

# Preparation of Macro Reversible Addition–Fragmentation Chain Transfer Copolymers and Their Application in Pigment Dispersion

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**ABSTRACT:** By using reversible addition–fragmentation chain transfer (RAFT) controlled polymerization, we prepared styrene–maleic anhydride copolymers with RAFT end groups. The resulting copolymers were characterized by Fourier transform infrared and <sup>1</sup>H-NMR spectroscopy. The molecular weights and molecular weight distributions were determined with gel permeation chromatography. The dispersing ability of the hydrolyzed macro reversible addition–fragmentation chain transfer (macro-RAFT) copolymers was evaluated. An organic phthalocyanine blue pigment (P.B.15 : 3) was dispersed with the macro-RAFT copolymers by vigorous stirring and ultrasonic processing.

The properties (particle size and polydispersity index) of the pigment dispersions were measured. The results show that with prolonged ultrasonication time, the particle size and polydispersity index decreased first and increased slightly later. There were no remarkable differences in the particle size and particle size distribution between the macro-RAFT copolymer and poly(styrene-co-maleic anhydride) dispersed pigment dispersions. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 125: 915–921, 2012

**Key words:** copolymers; dispersions; dyes/pigments; particle size distribution

## INTRODUCTION

Textile inkjet printing has demonstrated superior properties over traditional screen-printing methods because of its higher pattern resolution, low pollution, and rapid response to the frequent shift of cloth fashion. Inkjet printing inks are categorized into two major types: dyed inks and pigmented inks. Pigmented water-based ink shows much more superiority than dyed ink because of higher light-fastness and washing fastness, suitability for all kinds of fibers and fabrics, and shorter printing procedure.<sup>1</sup> However, because of their low polarity, organic pigments have always existed in aggregation or coagulation powders. They are water-insolu-

ble, difficult to wet in aqueous media, and generally applied as aqueous dispersions.<sup>2,3</sup>

The dispersant plays an important role in the preparation of pigment dispersion. A traditional dispersant for organic pigments is a surfactant with a low molecular weight. They show some dispersability in water, but they cannot firmly adsorb on the surface of pigment particles. To disperse pigments in water with high stability, polymeric dispersants have been developed, which have a certain length of hydrophobic chain segments and some hydrophilic groups. Polymeric dispersants can adsorb on the particle surface via anchoring segments (hydrophobic chains) to form a layer around the particles, which extends into the surrounding medium to provide entropic stabilization.<sup>4</sup> Meanwhile, polymer chains can prevent particle aggregation by steric and static repulsion.

Polymeric dispersants have proven to have good properties in stabilizing pigments in aqueous media. These polymers have hydrophobic chains, which can attach to organic pigment surfaces by van der Waals forces and hydrophilic chains, which build a voluminous shell around the particles and intensify the charges on the surface to provide static and steric stabilization.<sup>5</sup> Recently, many studies of polymeric dispersants, such as diblock polymers<sup>6</sup> and graft polymers,<sup>7</sup> have been done. In our group,

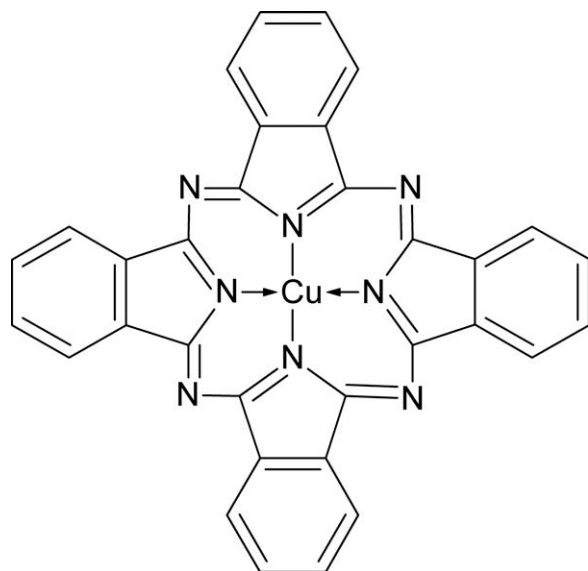
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**Figure 1** Structure of the organic phthalocyanine blue pigment.

