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Preparation and Characterization of Acrylic-Based Electronic Inks by In Situ Emulsifier-Free Emulsion Polymerization for Electrophoretic Displays

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Attempts were made to prepare monodispersed electronic ink particles by a new procedure, in situ emulsifier-free emulsion polymerization. Highly monodispersed poly(methyl methacrylate-*co*-ethylene glycol dimethacrylate) electronic ink particles containing blue dyes and charge control additives (E-81) were successfully prepared both in aqueous medium and in a mixture of water and methanol by emulsifier-free emulsion polymerization. On increasing either the concentration of oil blue N or E-81, the particle size decreased initially but then increased in the absence of methanol, whereas particle size progressively increases in the presence of methanol. The addition of methanol in the polymerization also influences the polymerization kinetic and the charge density of electronic ink particles. The resulting electronic inks were found to be smooth on the surfaces and particle sizes were 300−700 nm with a coefficient of variation of 0.3%. Electrophoretic mobility of the resulting electronic ink was -2.08 to -5.28×10^{-5} cm^2/V·s in the presence of charge control additives.

Introduction

Electronic papers (e-papers) have recently been of great interest for applications in information displays requiring low cost, lightweight, flexibility, and low power consumption. Compared to current displays, such as transmissive liquid crystal displays (LCDs)[1,2] or emissive technologies such as organic light diode displays (OLEDs),[3,4] field emission displays (FED, and plasma displays (PDP), the power consumption of electronic ink displays is very low.[5−10] There are several reasons for such low power consumption. First of all, electronic ink displays are fully reflective devices and require no backlights. Second, the generation of the image is based on a bistable mechanism, which does not require power consumption for image retention. The term bistability means that even if the external power turns off, the recorded image remains without power consumption. This bistability is one of the most representative properties for electronic ink displays, providing the electronic ink displays with a competitive edge compared with other display technologies. Colored electronic inks have attracted much attention because the fineness or resolution of the image is strongly dependent on the quality of ink, since full-color images capable of electrophoretic display systems are on the horizon. To achieve high-resolution and true bistability in electrophoretic display, the processes and materials involved in electronic inks must be finely tuned. The enhancement of image quality requires that electronic inks have a very small particle size within a narrow size distribution to produce better images with higher resolution and less edge roughness. Since smaller particle sizes together with uniform size distribution can impart a much more even charge on the particles, the image control becomes more precise and responsive within the given driving voltage. Thus, the particle size and size distribution are key parameters determining the quality of electronic inks. Conventionally, most electronic inks are produced by a pulverization method in which charge control additives and other additives are dispersed in a molten resin matrix, followed by cooling, crushing, pulverization, and classification/separation of the pulverized electronic ink particles within the intended particle size. This method has an inherent limitation to obtain narrow size distribution. These electronic ink particles made by pulverization

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usually contain fractions having significantly larger or smaller than average size and also have an irregular shape. The irregular size and shape of the electronic ink particles make it difficult to put a uniform charge on them. Without a uniform charge, electronic ink particles become very difficult to control in image quality, resulting in fogging and lower image density in the final product. As an alternative for overcoming this problem, the production of electronic inks with a polymerization method can be considered. The selection of the polymerization method depends on the expected size and size distribution of the electronic ink particles. With the dispersion polymerization method,[11−15] it is easy to synthesize particles with a relatively large particle size around 5 μm or less and a narrow particle size distribution, but it is difficult to retain other essential additives inside each particle. Electronic ink particles produced by the emulsion polymerization method[16−24] generally have particle sizes on a submicrometer scale or smaller. In the emulsion polymerization method, there are two methods for growing the particles: the seeded polymerization method and the coagulation method. However, both processes require rather complicated and numerous time-consuming reaction steps. Also the ionic and nonionic surfactant involved in the emulsion polymerization may have a detrimental effect on the electrophoretic response of particles.

