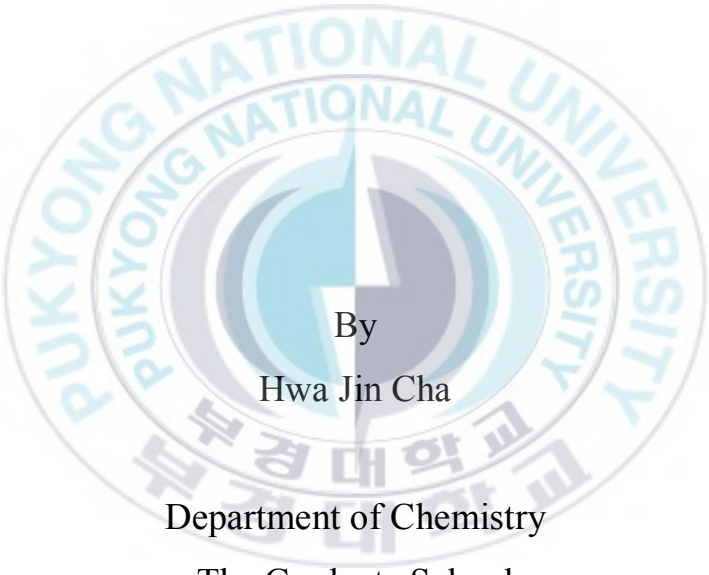
Thesis for the Degree of Master of Science

Preparation and Characterization of Electrophoretic Organic Ink Nanoparticles for Electronic Paper



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February, 2008

Preparation and Characterization of Electrophoretic Organic Ink Nanoparticles for Electronic Paper

(전자종이용 전기영동 유기 잉크 나노입자의 제조 및 특성 연구)

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A Dissertation

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February 26, 2008

Contents

I. Introduction ····· 1

1. Nanotechnology ····· 1

2. Applications of nanoparticles ····· 2

3. Techniques of free radical polymerization ····· 3

4. Polymer-surfactant systems ····· 5

5. Solubilization of dyes by polymer surfactant ····· 6

6. Electronic devices ····· 7

II. Experimentation and discussion ····· 9

1. Preparation of electronic ink nanoparticles by encapsulation method ····· 9

1.1 Materials ····· 9

1.2 Preparation of negatively charged color ink nanoparticles ····· 10

1.3 Preparation of positively charged color ink nanoparticles ····· 11

1.4 Characterization of color electrophoretic ink nanoparticles ····· 13

1.5 Result and discussion ····· 13

1.6 Conclusion ····· 28

2. Application of charged color ink nanoparticles for E-paper ····· 28

2.1 Materials ····· 29

2.2 Fabrication of electronic ink display ····· 29

2.3 Characterization of fabricated electronic ink display ····· 29

2.4 Result and discussion ····· 29

2.5 Conclusion ····· 34
III. References ····· 35

IV. Korean abstract····· 40

List of Figures

Figure 1. Synthetic process of negatively charged electrophoretic ink nanoparticles.

Figure 2. Synthetic process of positively charged electrophoretic ink nanoparticles

Figure 3. Schematic drawing on the structures of organic dyes; (a) acid blue 25, (b) acid yellow 76, (c) acid red 8.

Figure 4. Schematic drawing on the structure of organic dye encapsulated electronic ink particles

Figure 5. The SEM images of electronic ink particles with different colors; (a) red, (b) blue, (c) yellow.

Figure 6. The SEM images of blue color electronic ink particles with different SDS concentrations; (a) 1 wt%, (b) 3 wt%, (c) 5 wt%.

Figure 7. UV-vis spectra of (a) water dispersed acid blue 25, (b) before washing of blue color electronic ink nanoparticles (c) after washing 1st, (d) after washing 2nd, (e) after washing 3rd.

Figure 8. Variation of electrophoretic mobility vs. different

SDS concentrations of blue, red and yellow color electronic ink particles.

Figure 9. FT-IR spectra of (a) poly (styrene-co-4-vinyl pyridine), (b) poly(styrene-co-4-vinyl pyridine) with SDS , (c) poly(styrene-co-4-vinyl pyridine) with SDS and blue dye.

Figure 10. FT-IR spectra of (a) poly (styrene-co-4-vinyl pyridine), (b) poly(styrene-co-4-vinyl pyridine) with SDS , (c) poly(styrene-co-4-vinyl pyridine) with SDS and red dye.

Figure 11. FT-IR spectra of (a) poly (styrene-co-4-vinyl pyridine), (b) poly(styrene-co-4-vinyl pyridine) with SDS , (c) poly(styrene-co-4-vinyl pyridine) with SDS and yellow dye.

Figure 12. The SEM images of blue color electronic ink particles with different CTAB concentrations; (a) 1 wt%, (b) 3 wt%, (c) 5 wt%.

Figure 13. Variation of electrophoretic mobility vs. different CTAB concentrations of blue, red, and yellow colors electronic ink particles.

Figure 14. FT-IR spectra of (a) poly(styrene-co-4-vinyl pyridine), (b) poly(styrene-co-4-vinyl pyridine) with CTAB , (c) poly(styrene-co-4-vinyl pyridine) with CTAB and blue dye.

Figure 15. FT-IR spectra of (a) poly(styrene-co-4-vinyl pyridine), (b) poly(styrene-co-4-vinyl pyridine) with CTAB, (c) poly(styrene-co-4-vinyl pyridine) with CTAB and red dye.

Figure 16. FT-IR spectra of (a) poly(styrene-co-4-vinyl pyridine), (b) poly(styrene-co-4-vinyl pyridine) with CTAB , (c) poly(styrene-co-4-vinyl pyridine) with CTAB and yellow dye.

