

# Microemulsion Polymerization of Microlatex in Sublimation Ink for Cotton Fabric Ink Jet Printing

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**ABSTRACT:** A novel microlatex of styrene/2-ethylhexylacrylate (2-EHA)/2-hydroxyethyl methacrylate (2-HEMA)/N-(isobutoxy methyl) acrylamide (IBMA) copolymer was synthesized and mixed in sublimation inks to be inkjet printed on the cotton fabric to provide soft hand feel and good color fastness after heat-press. In the optimized microemulsion composition with highest monomer mixture amount, polymerizable maleate surfactants with moderate EO value attained smaller microemulsion droplet size in mono distribution and lower dosage than conventional POE surfactants in combination with anionic surfactants. With adopted semicontinuous process in microemulsion copolymerization at 65°C, the polymerizable surfactants stabilized the growth of microlatex particle size within 70 nm in 240 min and attained 100% of monomer conversion rate with two initiator systems, 2-2-azobis(2-methylpropionamide dihydrochloride (AAPH) and *tert*-butylhydroperoxide (TBHP)/sodium formaldehyde sulfoxylate (SFS). The microlatex particle size of two

surfactant systems increased with higher conversion rate and reaction temperature, which synchronized with initiator concentration. High polymer solid content was contributed mainly by IBMA monomer ratio requiring higher amounts of anionic surfactants and 2-HEMA as a cosurfactant in particle stabilization. Although the optimum ink containing high IBMA microemulsion exhibited small variation in viscosity, pH value and surface tension, disperse dyes in four colors had different interaction with the microlatex to demonstrate distinct printing durability and color performance. The resulted cotton fabric attained high K/S value for color strength, great AATCC grade for color fastness, and nearly zero color difference for negative dye particle diffusion or migration. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 122: 1872–1881, 2011

**Key words:** cotton; disperse dye; sublimation ink; fabric ink jet printing; microlatex; microemulsion polymerization; polymerizable surfactant; crosslinking

## INTRODUCTION

Recently, sublimation inkjet printing on polyester or materials treated with thermosetting primer is growing mostly in sign and advertisement industries because of quick product realization, environmental protection issue, and evolving printer with higher printing speed and lower cost. It would claim a much bigger market share if such simple process could be contrived for natural fibers. Cotton has been especially attempted in extending the process with sublimable disperse dyes by, e.g., pigmented melt-transfer paper, film-release paper, esterification of cotton, pretreatment with polyglycols, melamine-formaldehyde resin, etc.<sup>1</sup> However, the hand feel and fastness of such prints to washing and light exposure were not satisfied fairly. Even though the aqueous pigment inks containing UV-curable binder, e.g., polyurethane acrylate<sup>2</sup> or nanoscale binder,<sup>3</sup> could provide the solution for all types of fabrics,

the wet fastness were not outstanding with average grade of 3. Moreover, the UV light exposure system with few passes required to cure the polymer inks would be more costly than heat pressing method to fix the color in terms of instrument cost and life maintenance. Dyed fabric is practically superior to the pigment colored one in color saturation, brightness, rubbing, and washing durability.

To impart the affinity between functional groups of cotton and disperse dyes, this work envisioned that novel polymer or nanolatex should be generated. Such polymer on the fabric surface should be flexible for soft hand feel and well crosslinked for fastness achievement. Similar work on fabric finishing agent via latex preparation has been performed from copolymers, e.g., carboxylated butadiene-styrene-acrylonitrile,<sup>4</sup> butyl acrylate-styrene,<sup>5</sup> polyfluoroalkyl methacrylates,<sup>6</sup> styrene/butyl acrylate/glycidylmethacrylate,<sup>7</sup> and styrene/2-ethylhexyl acrylate/heptadecafluorodecyl acrylate.<sup>8</sup> Adopted polymerization therewith has been emulsion and miniemulsion. To be jet-printed through nozzles, the polymer *in situ* ink should be ultra small in particle size with mono-distribution. Microemulsion polymerization has been extensively reported<sup>9–12</sup> to provide thermodynamically stable, monodisperse nanoscale polymer

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latex with high polymerization rate, intrinsic control, and reproducibility of product properties. Their optimal efforts were to overcome application disadvantages of this polymerization: low polymer content at high surfactant concentration, by adopting bicontinuous microemulsion, semicontinuous process, inducing polymerization under instability temperature of microemulsion, using polymerizable surfactant or gemini surfactant, and applying redox initiation for stability against freeze-drying and rehydration.

To be applicable for textiles, the aqueous phase should be preferably prepared based on oil in water microemulsion. The ink formulation based on o/w microemulsion has been performed in our previous work<sup>13</sup> by optimizing component in Quasi-ternary phase diagram, investigating the disperse dye effect on the microemulsion system, and analyzing physico-chemical properties with ink jet printing quality assessment. Herein, we synthesized a new copolymer, styrene/2-EHA/2-HEMA/IBMA, with semicontinuous microemulsion polymerization. The process started by forming a monomer mixture microemulsion via titration into the solution of emulsifiers and distilled water at room temperature. After the thermal stability test, the obtained nano-sized (under 100 nm) microemulsions with mono-droplet size distribution were homogenized for uniform dispersion of micelles where copolymerization occurred. The polymerizations were carried out with the following steps (1) 50 wt % of monomer mixture microemulsion and 40 wt % of AAPH were added in the reactor and left to polymerize at 65°C for 60 min to form the seed. (2) The remaining amount of monomer mixture microemulsion and 60 wt % of AAPH were continuously added dropwise and left for 320 min to polymerize at steady 65°C. (3) The redox system of TBHP and SFS was used for postpolymerization under investigation temperature (25–65°C) left for 25 min to eliminate free monomers thus maximizing the conversion. We investigated the formulation systems based on conventional APEO-free POE surfactant system in the comparison with polymerizable maleate surfactant system, and discussed the effects of reaction time, redox reaction temperature, concentration of initiator and redox pair, surfactant contents, as well as monomer weight ratios on the overall monomer conversion rate and latex particle size. The optimal formulation was determined by attaining maximum monomer conversion rate, small particle size, high polymer solid content, and imparting least ink viscosity variation in sublimation inks. Based on the copolymer latex microemulsion with maximum concentration in four color inks, the compatibility of inks with the print-head of Mutoh RJ8000 printer was estimated by calculating the number of clogged nozzle and the hour of

printing durability. Finally, the printing quality of the above inks on cotton fabrics was evaluated after the sublimation process. The cotton fabric inkjet printed with inks containing our optimal IBMA copolymer presented good affinity between disperse dyes and cotton with fair rubbing fastness, good washing fastness, excellent light fastness, vivid color in high K/S value, minor color fading with small color difference and soft hand feel.