copolymers, such as poly(styrene-*co*-maleic anhydride) (PStMA) and poly(methyl methacrylate-maleic anhydride) (PMM), have been synthesized as polymeric dispersants for organic pigment dispersion.<sup>8–10</sup> It was shown that hydrolyzed PStMA can be used as an effective polymeric dispersant for pigment dispersion. The pigment dispersion had a small particle size, narrow distribution, and good stability, and was suitable for preparing pigmented water-based inkjet inks.

The reversible addition-fragmentation chain transfer (RAFT) method is a sophisticated form of controlled free-radical polymerization. It can be stopped and restarted at any time and is often referred to as *living polymerization*. RAFT polymerization, first introduced by group Moad and co-workers<sup>11,12</sup> at commonwealth scientific and industrial research organisation (CSIRO) in 1998, is one of the most convenient and versatile living radical polymerization techniques. It can be done through the addition of a certain amount of RAFT agent to a conventional free-radical polymerization. This technology has prominent advantages, including the ability to prepare polymers with a narrow molecular weight distribution, good compatibility with a wide range of monomers, facile experimental conditions that are similar to those of conventional radical polymerization, and synthesized polymers with reactive terminal groups [regarded as a macro reversible addition-fragmentation chain transfer (macro-RAFT) agent], which allow further chemical manipulation.<sup>12,13</sup> With RAFT-controlled polymerization, random copolymers can readily be prepared. Moreover, the macro-RAFT copolymers thus

synthesized had the advantage of carrying RAFT groups, which allow further chain extension via the addition of desired monomers at a controlled rate.<sup>14</sup>

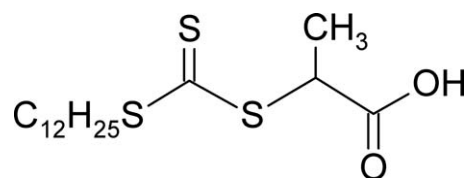
With RAFT-controlled radical polymerization, some amphipathic polymers (macro-RAFT agent) have been synthesized and used for dispersed media.<sup>15–17</sup> It was suggested that an amphipathic macro-RAFT agent can be used as a dispersant for pigment dispersion, with the hydrophobic segments as anchoring groups and hydrophilic groups as the water-soluble part. Moreover, according to the living feature of macro-RAFT agents, amphipathic polymers can extend the polymer chains with the addition of certain monomers. Therefore, it is feasible to functionalize the pigment surface by chain extension of an amphipathic macro-RAFT agent used for pigment dispersion with some monomers.

In this study, a trithiocarbonate RAFT agent, 2-[[[(dodecylsulfanyl) carbonothioyl] sulfanyl] propanoic acid, was synthesized. Macro-RAFT copolymers of styrene (St) and maleic anhydride (MA) were prepared through the RAFT process. The copolymers were characterized by Fourier transform infrared (FTIR) spectroscopy and gel permeation chromatography (GPC) analysis. The application of macro-RAFT copolymers for pigment dispersion preparation was evaluated.