Emulsifier-free emulsion polymerization can be a method that overcomes the aforementioned problems, because of the simplicity of the reaction process and the absence of external emulsifier. With this method, electronic inks are formed in situ by the polymerization of a mixture of monomer and dye in both aqueous and a methanol/water mixture. The properties of polymerized electronic inks particles can be controlled by the variation of the reaction medium and polymerization conditions. In this study, the synthesis of an acrylic-based polymerized electronic ink particle by the emulsifier-free emulsion polymerization for electrophoretic displays is demonstrated. The aim of this paper is to report the synthetic procedures of emulsifier-free emulsion polymerization of methyl methacrylate /ethylene glycol dimethacrylate containing blue dye for the electrophoretic displays and to examine the basic electrophoretic response of the prepared ink particles. The effects of the oil blue N concentration and the charge control additives in relation to electrophoretic mobilities are also discussed.

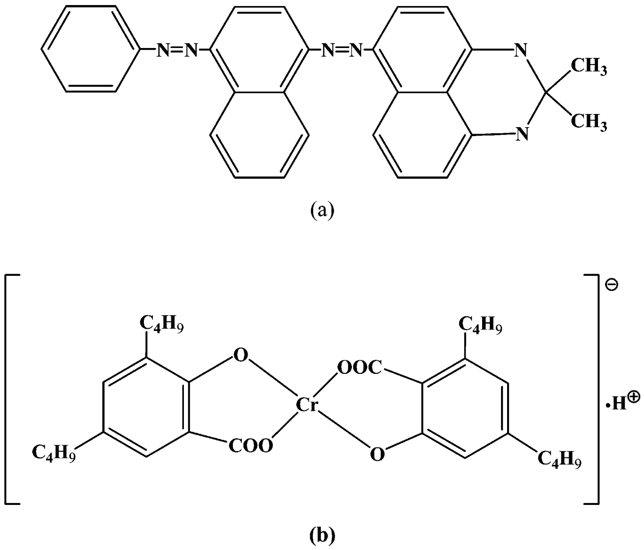

Figure 1. Chemical structure of (a) oil blue N and (b) E-81.

Experimental Section

Materials. Methyl methacrylate (MMA) was purified with 10 wt % aqueous sodium hydroxide solution and passed through an activated aluminum oxide column to remove inhibitor. Ethylene glycol dimethacrylate (EGDMA), oil blue N, and tetrahydrofuran (THF) were used as purchased from Sigma-Aldrich. Bis(3,5-di-*tert*-butylsalicylate) chromium (E-81) (Orient Co.) was selected as the negative charge control additive (Figure 1a). The initiator, 2,2′-azobis(2-methylpropionamidine) dihydrochloride (V-50) (Figure 1b) was obtained from Sigma-Aldrich and recrystallized in a water−acetone mixture (50/50 wt %). Anhydrous ethanol and methanol (absolute) were used as received from Sigma-Aldrich. Polychlorotrifluoroethylene (Dp × 4−10) dielectric suspending fluid was purchased from Halocarbon Product Corp.

Procedure of Electronic Inks by in Situ Emulsifier-Free Emulsion Polymerization. Emulsifier-free emulsion polymerizations were conducted using a batch process. All reactants and water, except for the initiator, were initially charged to a 500 mL glass reactor fitted with a PTFE-bladed paddle stirrer, four equally spaced baffles, a nitrogen inlet, a water-cooled reflux condenser, and a sample-taking syringe. The mixture of monomer and dye is prepared as follows. Purified methyl methacrylate and ethylene glycol dimethacrylate monomers are added to a 100 mL beaker. The ratio of MMA to EGDMA is selected to be 95/5 by weight. Oil blue N dye and charge control additives are added into the monomers in the presence of ultrasonic energy at room temperature. The monomer−dye mixture and dispersing medium (300 mL of water or a mixture of water and methanol) were initially charged to a 500 mL glass reactor. The mixture in the reactor was bubbled with nitrogen for about 10 min under 300 rpm agitation. The initiator in aqueous solution was injected using a glass syringe to start polymerization. The operation conditions were identical for all polymerizations carried out in this work. A representative polymerization recipe is presented in Table 1. The final product is washed with deionized water until the supernatant is transparent, filtered by vacuum, and then dried in a freeze-dryer.