Figure 17. Schematic drawing on the cross sectional structure of an electronic paper display using conductive color ink nanoparticles.

Figure 18. Variation of current vs. applied voltage curves on the SDS surfactant concentration in electrophoretic display.

Figure 19. Current-voltage curves of blue ink particles with CTAB and SDS in paraffin oil phase.

Figure 20. Current-voltage curves of blue, red, and yellow colored ink particles in paraffin oil-triethanolamine phase.

Figure 21. Photographs of blue color electronic paper display in (a) power-off and (b) power-on (20 V).

List of Tables

Table 1. Standard reaction conditions for polymer encapsulated electronic ink particles

Preparation and Characterization of Electrophoretic Organic Ink Nanoparticles for Electronic Paper

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Abstract

Color organic dyes (acid blue 25, acid red 8, acid yellow 76) were dispersed in methanol medium and polymerized with styrene and 4-vinyl pyridine (co) polymer using PVP (polyvinylpyrrolidone) as stabilizer. Highly monodisperised polystyrene electrophoretic ink particles containing organic dye and charge control additives were successfully prepared in nano size. Encapsulated organic dyes were more stable, and in order to improve their mobility, the SDS (sodium dodecyl sulfate) and CTAB (cetyltrimethyl ammonium bromide) were added as a charge control additive. These organic electrophoretic ink particles can be used as ink particles for blue color electronic paper, which is expected to substitute for the future display. Microscopy techniques (SEM) were used to investigate the size and morphology of electronic ink particles. The optical absorption of nanoparticle in water was measured using a UV–vis and chemical bonding of ink particles measured by FT-IR. The electrophoretic mobility was also measured by Z-potential measurement.

I. Introduction

1. Nanotechnology

Nanotechnology is concerned with materials and systems whose structures and components exhibit novel and significantly improved physical, chemical and biological properties, phenomena and processes because of their small nanoscale size. Structural features in the range of about 10^{-9} to 10^{-7} m (1 to 100 nanometers) determine important changes as compared to the behavior of isolated molecules (1 nanometer) or of bulk materials. For comparison, 10 nanometers are 1000 times smaller than the diameter of a human hair. We can exploit novel properties and phenomena of nano-based entities as we gain control of structures and devices at the atomic, molecular and supermolecular levels, and as we learn how to do manufacture efficiently and use these devices.[1-3] New behavior at the nanoscale is not necessarily predictable from that observed at large size scales. Important changes in behavior are caused not by the order of magnitude size reduction, but also by new phenomena such as size confinement, predominance of interfacial phenomena, quantum mechanics and Coulomb blockade. It is notable that all relevant phenomena at nanoscale are caused by the tiny size of the organized structure as compared to molecular scale,[4-5] and by the interactions at their predominant and complex interfaces. Once we are able to control feature size, we can enhance material properties and device functions beyond those that we currently know or even imagine. Reducing the dimensions of structures leads to entities with novel properties,

such as carbon nanotubes, quantum wires and dots, thin films, DNA based structures, and laser emitters.[6] Such new forms of materials and devices herald a revolutionary age for science and technology provided that we can discover and fully utilize the underlying principles.[7]

2. Applications of nanoparticles

Polymers for micro- and nanoelectronics from synthesis to electronics, bioanalysis in the micro- to nanoflow regime, mesoscopic phenomena in fluid systems, novel applications of atomic force microscopy, fundamentals and applications of uniform particles from micrometers to nanometers,[8] ordered molecular assemblies of nanoparticles, particle size assessment and characterization, and nanotechnology in catalysis. In fact, most of the materials studied at the present stage of investigation are nanoparticles. The studies on nanoparticles considered to some extent here are of course based on surface/ interface science, colloid science, polymer science,[9-11] materials chemistry, synthetic chemistry, electrochemistry, photochemistry, laser spectroscopy, microscopy, optics, and solid state physics. Biological sciences are extending the studies described in this book, various kinds of fundamental and applied research fields will be opened and activated, since particles are the most common morphology of materials. It covers analysis, synthesis, molecular design, droplets, medicine, food, cosmetics, blood, liposome, biocells, and even the cosmos will be clearly understood and properly used.[12-13] Fundamental and strategic studies will be developed, which are basically ascribed to the present results on nanometer-microsecond molecular diffusion control, femto Newton

interaction force control, and nanometer molecular/ particle arrangement.

3. Techniques of free radical polymerization

Free radical polymerization can be accomplished in bulk, suspension, solution, or emulsion.[14] Ionic and other nonradical polymerizations are usually confined to solution techniques. Each of the methods has advantages and disadvantage, as outlined in Table 1. In addition, work has also been done on solid and gas phase polymerization of vinyl monomers, but these is of lesser importance. Because polymers are not volatile, the term gas phase polymerization means, in effect, bulk polymerization in which monomer vapors diffuse to the polymerization site.

Bulk. Bulk polymerization is simplest from the standpoint of formulation and equipment, but it is also the most difficult to control, particularly when the polymerization reaction is very exothermic. This, coupled with problems of heat transfer as the monomer-polymer solution increases in viscosity, limits the use of bulk method in commercial production, although more efficient bulk processes have been developed in recent years. In cases where polymer is insoluble in monomer, polymer precipitates and the viscosity of the medium does not change appreciably. Problems still arise, however as a result of free radicals being occluded in the polymer droplet, which can lead to auto-acceleration, that is, a rapid increase in the polymerization rate.[15] In some instances, particularly with diene monomers, this occlusion effect may lead to the formation of insoluble crosslinked polymer nodules, a phenomemon refferred to as popcorn

polymerization.[16] The crosslinked nodules are usually of light weight and occupy considerably more volume than the monomers from which they are derived, which may cause fouling and even fracture of the polymerization apparatus. The major commercial uses of bulk vinyl polymerization are in casting formulations and low molecular weight polymers for use as adhesives, plasticizers, tackifiers, and lubricant additives.