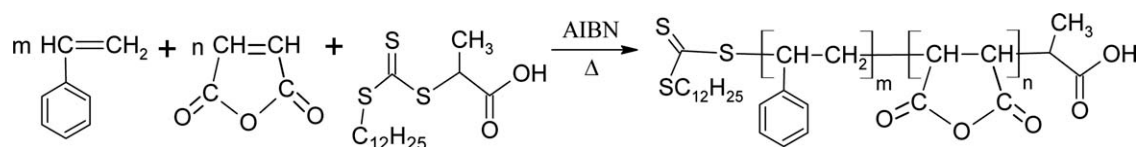
## EXPERIMENTAL

### Reagents

Water was distilled and deionized before use. The organic phthalocyanine blue pigment (P.B.15 : 3, Fig. 1), a gift from Changzhou North American Chemical Group (Changzhou, Jiangsu province, P.R. China), was used as supplied. Carbon disulfide, 1-dodecanethiol, tetrabutyl ammonium bromide, hexane, acetone, and 2-bromopropanoic acid (Sinopharm Chemical Reagent Co., Ltd.) were used as received. The monomers St and MA (Sinopharm Chemical Reagent Co., Ltd., Shanghai, P.R. China) were distilled *in vacuo* and kept refrigerated until use. The initiator, 2,2'-azobisisobutyronitrile (AIBN), was purified by recrystallization from ethanol.



**Figure 2** Structure of the RAFT agent 2-[[[(dodecylsulfanyl) carbonothioyl] sulfanyl] propanoic acid.



Scheme 1 Preparation of the macro-RAFT copolymers of St and MA.

### Synthesis of the RAFT agent

The RAFT agent, 2-[(dodecylsulfanyl) carbonothioyl] sulfanyl] propanoic acid (Fig. 2), was synthesized as follows:<sup>18,19</sup>

1. A 40% sodium hydroxide solution (4.00 g, containing 1.60 g, or 40 mmol, of NaOH) was added to a stirred mixture of 1-dodecanethiol (8.08 g, 40 mmol) and water (60 mL). Then, acetone (20 mL) and a tetrabutyl ammonium bromide solution [6.4 g, containing 1.28 g, or 4 mmol, of  $(C_4H_9)_4NH_4^+Br^-$ ] were added, and the turbid mixture became clear and transparent.
2. The resulting clear solution was stirred for 30 min, then cooled to near room temperature, and treated with carbon disulfide (3.42 g, 45 mmol) to give a clear orange solution. It was stirred for another 30 min, then cooled with an ice bath to an internal temperature of less than 10°C. 2-Bromopropanoic acid (6.273 g, 41 mmol) was added at a rate such that the temperature did not exceed 10°C. Then, a 40% sodium hydroxide solution (4.1 g, containing 1.64 g, or 41 mmol, of NaOH), was added, and the temperature was also kept lower than 10°C. When the exotherm had stopped, the ice bath was removed, and 60 mL of water was added.
3. The obtained orange solution was stirred at ambient temperature for 24 h, then diluted with water (20 mL), stirred, and cooled in an ice bath; then, hydrochloric acid was added at a rate that kept the temperature less than 10°C. With HCl addition, the yellow oil separated; stirring of the mixture was continued until the oil solidified. The solid was collected by suction filtration, washed with cold water, and dried under reduced pressure. The crude sample was purified by recrystallization from hexane four to five times with gentle stirring to give bright yellow microcrystals.

### Preparation of the macro-RAFT copolymers

The RAFT agents were reacted with St and MA in the presence of the initiator to give the macro-RAFT copolymers. A solution of 2-[(dodecylsulfanyl) car-

bonothioyl] sulfanyl] propanoic acid (0.75 g), AIBN (0.15 g), St (9.37 g), and MA (5.88 g) was prepared in dioxane (50 g) in a 250-mL, round-bottom flask. This was sparged with nitrogen for 10 min and stirred slightly. Then, the flask was heated to 70°C and maintained for a certain time under constant stirring. Although the reaction solution was transferred to cold water, the synthesized copolymers were precipitated. Copolymers of St and MA were synthesized with the same method without the RAFT agent (Scheme 1).

### Pigment dispersion

Pigment dispersion is normally carried out by mechanical milling or ultrasonication. The aim of these processes is to apply external force to break up pigment aggregates into small particles. During the breaking process, dispersants adsorb onto the surface of the pigment particles to prevent them from agglomerating to large ones.

A solution containing macro-RAFT copolymer, water, and sodium hydroxide was prepared in a 50-mL beaker. To this solution, P.B.15 : 3 was added, mixed, stirred, and then dispersed with a JY98-3D ultrasonic pulverizer (Scientz Co., Ningbo, Zhejiang province, P.R. China) at a power of 800 W (work model = 1 s/4 s pulse on/off) for 10 min. During the ultrasonication process, the dispersion was cooled with a cold water bath.