Characterization of Electronic Inks. The final conversion of monomer was measured by a gravimetric method. After evaporation of the most volatile components in a fumed cupboard, the samples were finally dried in a convection oven at 70 °C. Electronic ink particles were filtered with a mesh screen to remove the clusters of dye molecules that had not

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Table 1. Representative Recipe for Emulsifier-Free Emulsion Polymerization of P(MMA-*co*-EGDMA)

ingredient		amounts
monomer	MMA	28.5 g
	EGDMA	1.5 g
continuous phase[a]	water	240−300 mL
	methanol	0−60 mL
dye[b]	oil blue N	0.3−1.5 g
charge control additives[c]	E-81	0.03−0.45 g
initiator	V-50	0.15 g

[a] Total continuous phase is 300 mL. [b] Dye concentration is varied from 1 to 5 wt % of the total monomer base. [c] Charge control additive concentration is varied from 0.1 to 1.5 wt % of the total monomer base.

been incorporated into electronic ink particles and the aggregated electronic ink particles. The monomer conversions were calculated from the weights of fed monomers and dried polymers.

The particle size and size distribution of the electronic inks were measured by dynamic light scattering (DLS, Brookhaven) and field-emission scanning electron microscopy (FE-SEM, Hitachi S-4300). SEM specimens were prepared by redispersing the cleaned electronic inks in methanol and placing a drop of the suspension on a piece of cover glass, which was mounted with double adhesive tape on the carbon stud. The drop was dried in air at room temperature and then sputter-coated under vacuum with a thin layer of gold.

The percent dye incorporated into the electronic ink particles was determined with UV/vis spectrometry by sufficiently swelling the electronic ink particles in tetrahydrofuran (THF) for 5 days with stirring. Dried, blue-colored electronic ink particles were swelled in THF and the concentration of the THF was adjusted to 1 mg/mL. The dye content in blue electronic ink particles was determined by the absorbance at absorption maximum ($\lambda_{\max}$) at 644 nm.

The ζ-potential was measured by means of a Melvern Zetasizer 2000. The electrophoretic mobility (μ) was calculated by the conversion of the ζ-potential with the Smoluchowski relation, $\zeta = \mu\eta/\epsilon$, where η (=2.0 cP) and ϵ (=2.6) are the viscosity and dielectric constant of the suspending fluid, respectively.

Results and Discussion

Effect of Methanol Concentration. Oil blue N (1 wt %) was added to the polymerization systems that contained methyl methacrylate, ethylene glycol dimethacrylate, methanol, water, and V-50 (0.5 wt %). As the amount of methanol in the water−ethanol mixture is increased, the polarity of the reaction medium is decreased and the size of the P(MMA-*co*-EGDMA) particles is increased (Figure 2). On the other hand, the methanol concentration did not have much effect on the particle size distribution, which remains narrow throughout the experimented range (5−20 vol % of methanol of total continuous phase). A comparison of polymerization with and without the addition of oil blue N shows that the presence of oil blue N dyes in the polymerization mixture does effect the particle size as shown in Figure 3. The effects of composition of the continuous phase are summarized in Table 2. The conversion of monomer did not change much regardless of continuous phase composition, suggesting that the presence of methanol does affect the conversion of monomer. Also, Table 2 shows the incorporation of dye molecules in to electronic ink particles, which indicates how much dye is present in the final ink particles. The sample A1, which is prepared without methanol, shows about 2 wt % of incorporation, which means that 98% of dye fed disappeared somewhere outside of the polymer particles. However, the addition of methanol to the polymerization media has a dramatic effect on the dye holding or incorporating ability. As the methanol fraction is increased, the incorporation of dye is improved up to 97% of the theoretical value. In the absence of methanol, the tarlike product was indeed formed at the surface of the reactors, which explains the poor dye holding without addition of methanol. These results clearly demonstrate that the addition of methanol is the key parameter in improving the incorporation of dye inside of polymer particles. It can be also explained by the kinetic of emulsion polymerization. In emulsion polymerization, a considerable portion of polymerization is proceeding in the continuous phase, especially for monomers having a certain degree of water solubility. Acrylic monomers belong to that category. The monomers are diffused out from the monomer droplet and polymerized in the continuous phase. When the growing chain length reaches to a certain limit, such chains are no longer soluble in the continuous phase, separate from the continuous phase, and then start to form particles. Therefore, the incorporation of dye into the particle would depend on whether the dye molecules could be transferred from monomer droplets to the growing particles following the same path as the acrylic monomer. The dye, oil blue N, is completely miscible with acrylic monomers, but it has much lower solubility in water compared with acrylic monomers. Therefore, when using pure water as the continuous phase, the dye molecules cannot pass through the water phase from the monomer droplet to the growing particles and they remain in the monomer droplet. As a result, tarlike residues form at the end of the polymerization, and a poor degree of incorporation into the particles is shown. However, the addition of methanol brings much difference in the transfer of dye molecules from the monomer droplets to the growing particles. Since the solubility of dye is improved by addition of methanol to the water phase, the dye molecules now can go to the growing particles effectively, resulting in a high degree of incorporation into the particles. However, with addition of methanol, the solubility of acrylic monomer is also enhanced. Therefore, the addition of methanol certainly