## EXPERIMENTAL

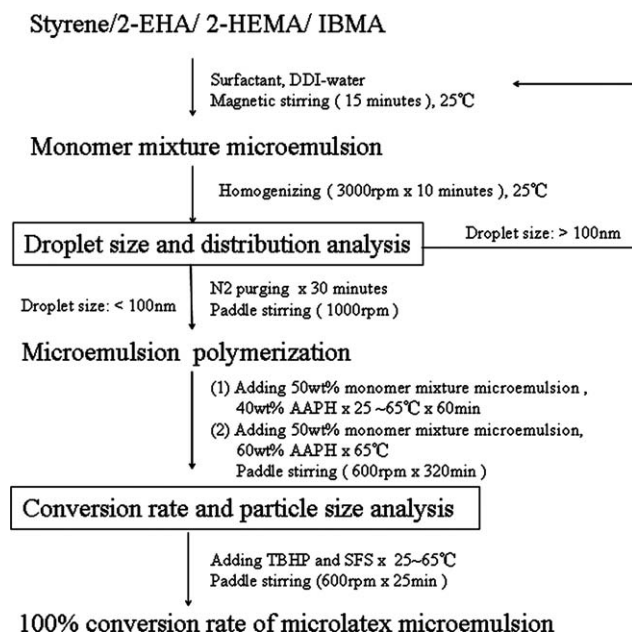
### Materials

Hydrophobic monomers, styrene (Aldrich), 2-ethylhexylacrylate (2-EHA, BASF), N-(isobutoxy methyl) acrylamide (IBMA, CYTEC), and hydrophilic monomer, 2-hydroxyethylmethacrylate (2-HEMA, Fluka), were vacuum distilled before use. 2-2-Azobis(2-methylpropionamide) (AAPH, Wako) was technical grade and used as supplied. Tert-butylhydroperoxide (TBHP, 70% aqueous solution, Sigma) and sodium formaldehyde sulfoxylate (SFS, BASF) was redox pair and directly applied to maximize monomer conversion. The APEO-free emulsifiers included nonionic surfactant polyoxyethylene tridecyl ether (Sinopol 2340, molecular formula:  $C_{13}H_{27}(C_2H_4O)_nOH$ ,  $n = 40$ , HLB = 18, SinoJapan Chemical), and biodegradable anionic surfactant, ammonium polyoxyethylene lauryl ether sulfate (Sinonate 1106SF, molecular formula:  $C_{12}H_{25}O \cdot (C_2H_4O)_n SO_3 \cdot NH_4$ ,  $n = 6$ , SinoJapan Chemical). To compare the emulsifier effect, the nonionic dodecyl polyethyleneoxide maleate (molecular formula:  $C_{12}H_{25}O \cdot C_4H_2O_2 \cdot (C_3H_6O)_n \cdot (C_2H_4O)_m \cdot OCH_3$ ,  $n = 2.3$ ,  $m = 17$  for Sinnoester CPM1, 34 for Sinnoester CPM2 and 43 for Sinnoester CPM3, Cognis) and anionic methacryloyloxyethyl maleate (molecular formula:  $C_{10}H_{12}O_6$ , Aldrich) were adopted to act as copolymerizable monomers for covalently incorporating surfactants in polymer chains without desorption from the latex particle surface.<sup>14</sup> Doubly distilled water was used as continuous polymerization media. The sublimation inks in which the obtained copolymers were directly applied were in four colors of magenta, yellow, cyan, and black by A-Text Worldwide Sdn Bhd.

### Preparation of monomer mixture microemulsion

Scheme 1 illustrates the typical procedure for the styrene/2-EHA/2-Hema/Ibma copolymer microemulsion.

The amounts of monomer mixtures, styrene/2-EHA/2-HEMA/IBMA, in required ratios were titrated to the aqueous solution containing surfactant combination and doubly distilled water. Different monomer ratios requiring minimum amount of



**Scheme 1** Preparation of styrene/2-EHA/2-HEMA/IBMA copolymer microemulsion.

distinct surfactant combinations were listed typically in Table I. The amount of water added was varied to maintain a constant total solution weight. The solution was loaded in a 500-mL beaker with magnetic stirring at room temperature until a clear, transparent microemulsion is obtained. The resultant microemulsion was then homogenized for 10 min by using a homogenizer (model: BOM-100D, Chemist Scientific Corp.) operated at 3000 rpm to ensure uniform microemulsion droplets subdivided into smallest size and to create a stable dispersion ideal for further processing. A cooling bath was used to avoid heating and control temperature at 25°C. The homogenized solution comprising microemulsion was obtained and analyzed for the size and distribution of droplets.

### Microemulsion polymerization

The 50 wt % of monomer mixture microemulsion was transferred to a four necked flask equipped with a paddle stirrer, thermometer, reflux condenser, and nitrogen inlet with N<sub>2</sub> purging for 30 min to remove oxygen. The microemulsion copolymerization started by adding 40 wt % of initiator as well as raising reaction temperature to 65°C and left for 60 min. The remaining amounts of monomer mixture and initiator were slowly added dropwise into the flask at the steady temperature of 65°C and stirring was maintained at 600 rpm for 320 min. To complete the monomer conversion, the redox pair of TBHP and SFS was added with stirring for another 25 min after the reacted mixture in the flask was cooled

down and kept at steady temperature for investigation (between 25 and 65°C). Each microlatex specimen thus obtained was characterized and applied in inks as follows.