Suspension. Suspension polymerization involves mechanically dispersing monomer in an noncompatible liquid, usually water, and polymerizing the resultant monomer droplets by use of a monomer soluble initiator. Monomer is kept in suspension by continuous agitation and the use of stabilizers such as poly(vinyl alcohol) or methyl cellulose. If the process is carefully controlled, polymer is obtained in the form of tranular beads, which are easy to handle and can be isolated by filtration or by spraying into a heated chamber (spray drying). A major advantage is that heat transfer is very efficient and the reaction is therefore easily controlled. Suspension polymerization cannot be used for tacky polymers such as elastomers because of the tendency for agglomeration of polymer particles. From the standpoint of kinetics and mechanism, suspension polymerization is identical to bulk polymerization. Suspension methods are used to prepare a number of granular polymers, including polystyrene, poly(vinyl chloride), and poly(methyl methacrylate).

Solution. Like solution, solution polymerization allows efficient heat transfer. Solvent must be chosen carefully, otherwise chain transfer reactions may severly limit the molecular weight. Because of problems in removing solvent completely from the resultant polymer, the method is best suited to applications where the

solution may be used directly, as with certain adhesives or solvent-based paints.

Emulsion. Developed at Goodyear Tire and Rubber Company in the 1920s, emulsion polymerization resembles suspension polymerization in that water is used as a dispersing medium and heat transfer is very efficient; but there is the similarity ends.[17-19] Monomer is dispersed in the aqueous phase by an emulsifying agent such as a soap or detergent. Initiator radicals, usually of the redox type, are generated in the aqueous phase and diffuse into soap micelles swollen with monomer molecules. As monomer is used up in the polymerization reaction, more monomer migrates into the micelles, and thus the reaction continues. Termination of polymerization occurs by radical combination when a new radical diffuses into the micelle. Because only one radical is present in the micelle prior to termination, extremely high molecular weights are obtainable, generally too high to be of practical value unless compounds called chain transfer agents are added, that control the degree of polymerization. The overall process is complex, with reaction kinetics differing significantly from that of bulk or solution processes. Emulsion polymerization is widely used in industry for large-scale preparations, and is particularly useful for manufacturing water-based paints or adhesives in which the emulsified product is used directly. Emulsion polymerization is also suitable for preparing tacky polymers because the very small particles are stable and resist agglomeration. A much less commonly used emulsion technique involves dispersing an aqueous solution of monomer in a nonaqueous phase. This is referred to as inverse or water-in-oil emulsion.

4. Polymer-surfactant systems

Polymerization and surfactants are used extensively in a wide variety of industrial, cosmetic, and pharmaceutical applications. In many, if not most, such cases their encounter is unintentional in the sense that they are added for their independent function rather for those arising out of their mutual interactions. For example, polymers are often used in formulation for controlling the rheology of solutions and suspensions and for altering the interfacial properties of solids. Surfactants are used for altering the wettability, solubilization and emulsification properties by changing the properties of the interfaces involved. When present together, polymers and surfactants can interact with each other leading to significant alterations in properties which are often considered undesirable. On the other hand, they may well be beneficial. Though limited, there are examples of systems in which the interaction between the polymer and the surfactant is exploited or circumvented to provide the beneficial effects sought from a formulation. Some of the potential benefits arising from the positive effects of polymer-surfactant interaction have been reviewed elsewhere.[20]

5. Solubilization of dyes by polymer-surfactant

Solubilization by surfactant micelles has been extensively studied. Both the physico-chemical aspects of micellar solubilization and applications of surfactant solubilization in a side variety of fields have been thoroughly reviewed.[21-22] In the presence of polymers, solubilization of small molecules by surfactants has been observed at concentrations below the surfactant critical micelle concentration (CMC).[23-25] Potential applications are expected in the fields of cosmetics (drug solubilization by polymer/surfactant complexes), water

processing (pollutants solubilization by polymer/surfactant complexes), fabric dyeing, etc, but only a limited number of physico-chemical studies on solubilization by polymer-surfactant systems have been published. Early studies observed the solubilization of the water-insoluble dye, yellow OB, by nonionic polymers such as polyvinylpyrrolidone and polyethylene glycol in the presence of anionic surfactants such as sodium dodecyl sulfate (SDS) and sodium octylbenzene sulfonate,[24-25] and by the anionic polymer polyacrylic acid in the presence of nonionic surfactant.[26-27] In the case of ionic polymers with surfactants of opposite charge, solubilization was observed at a concentration far below the surfactant CMC and before the polyion-surfactant complexes were precipitated.[28-29] The solubilization at concentrations below the surfactant CMC observed in most. Polymer-surfactant systems were ascribed to the formation of hydrophobic domains in polymer-surfactant complexes formed in aqueous solution.

6. Electronic devices

Electronic papers (e-papers) have recently been of great interest application in information displays requiring low cost, lightweight, flexibility, and low power consumption. Compared to current displays, such as transmissive liquid crystal displays (LCDs)[30-31] or emissive technologies such as organic light diode displays (OLEDs),[32-33] field emission displays (FED) and plasma displays (PDP), the power consumption of electronic ink displays is very low.[34-39] 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 of 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 imge quality requires that electronic inks have a very small particle size within an 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 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 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,[40-44] it is easy to synthesize particles with a relatively large particle size around 5μm 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[45-53] generally have particle sizes on a submicrometer scale of smaller.