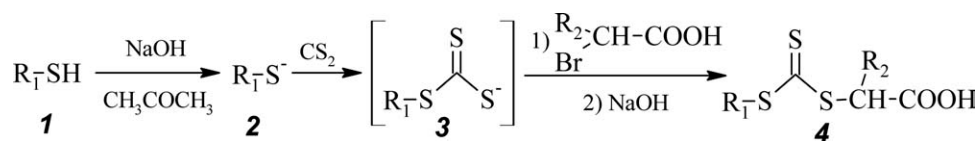
### Measurements

#### FTIR spectra

FTIR spectra were recorded on a Nicolet NEXUS 470 spectrometer (Thermo Fisher Scientific, Inc., Vernon Hills, Illinois, USA) with a deuterated triglycine sulfate (DTGS) detector. The dried samples mixed with KBr were compressed into a disc for FTIR scanning. The measurement was performed with 32 runs of scanning and at a resolution of 2  $cm^{-1}$ .

#### GPC analysis

The molecular weights and molecular weight distributions were determined with GPC. Analyses were carried out with a Waters 1515 high performance liquid chromatography (HPLC) system (Waters Corp., Milford, Connecticut, USA) fitted with a



Scheme 2 Synthesis route of the trithiocarbonate RAFT agent with carbon disulfide.

series of HP PLgel MIXED-C columns ( $3 \times 10^{-6}$  and  $5 \times 10^{-6}$  L). The polymers were dissolved in *N,N'*-dimethylformamide (chromatography pure) and filtered with a 45- $\mu\text{m}$  filter. The molecular weight was determined from Waters 2414 refractive index data analyzed with Waters Breeze GPC software, with all of the molecular weights being relative to polystyrene standards.

#### Particle size and its distribution

The particle size was measured at 25°C with a Malvern NANO-ZS 90 instrument (Malvern Instrument Ltd., Malvern, Worcestershire, UK) at a fixed scattering angle of 90°. The dispersion was diluted with distilled water before measurement. Dynamic light scattering measurements gave a Z-average size, which was the intensity mean of the particle diameter, and the polydispersity index (PDI), which provided information about the width of the particle size distribution.

## RESULTS AND DISCUSSION

### Preparation of the RAFT agent

In RAFT radical polymerization, a variety of thiocarbonythio compounds [ $\text{Z}-\text{C}(=\text{S})-\text{S}-\text{R}$ ], including dithiobenzoates, trithiocarbonates, xanthates, dithiocarbamates, and other compounds, were used. In this research, a RAFT agent with trithiocarbonates structure was synthesized according to the reaction mechanism of a carbodithionate salt with an alkylating agent, as shown in Scheme 2.<sup>20,21</sup>

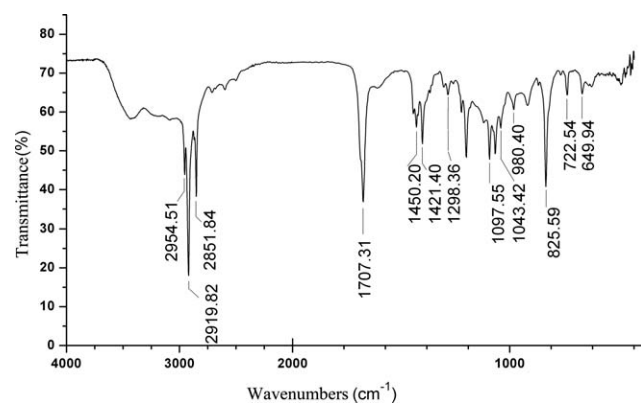


Figure 3 FTIR spectrum of the RAFT agent.