### Characterization of microlatex microemulsion

The conversion of the microemulsion polymerization of the microlatex was measured with gas chromatography (Shimadzu GC-14B) by injecting each synthesized sample into the capillary column. The samples were prepared as follows: 1.0 mL of the microlatex was diluted with 2.0 mL of an aqueous solution containing saturated hydroquinone to inhibit further polymerization of monomers, and 2.0 mL of cyclohexanone was added as internal standard to ensure results. Samples were shaken and decanted to force the equilibrium of the monomers' concentration between the liquid and gas phase. The upper organic phase where monomers were quantitatively extracted was taken for the GC analysis. To measure the solid content of the microlatex, 10 g of sample was dried for 30 min at 100°C in infrared moisture determination balance (model AD-4714A, A and D Co.). The solid content was expressed by the calculation of mass loss during evaporation, i.e., solid content (%) = 100% – moisture content readings (%). The characteristics of the copolymer latex were determined using a MP-6100 pH meter for pH measurement, Du Noüy Tension-meter for surface tension measurement, Brookfield DV-II+ Viscometer for apparent viscosity measurement and Zeta Plus<sup>TM</sup> particle analyzer for particle size evaluation and distribution. The thermodynamic stability test was performed with three cycles of 5°C for 3 h and 70°C for another 3 h.

### Application of inks based on microlatex microemulsion

Each synthesized microlatex microemulsion was added directly into the sublimation inks with gentle stirring for 30 min when the uniform mixture was attained. The concentration of the copolymer microemulsion in the ink was determined by controlling the ink viscosity verified within 1 cps. The compatibility of the produced inks with print-head, Epson 10000, on Mutoh RJ8000 ink jet printer was determined in terms of nozzle clogging and printing durability before the ink jet printing quality evaluation on fabrics.

### Evaluation of ink jet printing on cotton fabrics

The ink jet printing quality was conducted on well performed inks and 100% knitted cotton fabrics. The color of the printed samples was then fixed via

**TABLE I**  
**Preparation of Monomer Mixture Microemulsion (Excluding SA0-1 and SA0-2) with Required Minimum Amounts of Surfactant Combination and Water by Attaining Nano-Sized Droplet and Thermodynamic Stability (Temperature = 25°C)**

Sample code	Monomer ratio (wt %) (styrene: 2-EHA: 2-HEMA: IBMA)	Surfactants (wt %) (SS <sup>a</sup> , C1M <sup>b</sup> , C2M <sup>c</sup> , and C3M <sup>d</sup> )	Water (wt %)	Average size of droplets (nm)/ Size distribution	Average size of droplets (nm)/ Size distribution (after thermal stability test)
SA0-1	5% (1 : 1 : 2 : 0)	0.5% SS (1 : 1)	94.5%	105.6 Broad distribution	110.5 Broad distribution
SA0-2	5% (1 : 1 : 3 : 0.5)	0.6% SS (1 : 2)	94.4%	108.8 Broad distribution	121.3 Broad distribution
SA1	5% (1 : 1 : 2 : 0)	0.8% SS (1 : 1)	94.2%	55.8 Monodisperse	56.0 Monodisperse
SA2	5% (1 : 1 : 3 : 0.5)	0.8% SS (1 : 2)	94.2%	56.5 Monodisperse	55.8 Monodisperse
SA3	5% (1 : 1 : 4 : 2)	1.5% SS (1 : 2)	93.5%	58.6 Monodisperse	59.0 Monodisperse
SB0	10% (1 : 1 : 2 : 0)	1.0% SS (1 : 1)	88.0%	56.0 Monodisperse	56.5 Monodisperse
SB1	10% (1 : 1 : 3 : 0.5)	1.5% SS (1 : 1)	88.5%	55.0 Monodisperse	55.7 Monodisperse
SB2	10% (1 : 1 : 3 : 1)	2.0% SS (1 : 2)	88.0%	59.8 Monodisperse	60.3 Monodisperse
SB3	10% (1 : 1 : 4 : 2)	2.0% SS (1 : 3)	88.0%	58.7 Monodisperse	60.6 Broad distribution
SC0	15% (1 : 1 : 2 : 0)	1.3% SS (1 : 1)	83.7%	57.3 Monodisperse	57.7 Monodisperse
SC1	15% (1 : 1 : 3 : 0.5)	2.0% SS (1 : 2)	83.0%	60.3 Monodisperse	61.2 Monodisperse
SC2	15% (1 : 1 : 3 : 1)	2.0% SS (1 : 3.5)	83.0%	63.4 Monodisperse	64.5 Broad distribution
SC3	15% (1 : 1 : 4 : 2)	2.5% SS (1 : 3.5)	82.5%	64.5 Broad distribution	65.8 Broad distribution
MA1	5% (1 : 1 : 2 : 0)	0.2% C3M (1 : 0.5)	94.8%	53.8 Monodisperse	53.9 Monodisperse
MA2	5% (1 : 1 : 3 : 0.5)	0.2% C2M (1 : 0.5)	94.8%	54.9 Monodisperse	55.2 Monodisperse
MA3	5% (1 : 1 : 4 : 2)	0.2% C1M (1 : 0.5)	94.8%	55.6 Monodisperse	55.8 Monodisperse
MB0	10% (1 : 1 : 2 : 0)	0.4% C3M (1 : 0.5)	89.7%	54.1 Monodisperse	54.7 Monodisperse
MB1	10% (1 : 1 : 3 : 0.5)	0.4% C2M (1 : 0.5)	89.6%	54.0 Monodisperse	54.5 Monodisperse
MB2	10% (1 : 1 : 3 : 1)	0.2% C2M (1 : 1)	89.8%	55.2 Monodisperse	55.6 Monodisperse
MB3	10% (1 : 1 : 4 : 3)	0.4% C1M (1 : 1)	89.6%	55.5 Monodisperse	55.8 Monodisperse
MC0	18% (1 : 1 : 2 : 0)	0.7% C3M (1 : 0.5)	81.3%	54.3 Monodisperse	55.2 Monodisperse
MC1	18% (1 : 1 : 3 : 0.5)	0.6% C2M (1 : 1)	81.4%	54.8 Monodisperse	55.0 Monodisperse
MC2	18% (1 : 1 : 3 : 1)	0.6% C2M (1 : 2)	81.4%	56.5 Monodisperse	56.9 Monodisperse
MC3	18% (1 : 1 : 4 : 3)	0.6% C2M (1 : 2)	81.4%	56.0 Monodisperse	57.2 Broad distribution

<sup>a</sup> The combination ratio, Sinopol 2340 : Sinonate 1106SF.