II. Experimentation and Discussions

1. Preparation of electrophoretic ink nanoparticles by encapsulation method

1.1. Materials

Methanol was used as solvent and purchased for Junsei Chemical Co. Styrene monomer was purchased for Aldrich Chemical Co. and inhibitor was removed with added 10 wt% NaOH solution. 4-Vinyl pyridine, poly(N-vinyl pyrrolidone) (PVP), sodium dodecyl sulfate(SDS), 2,2'-azobis (isobutyronitrile)(AIBN) were also purchased from Aldrich Chemical Co. and used without further purification. Acid blue 25, acid red 8 and acid yellow 76 used as organic dye were purchased

from Aldrich Chemical Co. and used without purification. House-distilled water was passed through a four-cartridge Barnstead Nanopure II purification system consisting of macropure pretreatment for removing trace organics, two-ion exchangers and 0.2 mm hollow-fiber final filter for removing particles. Its resistivity was 18.3 MΩ and used in all the experiments.

1.2 Preparation of negatively charged color ink nanoparticles

Preparation of electronic ink nanoparticle was done in the following process. Organic dyes (0.3 g) and poly(N-vinyl pyrrolidone) (PVP, 0.3 g) were added to a solution of methanol (48 mL) and distilled water (12 mL). Different concentration of 1 wt% (0.06 g), 3 wt%(0.18 g), and 5 wt%(0.3 g) sodium dodecyl sulfate (SDS) were each added in a reaction mixture. After stirring for 2 h, styrene (0.042 mol, 4.8 ml) and 4-vinyl pyridine (0.01 mol, 1.2 ml) were slowly added to reaction medium. 2,2'-Azobis (isobutyronitrile)(AIBN) (0.15 g) was added in methanol (5 ml) and sonicated for 3 min. Initiator of solution was injected using a glass syringe, and the polymerization was allowed to proceed for 9 h at 65 ºC under the nitrogen air. After the (co) polymerization process, the reaction mixture was washed with water for 5 times and isolated using centrifugation and dried in a freeze-drier. In this synthesis, the styrene/4-vinyl pyridine weight ratio in the monomer mixture was fixed at 80:20 and methanol/water as solvent was also has 80:20 ratio. And as organic dye, acid blue 25, acid red 8, and acid yellow 76 were used.

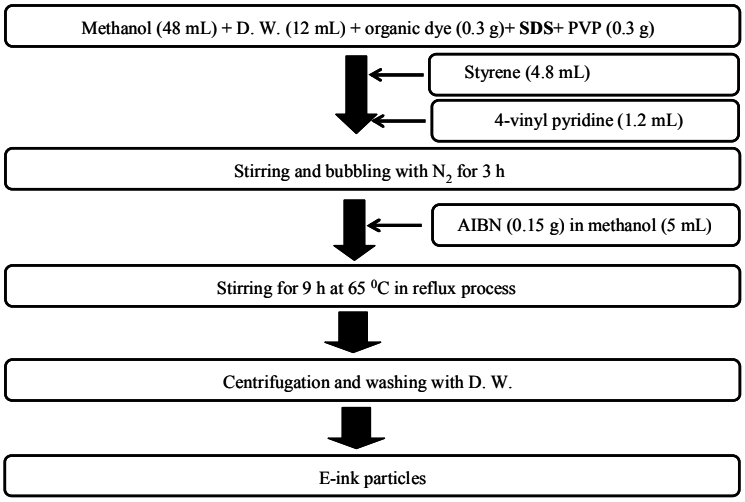


Figure 1. Synthetic process of negatively charged electrophoretic ink nanoparticles.

1.3 Preparation of positively charged color ink nanoparticles

Preparation of positive charged color ink nanoparticles was the same procedure with the negatively charged color ink nanoparticles except using cationic surfactant. Organic dye (0.3 g) and poly(N-vinyl pyrrolidone) (PVP, 0.3 g) were added to a solution of methanol (48 mL) and distilled water (12 mL). Different concentrations of 1 wt% (0.06 g), 3 wt% (0.18 g), and 5 wt% (0.3 g) cetyl trimethyl ammoniumbromide (CTAB) were added in a reaction mixture. After stirring for 2 h, styrene (0.042 mol, 4.8 ml) and 4-vinyl pyridine (0.01 mol, 1.2 ml) were slowly added to reaction medium. 2,2'-Azobis (isobutyronitrile)(AIBN) (0.15 g) was added in methanol (5 ml) and sonicated for 3 min. Initiator of solution was injected using a glass syringe, and the polymerization was allowed to proceed for 9 h at 65 ºC under the nitrogen air. After the (co) polymerization process, the reaction mixture was washed with

water for 5 times and isolated using centrifugation and dried in a freeze-drier. In this synthesis, the styrene/4-vinyl pyridine weight ratio in the monomer mixture was fixed at 80:20(v/v) and methanol/water as solvent was also 80:20(v/v) ratio. And as organic dye, acid blue 25, acid red 8, and acid yellow 76 were used.