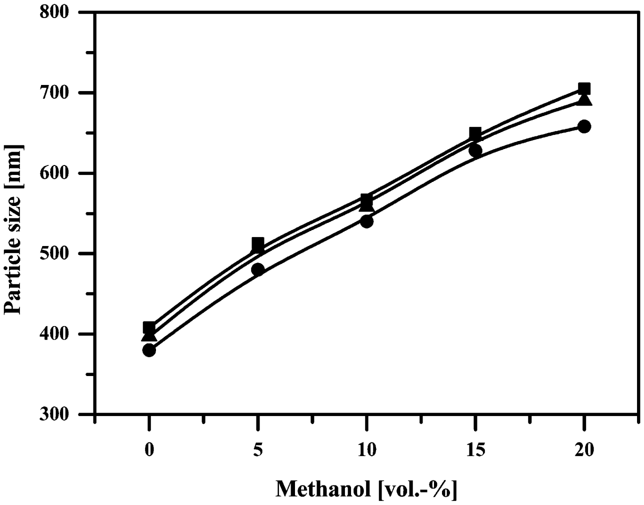


Figure 2. Dependency of electronic ink particle size on the concentration of methanol and oil blue N content: (●) no oil blue N, (▲) 1 wt % oil blue N, and (■) 5 wt % oil blue N.

Table 2. Final Conversion of Monomer and Incorporation of Dye into Polymer Particles as a Function of Water Concentration

sample	monomer MMA	monomer EGDMA	oil blue N (g)	continuous phase (W/M)[a]	absorbance (intensity)[b]	incorporation of dye (%)[c]	conversion of monomer (%)
A-1	28.5	1.5	0.3	100/0	0.02	2	99.2
A-2	28.5	1.5	0.3	95/5	0.048	15	98.6
A-3	28.5	1.5	0.3	90/10	0.074	35	99.1
A-4	28.5	1.5	0.3	85/15	0.096	52	98.8
A-5	28.5	1.5	0.3	80/20	0.155	97	98.7

[a] W/M = water/methanol volume ratio. [b] Absorbance at $\lambda_{\max}$ 644 nm. [c] Calculated by UV calibration curve and based on the total dye charged to the reactor.

