
## RESULTS AND DISCUSSION

### Synthesis of Core-Shell Latex

Molar ratio of the monomer is the main factor that can determine the properties of the core-shell latex. Table I shows the properties of core-shell latex prepared under different conditions. Runs 1–4 demonstrate that the core-shell latex has small particles, high freeze-thaw stability, excellent washing fastness, and minor change handle feeling of the printed fabrics when the molar ratio of BA, MMA, and St is about 6 : 2 : 2. It is known that the branched level of the copolymer increases with an increase of the amount of MMA and St and thus lead to a large particle size.<sup>7</sup> In addition, the printed fabrics will be felt hard when the amounts of hard monomers (MMA and St) are large enough. On the other hand, the rub and washing fastness of the printed fabrics will become poor if the amounts of MMA and St are small enough because the formed film that covers onto the pigment surface is lack of enough elasticity and hardness.



**Figure 3.** DSC curves of (a) core-shell latex and (b) traditional latex.



**Figure 4.** TGA scans for (a) core-shell latex and (b) traditional latex. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

The amount of ANPS in the polymerization can also influence on the properties of the core-shell latex. Runs 3 and 5–7 in Table I show that the higher is the amount of ANPS, the smaller is particle size and the higher is freeze-thaw stability of core-shell latex, and the poorer washing fastness of the printed fabrics will be obtained. The repulsive forces among the core-shell latex will increase by increasing the amount of ANPS that is adsorbed onto the latex surface in the polymerization, thus leading to small particles and high stability. However, high amount of ANPS in the polymerization can improve the wetting ability of formed film by water for introducing some  $-\text{SO}_3^-$  groups, which results in poor washing fastness.

The amount of APS is another important factor that can affect the properties of the core-shell latex. Runs 3 and 8–10 in Table I indicate that the core-shell latex has small particles, high freeze-thaw stability, and excellent pigment fixing when the amount of APS is higher than 1.0%. The reason may be due to the fact that the monomer conversion is low when the amount of APS is small, and then the unreacted monomers penetrate into the media to destroy the stability of the core-shell latex, thus leading to a large particle size. From aforementioned analyses, it is concluded that the Sample 3 is the most suitable latex for the pigmented ink. For further demonstrations, all the core-shell latex that mentioned as follows is referred to the Sample 3.

### Morphology of the Core-Shell Latex

Figure 1 shows that the morphology of core-shell latex [Figure 1(a)] is different from the core latex [Figure 1(b)], shell latex [Figure 1(c)], and traditional latex [Figure 1(d)]. It is clear that the particle of core-shell latex is larger than that of the core latex, shell latex, and traditional latex. This indicates that the latex with core-shell structure is successfully synthesized in this work. The polymerization procedure of core-shell latex may be depicted as Figure 2. First, the core latex is synthesized by the polymerization of BA using APS as initiator. Second, ANPS, St, and MMA are homogeneously encapsulated the core latex when they are slowly added into the core latex emulsion with mild

**Table II.** The Stability of the Core-Shell Latex

Samples	Stability (%)	
	$S_C$	$S_T$
Core latex	87	Coagulation
Shell latex	95	3.3
Traditional latex	93	19.9
Core-shell latex	91	3.1

stirring. Third, the temperature is elevated and some active oligomers with free radicals are produced. Finally, the active oligomers diffuse into the monomer layer that encapsulates the core latex and initiate the polymerization.

### DSC Analyses

The glass transition temperature of the core-shell latex was studied by DSC analysis. Figure 3 represents the DSC plots of the core-shell latex [Figure 3(a)] and traditional latex [Figure 3(b)]. It is observed from the figure that the core-shell latex has two glass transition temperatures ( $-22^\circ\text{C}$  and  $89^\circ\text{C}$ ), whereas only one glass transition ( $-2.8^\circ\text{C}$ ) is observed in the traditional latex. These differences indicate the presence of the both polymers in core-shell latex.