In the basic conditions, thiol (**1**; with Z group) ionized to the anionic form (**2**). The addition of carbon disulfide to **2** gave the thiocarbonylthio salt (**3**). Without the need for isolation, the trithiocarbonate could be made to interact with the alkylating agent, with the appropriate R group. The intermediate sodium salt (**3**) was not stable and was easily oxidized in air; therefore, the synthesis was processed in one pot, and the alkylating agent reacted with **3** *in situ*.

The synthesized RAFT agent was characterized with FTIR and <sup>1</sup>H-NMR spectroscopy. As shown in Figure 3, the wave numbers of groups vibration were as follows:  $\nu(\text{O}-\text{H})$ , 3437.01  $\text{cm}^{-1}$ ;  $\nu(\text{C}-\text{H})$ , 2954.51, 2919.82, 2851.84  $\text{cm}^{-1}$ ;  $\nu(\text{C}=\text{O})$ , 1707.31  $\text{cm}^{-1}$ ;  $\nu(\text{C}-\text{S})$ , 1209.87  $\text{cm}^{-1}$ ;  $\nu(\text{C}=\text{S})$ , 1097.55  $\text{cm}^{-1}$ . The chemical shifts of hydrogen atoms were as follows:  $\delta$  (ppm): 10.89 (br, 1H,  $\text{CO}_2\text{H}$ ), 4.87 (q,  $J = 7.4$  Hz, 1H,  $\text{SCH}$ ), 3.36 (t,  $J = 7.4$  Hz, 2H,  $\text{CH}_2\text{S}$ ), 1.70 (quint,  $J = 7.4$  Hz, 2H,  $\text{CH}_2\text{CH}_2\text{S}$ ), 1.63 (d,  $J = 7.4$  Hz, 3H,  $\text{SCHCH}_3$ ), 1.39 (sext,  $J = 7.44$  Hz), 1.26 [br, 16H,  $\text{CH}_3\text{CH}_2(\text{CH}_2)_8$ ], 0.88 (t,  $J = 6.7$  Hz, 3H,  $\text{CH}_3\text{CH}_2$ ).

### Preparation of the macro-RAFT copolymers

A trithiocarbonate RAFT agent with a dodecylsulfanyl Z groups (shown in Fig. 2) was used to prepare macro-RAFT copolymers.

FTIR spectra of the macro-RAFT copolymer and PStMA are shown in Figure 4. In the FTIR spectra, wave numbers of 1454, 1495, and 1602  $\text{cm}^{-1}$  were attributed to the in-plane stretching vibrations of  $-\text{C}=\text{C}-$  in benzene. There were symmetric and asymmetric stretching vibrations of  $\text{C}=\text{O}$  at wave numbers of 1778 and 1856  $\text{cm}^{-1}$ , and the absorption

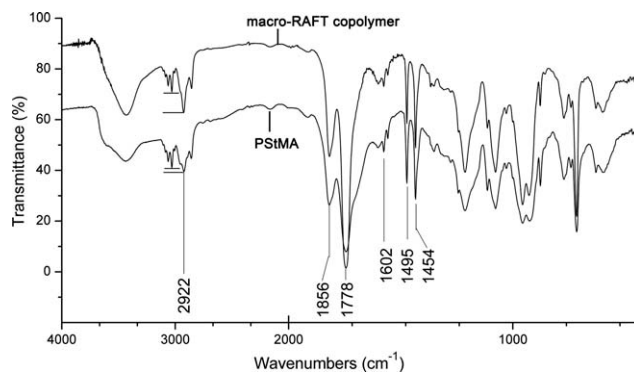


Figure 4 FTIR spectra of the copolymers.

**TABLE I**  
Molecular Weight and Molecular Weight Distribution Values of the Copolymers

| RAFT (%) <sup>a</sup> | $M_n$   | $M_w$   | PDI  |
|-----------------------|---------|---------|------|
| 0                     | 152,410 | 233,339 | 1.50 |
| 1.0                   | 75,551  | 107,029 | 1.42 |
| 2.5                   | 60,561  | 79,693  | 1.32 |
| 5.0                   | 42,518  | 55,134  | 1.30 |
| 7.5                   | 33,296  | 43,010  | 1.29 |
| 10.0                  | 18,936  | 21,806  | 1.15 |

$M_n$  = number-average molecular weight;  $M_w$  = weight-average molecular weight.