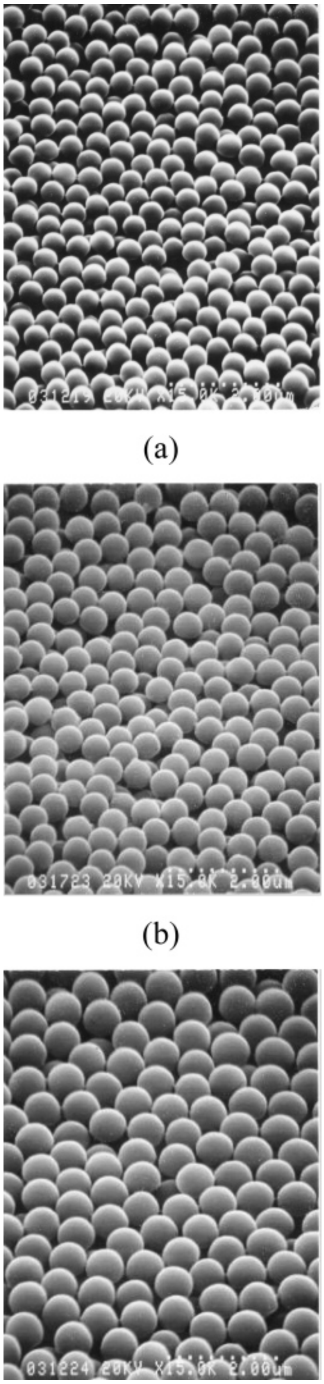


Figure 3. Scanning electron micrographs of electronic ink particles made with 5 wt % oil blue N and a varying methanol concentration: (a) 0 vol %, (b) 10 vol %, and (c) 20 vol %.

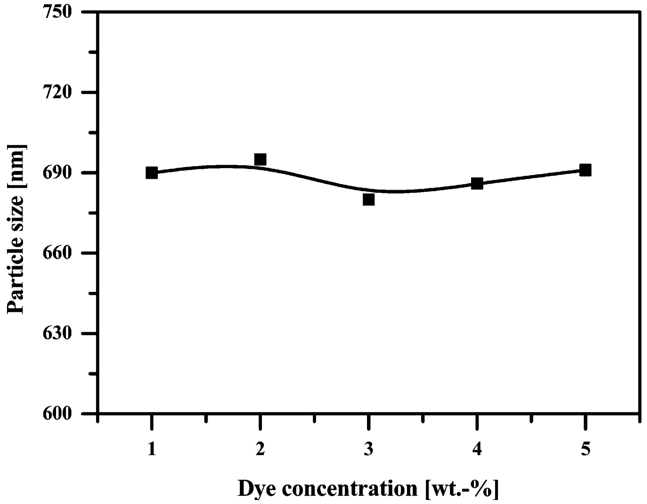


Figure 4. Dependency of electronic ink particle size on the concentration of oil blue N in the polymerization mixture at 20 vol % methanol.

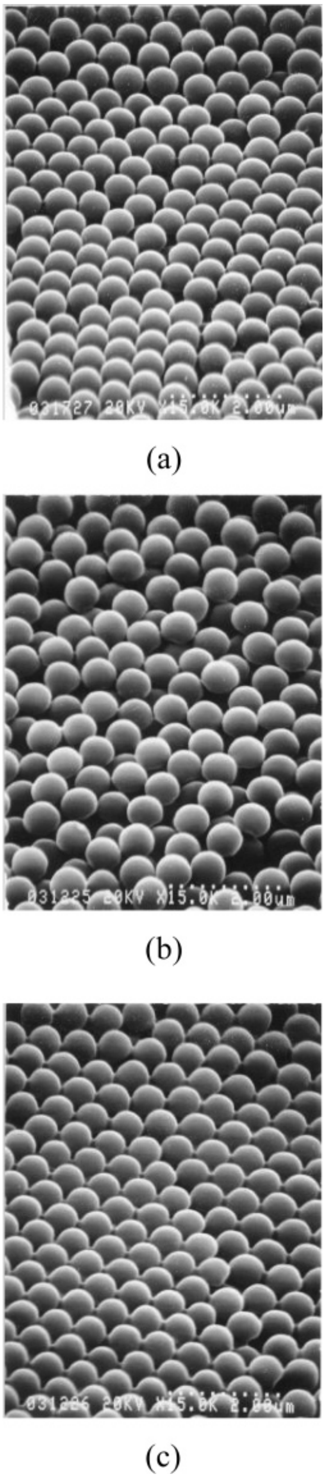
has some effect on the nucleation and particle stability, not to mention to the reactivity of growing radicals. These features are outside the scope of the current work and will be the subject of further study.