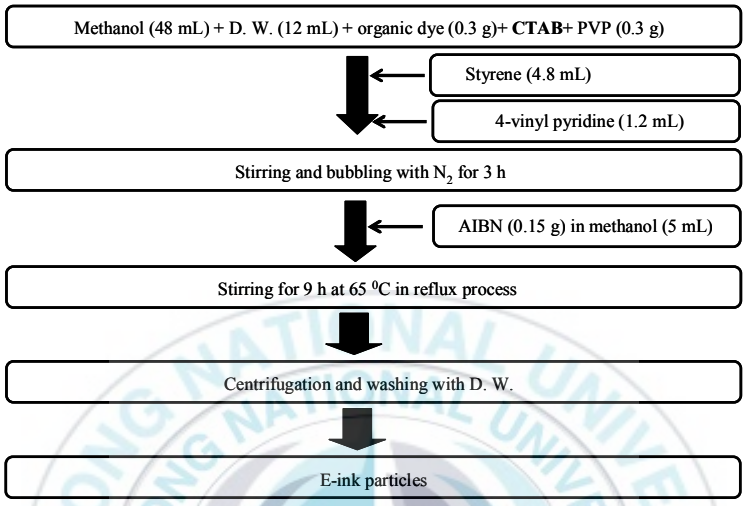


Figure 2. Synthetic process of positively charged electrophoretic ink nanoparticles

Table 1. Standard reaction conditions for polymer encapsulated electronic ink particles

	components	amounts
Monomer	Styrene	4.8 mL
	4-VP[1)]	1.2 mL
Dispersion medium[2)]	Methanol	48 mL
	Water	12 mL
Organic dye	Acid blue 25	0.3 g
	Acid red 8	
	Acid yellow 76	
Stabilizer	PVP[3)]	0.3 g
Initiator	AIBN[4)]	0.15 g
Surfactant	CTAB[5)]	0.06~0.3 g[7)]

	SDS[6]	

[1] 4-vinyl pyridine. [2] Total dispersion medium is 60 mL. [3] poly(vinylpyrrolidone). [4] 2,2'-azobis (isobutyronitrile). [5] cetyl trimethylammonium bromide. [6] Sodium dodecylsulfate. [7] Surfactant concentration is varied from 1 to 5 wt% of total monomer base.

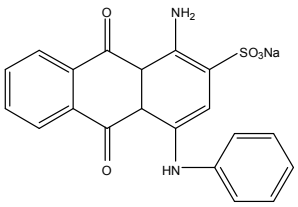
1.4. Characterization of color electrophoretic ink nanoparticles

The size and shape of electrophoretic ink nanoparticles were observed by images of scanning electron microscope (SEM, HITACHI (Japan), S-2400). Optical property of synthesized nanoparticles was identified through UV–vis absorption spectrum measurements (HITACHIU-2001) by observing absorption band. Chemical bonding of electronic ink nanoparticles were observed by FT-IR measurements (Perkin Elmer, USA). The electrophoretic mobility (μ) was measured using a Zetaplus 1246 (Brookhaven Instruments Corporation, USA) and calculated by the conversion of the the ξ–potential with the Smoluchowski relation, $\xi = \mu\eta/\varepsilon$, where η (=1.804 cP) and ε (=24.30) are the viscosity and dielectric constant of the suspending fluid, respectively.

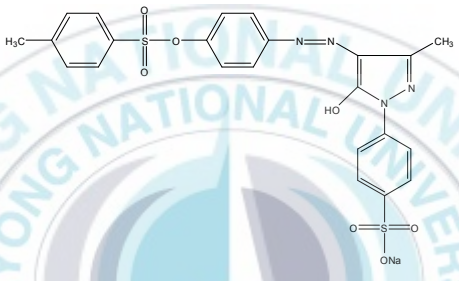
1.5 Results and discussion

Organic electronic ink particle was obtained using dispersion polymerization of styrene and 4-vinyl pyridine in aqueous methanol medium with poly (N-vinyl pyrrolidone) as a stabilizer.[54-55] Sodium dodecyl sulfate was roll of charge control additives. Free radical (co)polymerization of 4-vinyl pyridine monomer contains organic dye and surfactant. And styrene could make more stable electrophoretic nanoparticles. In this work, methanol/water mixture was used because the styrene monomer did not disperse in water. The charge

control additives are necessary in order to provide electrophoretic response to the ink nanoparticles.



(a)



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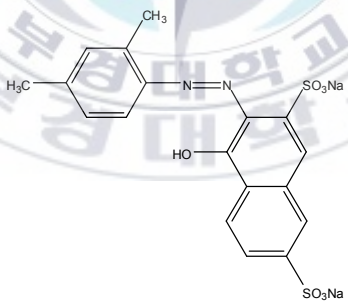


(c)

Figure 3. Schematic drawing on the structures of organic dyes; (a) acid blue 25, (b) acid yellow 76, (c) acid red 8.

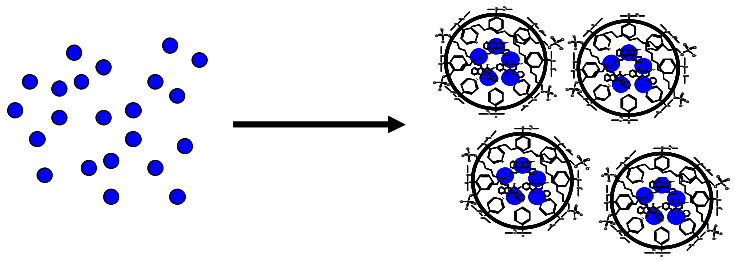
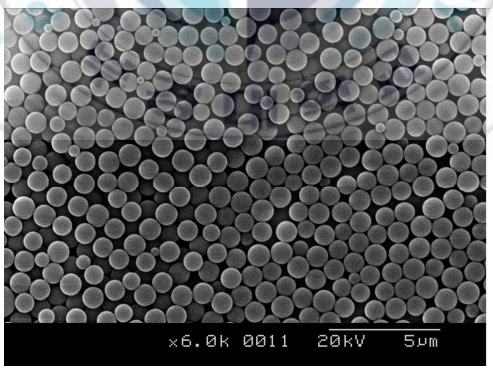
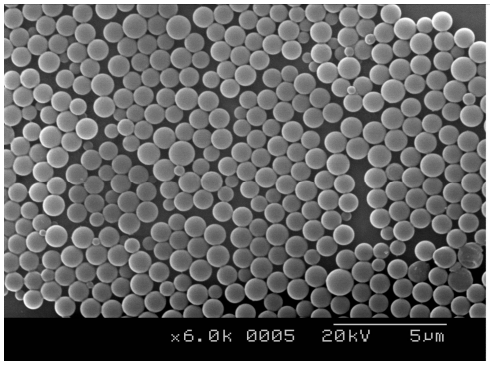