<sup>a</sup> The amounts of RAFT agent are weight fractions relative to all of the monomers.

intensity at  $1856\text{ cm}^{-1}$  was much weaker than that at  $1778\text{ cm}^{-1}$ , which was attributed to the remarkable characteristic of cyclic anhydrides (five-membered rings). We deduced from these absorption bands that there were St and MA units in the synthesized copolymers.

It was proven from the FTIR spectra that St and MA copolymerized according to RAFT living radical polymerization with the trithiocarbonate RAFT agent. As shown in the FTIR spectra (Fig. 4), there were some differences in the absorption intensity in some bands between the macro-RAFT copolymer and PStMA. The relative absorption intensities of the macro-RAFT copolymer at wave numbers of  $2922$  and  $1778\text{ cm}^{-1}$  were much stronger than that of PStMA. Wave numbers of  $2922$  and  $1778\text{ cm}^{-1}$  were attributed to the stretching vibrations of C—H in  $-\text{CH}_2-$  and C—O in  $\text{O}=\text{C}=\text{O}$ , respectively. So, it was certain that the RAFT agent with dodecyl and carboxyl groups copolymerized with St and MA according to the RAFT living radical polymerization process.

The average molecular weights and molecular weight distributions (PDI = Weight-average molecular weight/Number-average molecular weight) of the copolymers are shown in Table I. The average molecular weights and molecular weight distributions

**TABLE II**  
Effect of the Ultrasonication Time on the Pigment Dispersion

| Time (min) | Particle size (nm) | PDI   |
|------------|--------------------|-------|
| 1          | 190.7              | 0.375 |
| 2          | 170.4              | 0.214 |
| 3          | 166.8              | 0.230 |
| 4          | 169.1              | 0.207 |
| 5          | 165.9              | 0.217 |
| 7          | 164.8              | 0.225 |
| 9          | 162.4              | 0.211 |

St/MA = 3 : 2 (mol/mol), RAFT agent = 7.5% (w/w to monomer), AIBN = 10% (w/w to monomer), and copolymer = 10% (w/w to pigment).

**TABLE III**  
Effect of the Amounts of Macro-RAFT Copolymers on the Pigment Dispersions

| Copolymers (wt %) <sup>a</sup> | Particle size (nm) | PDI   |
|--------------------------------|--------------------|-------|
| 3                              | 175.2              | 0.234 |
| 5                              | 156.8              | 0.228 |
| 7                              | 154.8              | 0.219 |
| 10                             | 172.6              | 0.313 |
| 20                             | 169.7              | 0.292 |

<sup>a</sup> The amounts of the copolymers are weight fractions relative to the pigment. Copolymers: St/MA = 3 : 2 (mol/mol), RAFT agent = 2.5% (w/w to monomer), and AIBN = 10% (w/w to monomer).

of the macro-RAFT copolymers were smaller than that of PStMA. Furthermore, they decreased dramatically with increasing amounts of RAFT agent. The narrow molecular weight distributions showed the characteristics of RAFT living radical polymerizations.

From the previous analyses of the FTIR spectra and the molecular weights and molecular weight distributions of the copolymers, we concluded that with the addition of RAFT agent, St and MA copolymerized according to RAFT living radical polymerization (Table II).

### Pigment dispersion

#### Ultrasonication time

The pigment dispersion with the hydrolyzed macro-RAFT copolymers was evaluated. There were St and MA units in the macro-RAFT copolymers. The St hydrophobic region, especially benzene, interacted with organic pigments. The hydrophilic maleic acid or its salt hydrolyzed from MA provided dispersion stability, depending on steric and electrostatic repulsions.