<sup>b</sup> The combination ratio, Sinnoester CPM 1 : Methacryloyloxyethyl maleate.

<sup>c</sup> The combination ratio, Sinnoester CPM 2 : Methacryloyloxyethyl maleate.

<sup>d</sup> The combination ratio, Sinnoester CPM 3 : Methacryloyloxyethyl maleate.

heat-press by a thermo *trans*-printing machine at 200°C for 30 s. Color strength and fading of the prints were determined by reflectance measurement using a spectrophotometer (Spectraflash 600, Data-Color). The color fading was calculated as the color difference between the prints on the first day and the 30th day. Along with the examination a fabric softness test was done by hand touch. The color fastness of ink jet printed cotton fabrics to washing, rubbing, and light were evaluated according to AATCC 61-2003-2A, AATCC 8-1995, and AATCC16-1998A, respectively.

## RESULTS AND DISCUSSION

Our interest in O/W microemulsion polymerization is due to its unique properties of transparency, low viscosity, great stability, and controllable production, which meet the aqueous ink formulation requirement for ink jet printing. To make the resulting co-

polymer directly applicable in inks, we attempted to optimize the method to maintain produced microlatex particle size similar to the originally formed microemulsion.

### Effects of monomer weight ratio and surfactants on O/W microemulsion formation

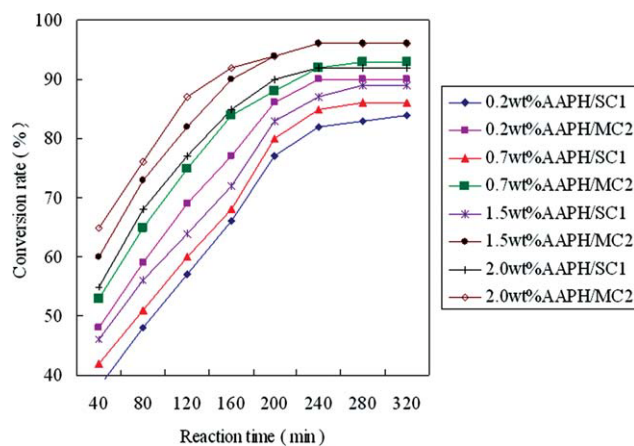
In Table I, the composition for each monomer mixture microemulsion was optimized by attaining nano-sized emulsion droplets with narrow and mono-modal distribution, i.e., monodispersed. By contrast, the peaks in the size distribution were separated from one another and were broadly distributed, i.e., the sum of two or more normal distributions and multimodal distribution. According to our former study,<sup>8</sup> the monomers of styrene and 2-EHA have been investigated in equal ratio to provide ideal hardness, penetration, and binding to the fiber. Herein, to facilitate the interconnection

between the linear polymer and fiber, the IBMA is copolymerized in the acrylic backbone to induce crosslinking and forms a network where the dispersed dye particles are capably embedded at sublimation temperature. The critical surfactant amounts of samples SA0-1 (less than 0.5wt %) and SA0-2 (less than 0.6 wt %) rendered monomer mixture emulsions with more than 105 nm of droplet size and broad size distribution. Those emulsions would not be microemulsion with considerable increase in droplet size after the thermal stability test. To compare microemulsions without IBMA monomer, samples SA1, SB0, SC0, MA1, MB0, and MC0 presented that nano-sized droplets of monomer mixture microemulsions still kept monodispersing with small variation in the thermal stability test when total monomer weight ratio was increased. Samples SC0 and MC0 attained smaller droplet sizes than samples SC1 and MC2 in the highest monomer mixture amount. With higher ratio of the IBMA monomer, the hydrophilic monomer, 2-HEMA, played as a cosurfactant to be incorporated more with higher ratio of surfactants. Especially the amount of anionic surfactants, Sinonate 1106SF and methacryloyloxyethyl maleate, increased to facilitate the inversion process of more hydrophobic monomers in water and stabilized the emulsion droplets. In the system of Sinopol 2340 and Sinonate 1106SF (SS), sample SB1 maintained the smallest droplet size after the stability test to imply that the equal ratio of two surfactants (1 : 1) within the amount of 1.5 wt % could reduce and stabilize the microemulsion droplet size between 55.0 and 56.0 nm when 2-HEMA and IBMA with the ratio of (3 : 0.5) were added in total monomer amount of 5–10 wt %. With the same monomer ratio of (1 : 1 : 3 : 0.5) and surfactant ratio of (1 : 2), samples SA2, SB2, and SC1 presented mono-distribution of droplet size when the monomer amount was increased from 5 to 15%. However, the higher IBMA ratio of 2 in more than 10 wt % of monomer mixture would limit 2-HEMA and Sinonate 1106SF from solubilizing and stabilizing to show a larger droplet size with broader distribution. Compared with the system of Sinnoester CPM 1, 2, 3, and methacryloyloxyethyl maleate, only 0.2–0.4 wt % of surfactants containing 0.5 of anionic surfactant ratio were required in samples MA1, MA2, MA3, MB1, MB2, and MB3 to produce much smaller emulsion droplet size than those in the SS system with the same monomer content. With higher proportion of IBMA and more content of monomer mixture, less EO value of nonionic Sinnoester CPM was introduced and Sinnoester CPM 2 was rendered the most effective emulsification in combination with methacryloyloxyethyl maleate to keep the mono distribution of droplet size within 57.0 nm after the stability test. As the IBMA ratio increased to 3 in 18 wt % of

the monomer mixture, only 0.6 wt % of Sinnoester CPM 2 and methacryloyloxyethyl maleate (1 : 2) were required to form the microemulsion in smaller particle size of 56.0 nm. But the droplet distribution turned broad and was less stable after freeze-thawing test. Therefore, the emulsifying ability of polymerizable surfactants (Sinnoester CPM 1, 2, 3, and methacryloyloxyethyl maleate) is much higher than that of the combination surfactants (Sinopol 2340 and Sinonate 1106SF).