Figure 4. Schematic drawing on the structure of organic dye encapsulated electronic ink particles

Electronic ink particles of three colors were prepared as 5 wt% concentration of SDS as ionic surfactant and different organic dyes. Figure 5 (a), (b) and (c) show red, blue, yellow color ink particles. These images show 800 nm particle size and regular size distribution.



(a)



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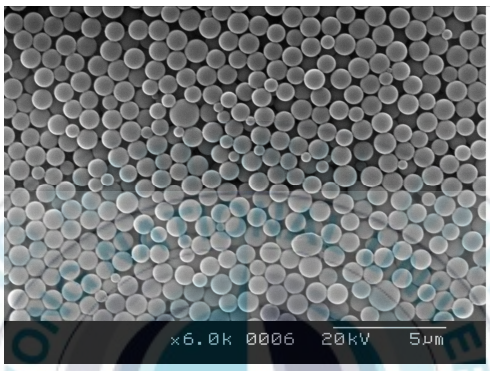
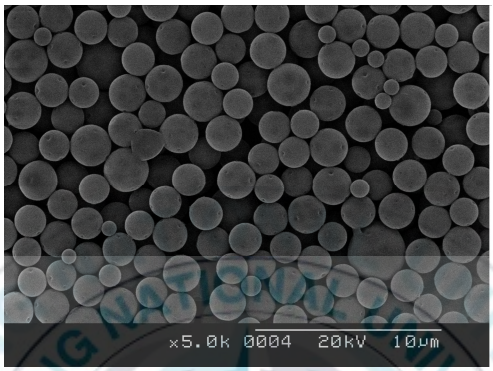


(c)

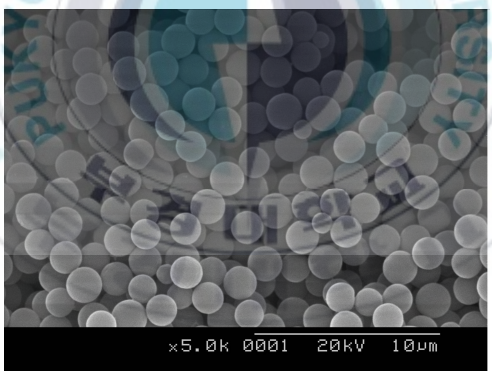
Figure 5. The SEM images of electronic ink particles with different colors; (a) red, (b) blue, (c) yellow.

We selected sodium dodecyl sulfate (SDS) as a charge control additive for adding (-) charge to the surface of ink nanoparticles. And cetyl trimethyl ammonium bromide (CTAB) was used for adding (+) charge to ink nanoparticles. The concentrations of SDS and CTAB employed were 1, 3, 5 wt%, in order to control the size of ink particles and amount of surface charge. The particle

diameter was decreased from 1.5 μm to 800 nm as the concentration of SDS was increased from 1 wt% to 5 wt%. Figure 6 shows the relationship between particle size and the concentration of surfactant. The surfactant can provide either more nucleation sites or more particle stabilization capability. Both are favorable for smaller particle size. The ink particles were spherical with uniformly smooth surface and size distribution is very small.



(a)



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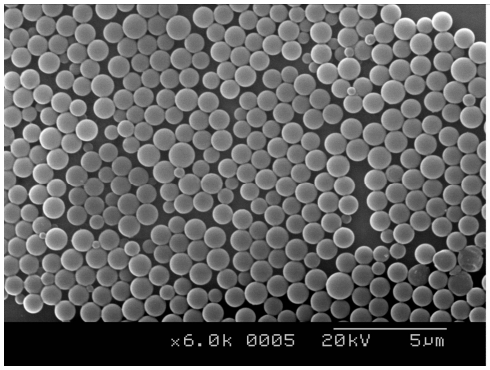


(c)

Figure 6. The SEM images of blue color electronic ink particles with different SDS concentrations; (a) 1 wt%, (b) 3 wt%, (c) 5 wt%.

Figure 7 shows UV-vis spectra of electronic ink particles. After the end of reaction, this ink particle was centrifuged at 3000 rpm and washing with distilled water 5 times. Ink nanoparticles were diluted in water and measured with UV-vis. In spite of several washing, electronic ink particles prepared by dispersion polymerization of styrene and 4-vinyl pyridine contain acid blue 25 as organic dye. This indicates that organic dye particles are encapsulated by polystyrene and 4-vinylpyridien (co)polymer. Encapsulation technology has been used to improve to the stability of the encapsulated products. Therefore these electronic ink particles can be used for electronic paper application.