The pigment dispersions were produced by ultrasonication mixture of the pigment, hydrolyzed macro-RAFT copolymers, and water. Ultrasonic waves of high intensity can generate cavitations in liquids. The cavitations can be used for many processes, for example, mixing and blending, deagglomeration, milling, and cell disintegration. In the ultrasonication process, the pigment aggregates were broken up into small particles because of ultrasonic cavitations. With longer time, the particle size of the pigment was smaller, and the particle size distribution (PDI) decreased. After about 5 min of ultrasonication, the particle size almost did not change, and PDI increased slightly. Except for deagglomeration, the effect of ultrasonic cavitation was to generate heat. With longer time, heat generation made the dispersions temperature increase. At higher temperatures, the Brownian movement of particles speeds up, and the smaller particles may interact with each

**TABLE IV**  
**Pigment Dispersions Dispersed with Different Dispersants**

| Dispersant             | Particle size (nm) | PDI   |
|------------------------|--------------------|-------|
| RAFT-StMA <sup>a</sup> | 175.3              | 0.251 |
| PStMA                  | 169.7              | 0.221 |
| PMM                    | 232.5              | 0.395 |

The amount of dispersant was 10% relative to the pigment, and the ultrasonication time was 10 min.

<sup>a</sup> St/MA = 3 : 2 (mol/mol), AIBN = 10% (w/w to monomer), and RAFT = 7.5% (w/w to monomer).

other and result in particle agglomerations again; this makes the particle size and PDI increase. Therefore, in the ultrasonic dispersing procedure, the dispersion temperature must be kept as low as possible, and too long a process is not desirable.

#### Amount of the macro-RAFT copolymers

Table III reveals that the particle size of the pigment dispersions decreased first and increased later with increasing amount of the macro-RAFT copolymers. The variation of the particle size distribution (PDI) was similar to that of the particle size. The smaller the particle size of the pigment was, the larger the surface areas was and, also, the higher the surface energy was. Small particles tended to aggregate to larger ones to reduce the surface energy. Therefore, there were much greater amounts of dispersants required to adsorb on the surface of particles to prevent them from aggregating.

However, too large amounts of the copolymers were not desirable. When the amount of copolymers was too high, a part of the copolymers dispersed in the water; this could increase the viscosity of the dispersion. This led to a lower dispersing efficiency. Moreover, the copolymers dispersed in water might have bridged two or more particles to form large aggregates.

#### Comparison with normal polymeric dispersants

Amphipathic copolymers as polymeric dispersants were used in preparation of the pigment dispersion. The particle size and particle size distribution of the pigment dispersion dispersed with St-MA RAFT copolymer, PStMA, and PMM are shown in Table IV. The pigment dispersions prepared by the macro-RAFT copolymer and PStMA had similar particle sizes and particle size distributions, whereas those prepared by PMM had larger values. The macro-RAFT copolymers polymerized with St and MA via the RAFT mechanism had a similar structure as PStMA, although the Z and R groups remained at the end or middle of the polymer chains. Mean-

while, the Z and R groups of the RAFT agent in this study were hydrophobic and hydrophilic, respectively; they had no side effects on the dispersing ability.

## CONCLUSIONS

Macro-RAFT copolymers were synthesized by RAFT controlled/living radical polymerization. They were characterized by FTIR spectroscopy and molecular weight analyses.

Macro-RAFT copolymers, with hydrophobic and hydrophilic units, have the potential ability to disperse pigments. An organic phthalocyanine blue pigment (P.B.15 : 3) was dispersed with macro-RAFT copolymers by vigorous stirring and ultrasonic processing. The properties of the pigment dispersions (particle size and PDI) were measured. The particle size and particle size distribution (PDI) had a relationship with ultrasonication time and the amounts of the macro-RAFT copolymers. With increased ultrasonication time, the particle size and PDI decreased first and increased slightly later. When the amounts of the copolymers were too low or high, the particle size and PDI were larger. The retention of Z and R groups in the polymer chains had no side effect on the pigment dispersion. There were no remarkable differences in the particle size or particle size distribution between the macro-RAFT copolymer and PStMA dispersed pigment dispersions.

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