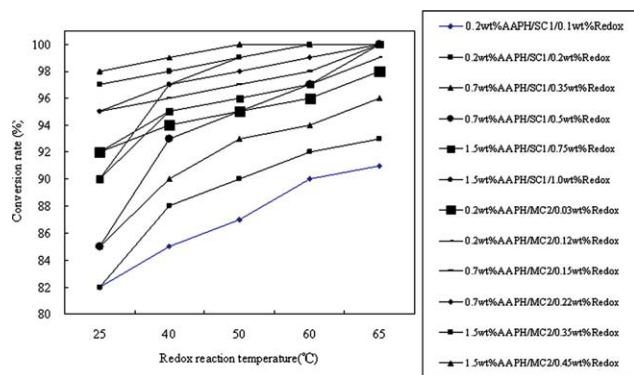
#### **Effects of reaction time, redox reaction temperature, concentration of initiator, redox pair, surfactant contents, and monomer weight ratio on microemulsion polymerization**

Since the initiation and propagation of monomer droplets occur synchronously in the microemulsion polymerization, the completion of reaction could be determined by the monomer conversion rate which much correlate with temperature, time, and the contents. We induced polymerization with our semicontinuous method below the instability microemulsion temperature of 70°C to control the growth step of the latex particles. Based on optimized microemulsion composition with highest monomer mixture amount and relatively lowest surfactant contents in Table I, experiments were proceeded from the sample SC1 formulated by conventional the POE surfactant system in comparison with the sample MC2 using the polymerizable maleate surfactant system. Kinetic studies have been performed in Figures 1–4 to illustrate the effects of reaction time, redox reaction temperature, concentration of initiator and redox pair, surfactant contents, as well as monomer weight ratios on the overall monomer conversion rate and latex particle size. In Figure 1, the conversion rate was intensively upgraded with increased concentration of AAPH. However, conversion rates were greatly increased in the presence of polymerizable maleate surfactants (MC2) even with much lower AAPH content, e.g., the rate comparison from 40 to 320 min: 0.2 wt %AAPH/MC2 > 1.5 wt %AAPH/SC1 > 0.7 wt % AAPH/SC1 > 0.2 wt % AAPH/SC1, and the comparison from 280 min to 320 min: 0.7 wt % AAPH/MC2 > 2.0 wt %AAPH/SC1 > 0.2 wt % AAPH/MC2. It can be assumed that the polymerizable maleate surfactants contained more active hydrogen atoms to contribute to higher monomer conversion rate. In the beginning of 80 min when the total composition has copolymerized in the microemulsion, sample MC2 achieved nearly 60% of conversion rate with only 0.2 wt % of AAPH while sample SC1 reached the rate of just 56% with higher content of 1.5 wt % thereof. With the content of 2.0 wt % AAPH, the final conversion of SC1 attained highest rate of 92%. However, the conversion rate of

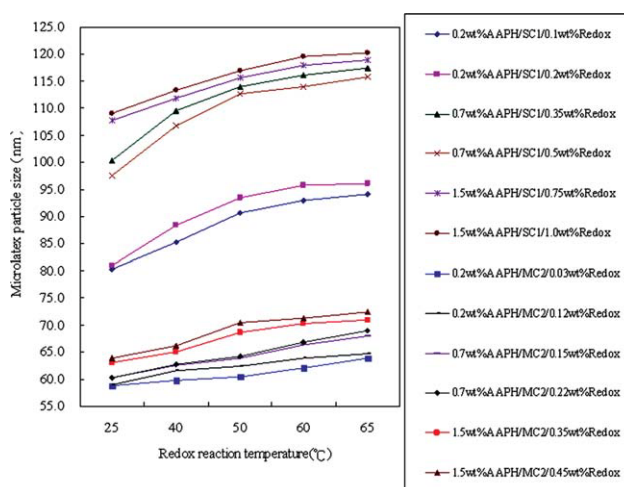


**Figure 1** Effect of AAPH initiator concentration on monomer conversion as a function of the reaction time at 65°C. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

MC2 after 200 min was similar to the one with 1.5 wt % AAPH and attained 96% upon 240 min. From 240 to 320 min, the attained conversion rates of 0.2 wt % AAPH/MC2, 1.5 wt % AAPH/MC2, 2.0 wt % AAPH/SC1, and 2.0 wt % AAPH/MC2 were similar, whereas the rates of other samples showed a slightly increasing tendency but kept constant after 280 min. The results could be assumed that the maleate surfactants copolymerized simultaneously with the monomer mixture at reaction temperature within the microemulsion droplet, where the propagation had limitation although a higher concentration or more amount of initiator was added. Another limitation in conversion was observed with further addition of the monomer mixture to the propagation chain from 80 to 240 min. It is assumed that monomers have a different reactivity ratio and solubility in polymerization loci. Sanghvi et al.<sup>15</sup> studied that the actual concentration of 2-HEMA within the monomer droplet would be

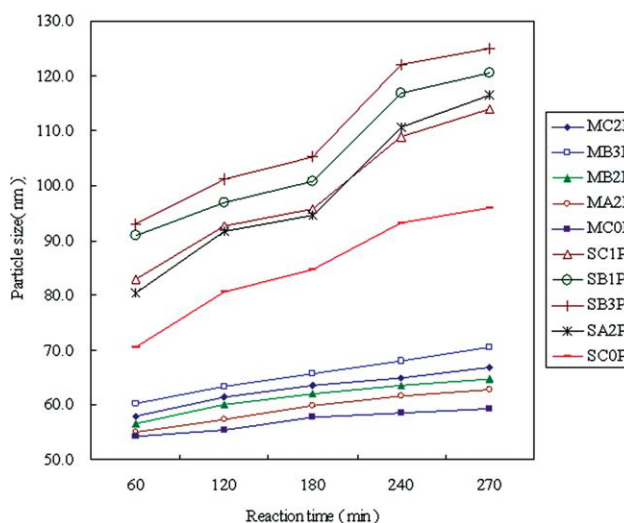


**Figure 2** Effects of redox pair concentration and reaction temperature on monomer conversion (redox pair: TBHP/SFS = 1/1, reaction time: 25 min). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 3** Effects of redox pair concentration and reaction temperature on particle size of microlatex (redox pair: TBHP/SFS = 1/1, reaction time: 25 min). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

smaller than the hydrophobic styrene in the feed due to low solubility of styrene and complete solubility of 2-HEMA in the aqueous phase. It caused different monomer distribution between microemulsion droplets and the aqueous phase to capably govern the reactivities of monomers. In this study, we tried to reduce free monomers and attain 100% conversion by further initiation with redox chemicals.