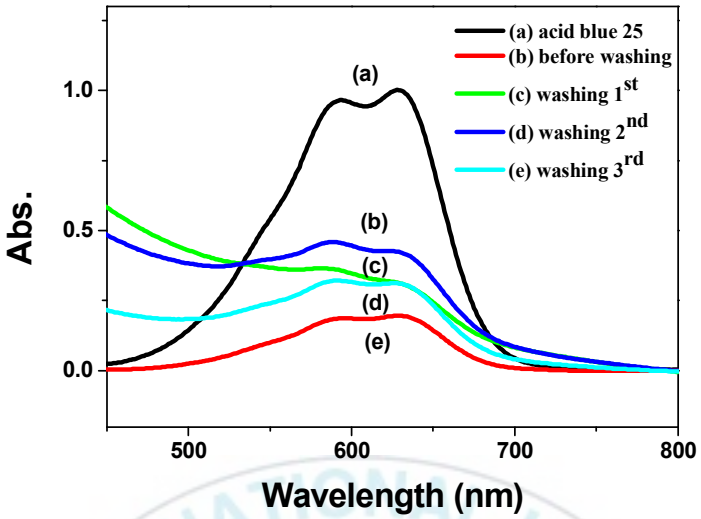


Figure 7. UV-vis spectra of (a) water dispersed acid blue 25, (b) before washing of blue color electronic ink nanoparticles (c) after washing 1st, (d) after washing 2nd, (e) after washing 3rd.

Figure 8 shows the electrophoretic mobility on the SDS surfactant concentration of the electrophoretic ink particles. The electrophoretic mobility value increased as the SDS surfactant concentration increased. Increasing the concentration of the SDS surfactant increases the number of effective charging sites of the ink particles, resulting in them having higher electrophoretic mobility. However, the surfactant used in this study is a SDS which is quite soluble in water. Therefore, some of the surfactant migrates from the particles to the water phase during the washing process, even though the particles are completely cleaned and dried before use. This migration of the surfactant has the combined effect with the

increase in the charge density of causing the electrophoretic mobility to show a maximum as shown in Figure 8. The maximum value of the electrophoretic mobility was -2.89 (μ/s)/ (V /cm) at a surfactant content of 5 wt%.

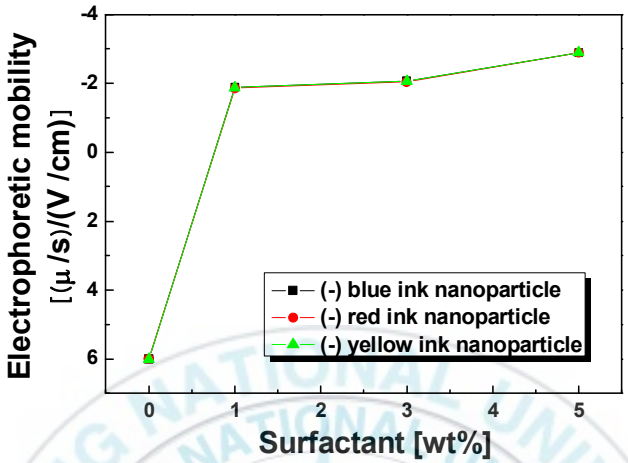
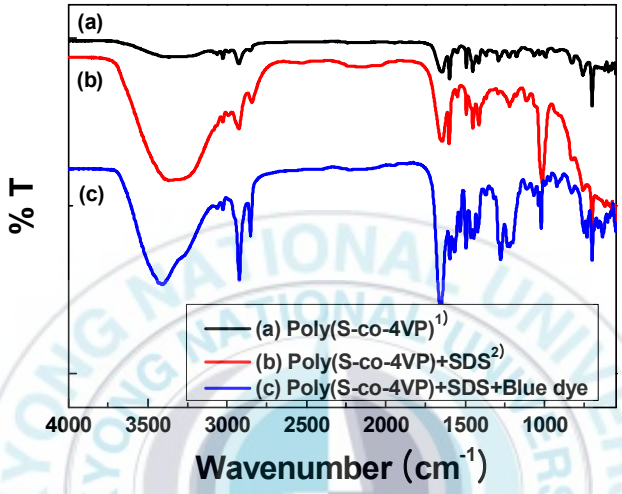


Figure 8. Variation of electrophoretic mobility vs. different SDS concentrations of blue, red and yellow colors electronic ink particles.

Figure 9 shows the FT-IR spectra of (a) poly(styrene-*co*-4vinyl pyridine), (b) poly(styrene-*co*-4vinyl pyridine) with SDS and (c) poly(styrene-*co*-4vinyl pyridine) with SDS and blue dye. In the spectrum of the (a) poly(styrene-*co*-4vinyl pyridine), it was observed the polystyrene characteristic peak at 1600 and 1475 cm^{-1} belong to C=C bands of phenyl ring. In the spectrum Figure 9 (b) and (c), it was possible to observe a broad band region at 3300-3600 cm^{-1} associated to the hydroxyl group. The peaks of 1330 and 1220 cm^{-1} belong to sulfonate (O=S=O) stretching band of SDS in spectrum of Figure 9 (b) and (c).

The bands in the region of 2800-3000 cm^{-1} correspond to the CH_2 and CH_3 group of polymer backbone. The intensity of the carbonyl peak at 1690 cm^{-1} was increased in Figure 9 (c). This indicates that blue dye was encapsulated with styrene and 4-vinyl pyridine.



[1)] Poly (styrene-co-4vinyl pyridine), [2)] Poly (styrene-co-4vinyl pyridine) with sodium dodecylsulfate

Figure 9. FT-IR spectra of (a) poly (styrene-*co*-4-vinyl pyridine), (b) poly(styrene-*co*-4-vinyl pyridine) with SDS , (c) poly(styrene-*co*-4-vinyl pyridine) with SDS and blue dye.