Effect of Oil Blue N Dye Concentration. Table 3 shows the effect of the oil blue N feed level on the incorporation of dyes and the final conversion of monomers in the final particles. The results indicated that the amount of the oil blue N dye in the polymerization feed did not have a significant effect on either the amount of dye in the polymerized particle or the final conversion of monomer. With further increases in the oil blue N feed levels from 1 to 5 wt %, the particle size slightly increased from 690 to 695 nm, as shown in Figure 4, but it is not that significant. Oil blue N dyes seems to have an inhibitory effect on the radical polymerization, considering that the increases in oil blue N dyes feed level decreased the final conversion of monomer. When the oil blue N loading was about 7 wt %, an irregular particle shape (aggregated form) was obtained (not shown), and the percentage conversion could not be precisely determined. An addition of 1 wt % oil blue N to the polymerization mixture shows a yield of 98.7%, which further decreases to 94.8 and 90.1% when the feed levels of oil blue N were increased to 3 and 5 wt %, respectively. At high oil blue N dye feed levels, the yield of electronic ink particles slightly decreased, which could be rationalized by the increased inhibitory effect of the oil blue N dyes caused by decreases in both the radical concentration and conversion. As shown in Figure 5, the scanning electron micrographs of electronic ink particles prepared in the mixture of water and methanol (20 vol % of total continuous phase) show that submicron-sized electronic ink particles with fairly narrow distributions could be

Table 3. Final Conversion of Monomer and Incorporation of Dye into Polymer Particles as a Function Dye Concentration

sample	monomer		oil blue N (g)	continuous phase (W/M)[a]	absorbance (intensity)[b]	incorporation of dye (%)c	conversion of monomer (%)
	MMA	EGDMA					
B-1	28.5	1.5	0.3	80/20	0.155	97	98.7
B-2	28.5	1.5	0.6	80/20	0.274	94.5	96.5
B-3	28.5	1.5	0.9	80/20	0.389	92.7	94.8
B-4	28.5	1.5	1.2	80/20	0.505	92	92.6
B-5	28.5	1.5	1.5	80/20	0.639	94.4	90.1

[a] W/M = water/methanol ratio. [b] Absorbance at λ_{max} 644 nm. [c] Calculated by UV calibration curve and based on the total dye charged to the reactor.


(a)

(b)

(c)

Figure 5. Scanning electron micrographs of electronic ink particles made with 20 vol % methanol and varying amounts of oil blue N: (a) 1 wt %, (b) 3 wt %, and (c) 5 wt %.

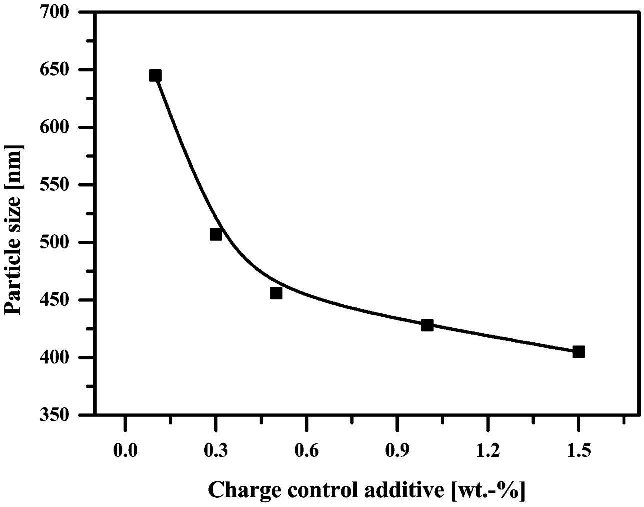


Figure 6. Dependency of electronic ink particle size on the concentration of charge control additives in the polymerization mixture at a 20 vol % methanol and 5 wt % oil blue N.

obtained, ranging from 690 to 700 nm with different concentration of oil blue N dye inside.

Effect of Charge Control Additives. To provide electrophoretic response to the particles, charge control additives are necessary. Therefore, ink particles containing charge control additives were polymerized in a 80/20 water−methanol mixture while the concentration of charge control additives was varied from 0.1 to 1.5 wt %. The particle diameter was decreased from 650 to 405 nm as the charge control additive was increased. Figure 6 shows the relationship between particle size and the charge control additive concentration. In emulsifier-free emulsion polymerization, the particle size is mainly determined by particle stability and nucleation rate. Since charge control additives are either negative or positive charge producing species, they could act as a kind of surfactant when they are exposed on the interface. Therefore, they can provide either more nucleation sites or more particle stabilization capability. Both are favorable for smaller particle size.