**Figure 4** Effects of different monomer ratios and surfactant contents on particle size of microlatex during the reaction time when 100% conversion of SC1 and MC2 were attained (SA2P, SB1P, SC0P, SC1P : [AAPH] = 1.5 wt %, [50% TBHP and 50% SFS] = 1.0wt%, MC0P, MC1P, MC2P, MC3P : [AAPH] = 1.5 wt %, [50% TBHP and 50% SFS] = 0.35wt%, polymerization reaction: 65°C from 60 min to 240 min, redox reaction: 60°C from 245 to 270 min). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

The concentration of the redox pair and reaction temperature posed synchronizing effects on the monomer conversion rate in Figure 2. The TBHP and SFS were added in equal ratio with the investigated dosage (by 50–100% of AAPH weight) after the polymerization proceeded at 65°C for 4 h. Originally obtained conversion rate was not observed to be upgraded with any amount of redox chemicals if the redox reaction temperature was set at 25°C. From 40 to 65°C, the comparison manifested that the conversion rate was greatly enhanced in the presence of polymerizable maleate surfactants and that the polymerization rate was much higher even with much lower redox concentration. The results of microlatex particle size gave the determination of the above effects in Figure 3. The average particle size of microlatex produced by polymerizable maleate surfactant system (MC2) ranged from 60 to 70 nm, which was slightly larger than the originally formed microemulsion droplets (56.5 nm). However, the microlatex particle prepared by the conventional POE surfactant system (SC1) was generally one to two times that of the microemulsion droplets to imply that microemulsion polymerization without appropriate steric stabilization proceeded in the coalescence of one to two droplets. It can be shown in the system of 0.7 wt % AAPH/SC1/0.35 wt % redox, 1.5 wt % AAPH/SC1/0.75 wt % redox, and 1.5 wt % AAPH/SC1/1.0 wt % redox, which of particle sizes in original state (at 25°C) were above 100 nm to be unstable and producing larger latex particle relatively from 40 to 65°C. The systems of 0.2 wt % AAPH/SC1/0.1 wt % redox and 0.2 wt % AAPH/SC1/0.2 wt % redox presented smaller microlatex particle size (<95 nm) probably due to low dosage of initiators, leading to a very mild propagation but slower or much incomplete conversion rate shown coordinately in Figure 2. Therefore, the SC1 system could be optimized with 0.5 wt % of the redox pair and the amount of AAPH in the range between 0.2 and 0.7 wt % to obtain the particle size of 95–115 nm at 65°C. In the comparison with the MC2 system, slow increase of particle size was observed in the samples with 0.2 wt % of AAPH and 0.03–0.12 wt % of redox pair when the redox reaction temperature was raised from 25 to 65°C. The microlatex particle size was enlarged dramatically from 63 to 70 nm when the system containing 0.7 wt % of AAPH was added with the redox pair in the amount between 0.12 and 0.15 wt % at the temperature varying from 50 to 65°C. If the content of AAPH was raised to 1.5 wt % and the redox pair from 0.35 to 0.45 wt %, the particle size was increased considerably from 65 to 70 nm at the temperature between 40 and 50°C. However, the propagation kept nearly constant with the particle size increasing not more than 73 nm at 65°C to possibly infer the synchronization of termi-

nation induced by those overweighted initiators. Combining the discussion with those monomer conversion rates at 100% in Figure 2, the contents of AAPH (1.5 wt %) and the redox pair (0.45 wt %) assisted the MC2 system to complete copolymerization at 50°C by forming a maximum latex particle size of 70 nm. For the SC1 system, higher redox reaction temperature of 60°C was required with a much larger particle size of 120 nm. Lower contents of 0.7 wt % AAPH and 0.22 wt % redox pair in the MC2 system were preferred with lower particle size (66.8 nm) and almost complete conversion rate (99%). The latex particle sizes of both systems increased with higher polymerization rate and reaction temperature to imply more significant nucleation in the microemulsion droplets. The copolymerized surfactant covalently bond around the latex particle surface to form a polar shell and enhance stabilizing efficiency.

In Figure 4, the effects of lower monomer ratios and higher surfactant concentration on reducing the particle size of microlatex were illustrated when the above optimal condition of polymerization was found accordingly. The initial composition of 50 wt % monomer mixture, 100 wt % emulsifiers, 40 wt % AAPH, and 50 wt % distilled water proceeded polymerization within the O/W microemulsion region to form smallest particle size in 60 min. As the remaining amounts of mixed monomer and initiator were continuously added dropwise to the copolymerizing microemulsion with stirring in 240 min, the slow increased particle size probably meant that more monomers diffuse into the seeded polymer particle and further copolymerized gradually when AAPH initiator decomposed and primary radicals reacted in the hydrophobic monomer (styrene, 2-EHA, IBMA), swollen micelles, and with hydrophilic monomers (2-HEMA) dissolved in aqueous phase. It applies to the control of the termination mechanism by such chain transfer reaction to the monomer.<sup>16</sup> When the polymerization was accelerated by adding redox pair of TBHP and SFS for another 25 min, samples stabilized by the polymerizable maleate surfactant system (C2M) produced much smaller and steadier latex particle growth with higher monomer content than that stabilized by conventional POE surfactant system (SS). The smallest latex particle sizes in two systems with most steady latex particle growth were observed in samples SC0P and MC0P containing highest monomer amount without IBMA. In SS system of formed latex polymers (SA2P, SB1P, SB3P, SC0P, SC1P), the particles increased dramatically from the reaction time of 180 min. Sample SC1P containing highest monomer weight ratio of 15 wt % attained smaller particle size than sample SA2P on the reaction time of 240 min to imply the effective stabilization of the surfactant system of 2.0

wt % SS(1 : 2). Samples SA2P, SB1P, and SB3P caused larger particle sizes in accordance with higher monomer weight ratio and raised IBMA content. In C2M system thereof (MA2P, MB2P, MB3P, MC0P, and MC2P), the particle size of latex increased slightly with higher monomer ratio, although the surfactant dose was raised from 0.2 to 0.6 wt %. Sample MC2P with highest monomer ratio and IBMA content presented more steady growth of smaller particle size than sample MB3P. Furthermore, samples SB3P and MB3P were compared, respectively, in two systems to show their largest particle size and low solid content probably caused by the incomplete conversion rate in Table II. The two systems were similar in requiring a higher ratio of anionic surfactants to stabilize latex particle growth. Therefore, maintaining stable droplets throughout the reaction process is essential to achieve high polymer content in microemulsion polymerization.