### TGA Analyses

Figure 4 represents the TGA plots of the traditional latex and core-shell latex. Unlike the traditional latex, the core-shell latex was found to decompose in two stages. The first weight loss appeared at  $230^\circ\text{C}$ , which may be ascribed to the “weak links” of PBA in the core-shell latex. The second weight loss appeared at  $400^\circ\text{C}$ , and the temperature corresponding to 50% weight loss ( $T_{50}$ ) of core-shell latex shifted to higher temperature region than the traditional latex. This may be caused by the shell polymers. These results further indicate two types of polymers existed in the core-shell latex.

### Stability of the Core-Shell Latex

Table II shows that the shell latex and core-shell latex have outstanding centrifugal stability and freeze-thaw stability. Unlike the core latex, some  $-\text{SO}_3^-$  which can produce repulsive forces are introduced onto the latex surface for ANPS taking part in the polymerization in shell latex and core-shell latex. Therefore, desorption of ANPS from latex is effectively avoided, even at centrifugal or freeze-thaw conditions. Moreover, Table II also

**Table III.** Physical Properties of the Pigmented Ink Consisted of Core-Shell Latex

Pigmented ink	$D_n$ (nm) <sup>a</sup>	$\eta$ (mPa s)	Surface tension (mN/m)	Stability (%)	
				$S_T$	$S_C$
Yellow	167.6	6.32	31	1.7	87
Cyan	147.3	5.47	29	2.5	89
Magenta	154.2	5.23	28	1.3	92
Black	137.8	6.25	30	1.4	90

<sup>a</sup>Note: The maximum standard deviation was about 2.3.

**Table IV.** Printing and Color Performance of the Pigmented Ink with Core–Shell Latex<sup>a</sup>

Pigmented ink	B (%)	K/S value	Rub fastness (level)		Washing color fastness (level)		Softness of printed fabrics (by touch)
			Dry	Wetting	Color change	Staining	
Yellow	0.8	2.63	4–5	4	4	4–5	Soft
Cyan	0.7	4.37	3–4	3	4	4–5	Soft
Magenta	0.4	5.41	3–4	3	4	4–5	Soft
Black	0.4	4.59	3–4	3	3–4	4–5	Soft

<sup>a</sup>Note: Baking 3 min with 130°C.

indicates that the copolymer with high  $T_g$  may help to improve the stability to temperature of the latex. Therefore, considering the stability of pigmented ink and handle feeling of printed fabrics, the core–shell latex may be the most suitable for formulation of pigmented ink for textile inkjet printing.

#### Properties of the Pigmented Ink and Color Performance of the Printed Fabrics

Table III shows the physical properties of the pigment ink that contains 20 wt % core–shell latex. The particles, surface tension, and apparent viscosity of pigmented inks were small and the freeze–thaw and centrifugal stability were excellent. This makes it applicable for use in Mimaki JV4–180 inkjet printing machine. To further understand the properties of the pigmented ink, the printing and color performance are also investigated, and the results are shown in Table IV. It can be seen that the clogging nozzle rate is small, and the printed fabrics with this pigmented ink shows high rub fastness, washing color fastness, and softness hand feeling, which can satisfy the national quality criteria of the textiles. Unlike the traditional emulsion, the core–shell latex consists of two types of polymers, the core polymer with low  $T_g$  adjusting the handle feeling of the printed fabrics and the shell copolymer with high  $T_g$  reducing the viscoelasticity of the latex. Therefore, the core–shell latex can improve the printing performance of the pigmented ink.

#### CONCLUSIONS

The core–shell latex was successfully synthesized with reactive emulsifier (ANPS). The prepared latex exhibited high freeze–thaw stability and centrifugal stability when the molar ratio of BA, MMA, and St was about 6 : 2 : 2, ANPS to St and APS to St based on the weight ratio were about 15% and 1.0%, respectively. The core–shell latex and the pigment dispersions worked very well without any nozzle-blocking problem. The printed fabrics with the pigmented inks consisted of 20% core–shell latex showed excellent color fastness and softness of the handle feeling.

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