Electrophoretic Mobility. As shown in Figure 7, the content of the charge control additive has an effect on the electrophoretic mobility of the electronic ink particles. The electron mobility was measured by electrophoretic ink particle dispersion, which is redispersed after cleaning and drying of the synthesized particles. The electronic ink particles for this study were spherical with a uniformly smooth surface (Figure 5). The electrophoretic mobility value increased along with an increase in charge control additive concentration. But it shows a maximum and then decreases with a further increase of charge control additive. The maximum value

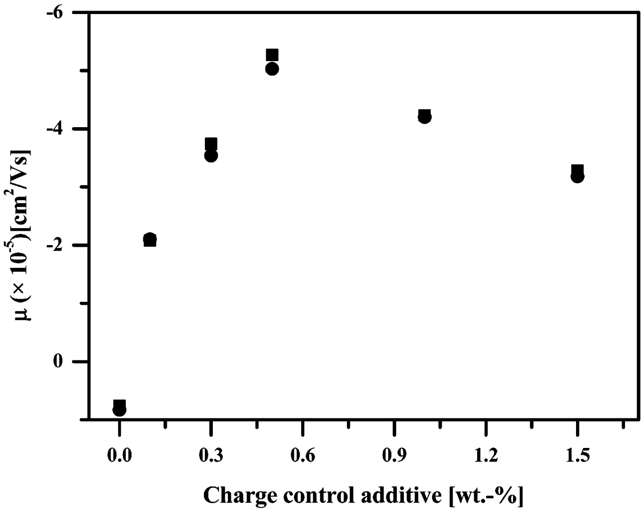


Figure 7. Effect of charge control additives in electronic ink particles on electrophoretic mobility: (■) 3 wt % and (●) 5 wt % oil blue N.

of the electrophoretic mobility was 5.27×10^{-5} cm^2/V·s at the charge control additive content of 0.5 wt %. An increase in the concentration of charge control additives will increase the number of effective charging sites of the electronic ink particles, resulting in higher electrophoretic mobility. However, the charge control additive E-81 is a Cr complex that is quite soluble in water. Therefore, some E-81 migrates from the particle to the water phase during the redispersing process, even though the particles are completely cleaned and dried before use. Since the particle sizes keep decreasing with an increase of charge control additive, there will be more interface between the particle and water, allowing a higher degree of migration from particles to water. Such migrated E-81 has an effect of hampering the electrophoretic movement of ink particles. Therefore, combined with an increase of charge density, a maximum in electrophoretic mobility is seen, as in Figure 6.

Conclusion

Electronic ink particles with narrow size distribution are prepared by one-shot, in situ emulsifier-free emulsion polymerization using a mixture of acrylic-based monomer dye (oil blue N) and charge control additive (E-81). The particle size was found to decrease either upon increasing charge control additives or upon increasing the fraction of water in the water−methanol mixture. The ink-holding ability or the degree of incorporation of dye into the particle is strongly dependent on the polarity of the polymerization medium. By adding methanol, the polarity of the polymerizing medium can be lowered and the degree of incorporation can be improved from 2% to 98% of the theoretical value. Regarding the use of charge control additive, a relatively small amount was sufficient or optimum for electrophoretic movement of the ink particle. Excessive use of charge control additives rather decreased the electrophoretic movement. This may be the result of the smaller particle size, which will facilitate the migration of charge control additives from the particles to the water. In further applications, monodispersed blue electronic ink particles are expected to find great usefulness in electrophoretic displays (see the Supporting Information).

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Supporting Information Available: Figures illustrating in-plane electrophoretic display cells and schematic operation mechanisms; optical microscopy of the initial state, with and without applied voltage, and with reverse applied voltage; and photographs of an in-plane electrophoretic display cell. This material is available free of charge via the Internet at http://pubs.acs.org.

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