Comparing the latex properties of the two systems as shown in Table II, higher solid content was attained by the C2M system and more contents of monomers, especially IBMA. Without IBMA, samples SC0P and MC0P were common in the highest monomer ratio, 100% monomer conversion rate, lowest solid content, and lowest viscosity. The increased amount of IBMA rendered considerably higher viscosity and higher solid content, except for SB3P and MB3P. The surface tension thereof was also reduced with higher surfactant amount, especially with anionic surfactant and higher HLB value (C2M versus C1M). Generally, system SS produced latex with lower pH value (5.2–5.8), lower surface tension (43.0–44.5 dyn/cm), but higher viscosity (23.4–25.5 cps) than the system C2M with pH value in the range of 6.0–6.9, surface tension of 44.0–49.8 dyn/cm, and viscosity of 12.2–15.0. The obtained properties were compatible with applied sublimation inks and submitted to the following application evaluation.

#### Ink jet printing performance of sublimation inks containing microlatex microemulsion

The above results provided microlatex microemulsion of styrene, 2-EHA, 2-HEMA, and IBMA copolymers that were stabilized by polymerizable maleate surfactant and POE surfactant also ready for ink preparation. To optimize application conditions of sublimation inks containing copolymer latex microemulsion on 100% knitted cotton fabrics, the concentration of copolymer latex microemulsion was investigated for samples SA2P, SB3P, SC0P, SC1P, MA2P, MB3P, MC0P, and MC2P with relative amounts of IBMA and solid content. Since ink viscosity correlates closely with the printing velocity and printing

**TABLE II**  
The Properties of Copolymer Microlatex Via O/W Microemulsion Polymerization

Samples	Monomer conversion rate (%)	Solid content (wt %)	pH value	Viscosity (cps)	Surface tension (dyne/cm)
SA2P	100	25.3	5.8	24.5	44.2
SB1P	100	25.8	5.5	24.6	44.0
SB3P	97	25.0	5.2	25.5	43.5
SC0P	100	25.4	5.6	23.4	44.5
SC1P	100	28.0	5.2	25.3	43.0
MA2P	100	36.3	6.7	13.0	49.1
MB2P	100	37.8	6.6	14.2	48.7
MC0P	100	35.7	6.9	12.2	44.0
MC2P	100	39.6	6.0	14.5	47.3
MB3P	98	37.5	6.7	15.0	49.8

consistency in our former study, each concentration was adjusted without making original ink viscosity increase more than 1 cps. The ink jet printing performance of microlatex in sublimation inks was determined with a number of nozzles clogged after the printing durability test and series of color evaluation in Tables III and IV.

Due to a different dye chemical structure and formulation nature in four color inks, the copolymer microemulsions displayed quite different conformations in ink media, which reflected in the viscosity variation. The effects of copolymer microemulsion addition on the viscosity properties of four color inks depend on concentration, copolymer substitution, viscosity, and particle size. Samples SC0P and MC0P were allowed in highest concentration with least viscosity variation due to zero content of IBMA causing much less chain conformation. Higher concentration of copolymer microemulsion tolerated in samples MA2P, MB3P, and MC2P could be ascribed to surfactant-induced intramolecular interactions and consequently to slight conformational changes of polymer chains, so leading to a small variation in the original ink viscosity. Also, the inherent stability, lower viscosity, and smaller particle size of these copolymer microemulsions could contribute to a higher content in inks. However, samples SA2P, SB3P, and SC1P had limited concentration less than 1% in inks due to the intermolecular connections promoted by the prevailing micelles in the system which caused conformation and interaction between polymer chains and composition in inks. It could be also assumed that SC1P with highest solid content and SB3P containing largest particle size in most amount of IBMA tended to clog more printer nozzles. Although SA2P contained less amount of monomer than SC1P, its larger particle size in Figure 4 reduced printing durability for 180 h and still clogged two nozzles after run. The observed nozzle clogging also meant lack of ink drop ejection to describe poor ink jetting behavior from the orifices



**TABLE III**  
**Compatibility of Copolymer Latex Microemulsion with**  
**A'Tex Sublimation Inks on Mutoh RJ8000 Ink Jet Printer**  
**(Printing Resolution: 360 × 360 dpi)<sup>a</sup>**

	Maximum concentration of copolymer latex microemulsion in four color inks	Printing durability (h)	Number of nozzle clogged
SA2P	Cyan: 0.2% Magenta: 0.2% Yellow: 0.7% Black: 0.5%	180	2
SB3P	Cyan: 0.2% Magenta: 0.2% Yellow: 0.5% Black: 0.5%	100	5
SC0P	Cyan: 0.8% Magenta: 0.8% Yellow: 1.5% Black: 1.0%	240	2
SC1P	Cyan: 0.4% Magenta: 0.5% Yellow: 0.7% Black: 0.7%	200	2
MA2P	Cyan: 2.3% Magenta: 2.5% Yellow: 2.8% Black: 2.8%	>240	0
MB3P	Cyan: 1.7% Magenta: 1.7% Yellow: 2.8% Black: 2.2%	200	2
MC0P	Cyan: 2.5% Magenta: 2.5% Yellow: 3.0% Black: 3.0%	>240	0
MC2P	Cyan: 1.7% Magenta: 2.2% Yellow: 2.8% Black: 2.2%	>240	0

<sup>a</sup> Each concentration was based on viscosity variation of blank inks within 1 cps.

of the print-head. Although the mean particle size of samples SC0P, SC1P, SA2P, SB1P, and SB3P in Figure 4 were much smaller than the diameter of

one nozzle (50 μm), the latex particles with poor steric stability tended to proceed in the coalescence of few particles or flocculation around the orifices of the print-head, possibly causing misdirection of the ink drop or prevention of drop ejection. Sublimation inks in cyan and magenta were influenced more easily by larger latex particle size and higher solid content with IBMA composition so that the latex microemulsion concentration was limited to be not as high as other two colors. The possible reason was that the dye structures of cyan and magenta which were mostly in anthraquinone form posed lower steric hindrance from IBMA copolymer structure to form agglomerates. The dye structures of yellow and black usually in diazo form had more satisfactory compatibility with the copolymer without increasing particle size. Yellow ink could contain highest amount of latex microemulsion to imply the highest compatibility or strongest steric stability between two nano-particles of yellow disperse dye and the latex. The best printing durability of more than 240 h were observed in MA2P, MC0P and MC2P without nozzle clogging. The two clogged nozzles of MB3P, however, could be also attributed to the large latex particle size with high content of IBMA causing inferior printing durability. IBMA is well known for undergoing a self-crosslinking reaction and a condensation reaction of the isobutoxymethyl groups with hydroxyl, carboxyl, amine, or amide groups in copolymer systems or in the cellulosic substrates to produce network polymer and isobutanol.<sup>17</sup> When the IBMA containing copolymer is applied on the cotton fabric, the crosslinking occurs upon heating by tying up the hydroxymethyl group as part of the polymer-to-substrate linkage.

When the cotton fabric was inkjet printed with each disperse ink sample, the prints with good edge acuity were observed during ink jet printing and sublimation. After 30 days, worse edge acuity with dye diffusion were found in samples SA2P, SC0P, and MC0P where color differences were more than 0.8 and up to 3.0. Moreover, samples SC0P and

**TABLE IV**  
**Evaluation of Disperse Dye Inks Containing Copolymer Latex on the 100% Cotton Fabrics by**  
**Mutoh RJ8000 Ink Jet Printer**

	Color strength K/S (C,M,Y,K)	Color fading (ΔE)	Color fastness			Hand feel
			Washing	Rubbing	Light	
SA2P	6.2, 7.3, 7.2, 6.6	0.8 <sup>a</sup>	3	3	4	Soft
SB3P	6.4, 7.7, 7.5, 6.8	0.3	4	4	4	Soft
SC0P	3.8, 4.6, 4.8, 4.0	3.0 <sup>a</sup>	1–2	2	4	Soft
SC1P	6.8, 7.9, 7.2, 7.0	0.4	3–4	3–4	4	Soft
MA2P	7.3, 8.4, 8.2, 7.3	0.3	3–4	3–4	4	Soft
MB3P	7.2, 8.5, 8.4, 7.8	0.1	4	4	4	Slight hard
MC0P	4.5, 4.9, 5.3, 5.0	3.0 <sup>a</sup>	1–2	2	4	Soft
MC2P	7.3, 9.0, 8.4, 7.5	0.1	4	4	4	Soft

<sup>a</sup> Slight dye diffusion on the cotton fabric after stored for 30 days.

MC0P presented worst washing and rubbing fastness with grades 1–2. Sample SA2P was not satisfying either with the two fastnesses at grade 3. Other samples still remained good edge acuity without obvious color difference which was lower than 0.5. As the concentration of latex microemulsion or IBMA content in inks increased, the color strength expressed as K/S value and color fastness in washing as well as rubbing were significantly improved. Therefore, the IBMA copolymer assured a stronger fixation of disperse dye with cotton fibers. The light-fastness of each sample was the same at grade 4 to imply that IBMA copolymer wouldn't affect the performance of disperse dyes under the light exposure. Compared with samples SA2P and SB3P, SC1P possessed best printing durability, highest color strength but moderate color fading ( $\Delta E = 0.4$ ), washing, and rubbing fastness (grade 3–4). Although SB3P gained highest washing and rubbing fastness with fair color fading, it was suggested to acquire adapted copolymerization condition to attain complete monomer conversion rate with small and stable particle size. Samples MB3P and MC2P attained similar properties in highest color strength, least color fading ( $\Delta E = 0.1$ ) and best color fastness in washing and rubbing (grade 4), but the hand softness was slight hard for MB3P. Therefore, MC2P acted as the best impregnation primer in applied inks and provided the cotton fabric with a soft crosslinked matrix to embed disperse dyes when heated in the sublimation process. Its network formation would also kinetically hinder the dye particle from diffusing or migrating.

### CONCLUSIONS

Styrene/2-EHA/2-HEMA copolymers functionalized with N-(isobutoxymethyl) acrylate have been successfully prepared by optimized semicontinuous microemulsion polymerization. We proved that our selected mixtures of polymerizable anionic and non-ionic surfactants in small quantities (0.2–0.6 wt %) gave 100% monomer conversion rate with the aid of mild redox initiation at 60°C. Contrary to the conventional POE surfactants, the polymerizable maleate surfactants capably maintained produced microlatex particle size (60–68 nm) not much more than the originally formed microemulsion which had the mean particle diameter of 55–60 nm with narrow particle size distribution and high stability. As the monomer mixture ratio and IBMA content increased, the polymer solid content in the C2M sys-

tem was enhanced up to 39.6% and most microemulsion droplets needed to be stabilized with higher amounts of anionic surfactants and 2-HEMA which played as a cosurfactant. The latex particle growth during copolymerization was effectively controlled by (1) our semibatch of termination reaction, (2) modified polymerization rate from reaction time, redox reaction temperature, and concentration of initiator and redox chemicals, (3) complete monomer conversion rate, and (4) covalent bond of copolymerized surfactants around the latex particle surface to form a steric hindrance from particle coalescence.

The copolymer latex microemulsion in high solid content was compatible with applied sublimation inks by exhibiting small viscosity variation and similar pH value and surface tension to the original inks. The optimum inks prepared from the microemulsion with high IBMA content could tolerate printing durability more than 240 h without nozzle clogging. The printed cotton fabric by the above inks attained color fixation via sublimation to present good edge acuity, nearly zero color fading, high color strength, soft hand touch, and excellent color fastness at grade 4.

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