The intensity of the sulfonate peak at 1330 and 1220 cm^{-1} was increased in Figure 10 (c). This indicates that red dye was encapsulated with styrene and

4-vinyl pyridine.

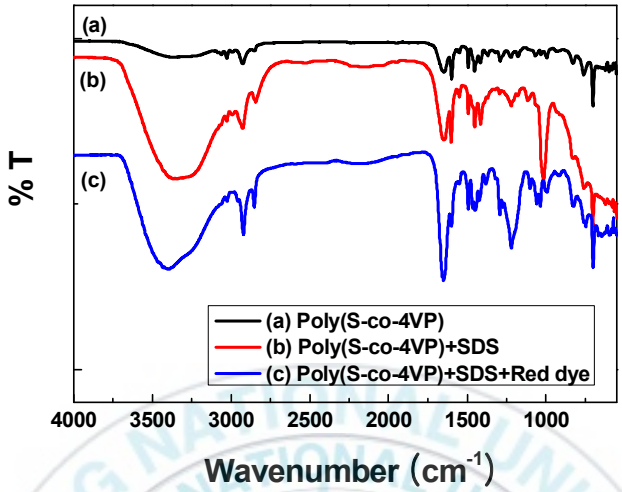


Figure 10. FT-IR spectra of (a) poly (styrene-*co*-4-vinyl pyridine), (b) poly(styrene-*co*-4-vinyl pyridine) with SDS , (c) poly(styrene-*co*-4-vinyl pyridine) with SDS and red dye.

The peak at 1490 cm^{-1} belong to N=N stretching band of yellow dye in Figure 11 (c).

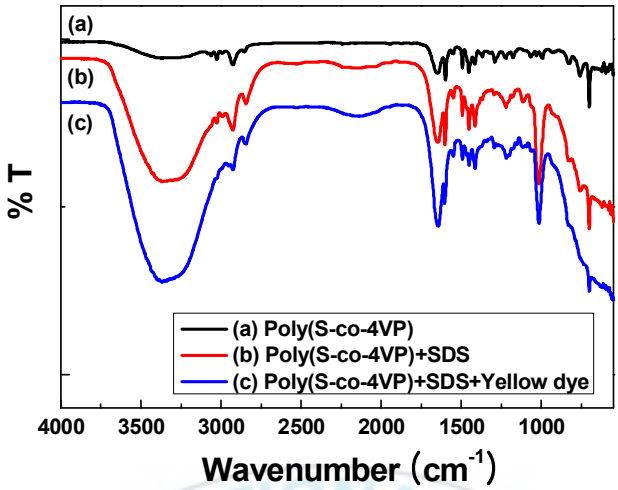


Figure 11. FT-IR spectra of (a) poly (styrene-*co*-4-vinyl pyridine), (b) poly(styrene-*co*-4-vinyl pyridine) with SDS , (c) poly(styrene-*co*-4-vinyl pyridine) with SDS and yellow dye.

Figure 12 shows SEM images of electrophoretic ink particles prepared by free-radical (co) polymerization. The nanoparticles have spherical shape and smooth surface. As increased the concentration of surfactant, particle size was decreased from 1.5 μm to 800 nm.

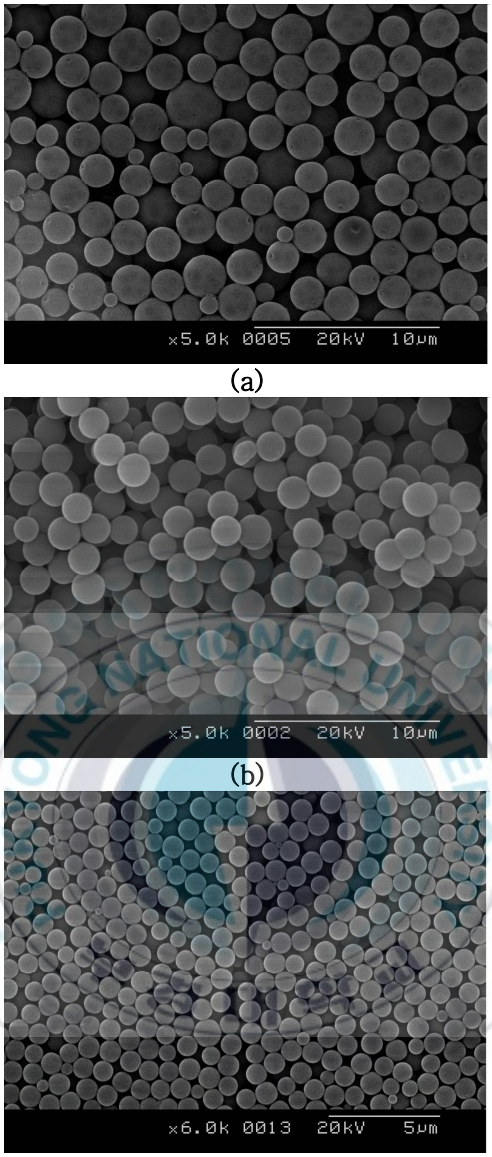


Figure 12. The SEM images of blue color electronic ink particles with different CTAB concentrations; (a) 1 wt%, (b) 3 wt%, (c) 5 wt%.

Figure 13 shows the electrophoretic mobility on the CTAB surfactant concentration of the electrophoretic ink particles. The electrophoretic mobility value increased as the CTAB surfactant concentration increased. Increasing the concentration of the CTAB surfactant increases the number of effective charging sites of the ink particles, resulting in them having higher electrophoretic mobility. The maximum value of the electrophoretic mobility was -2.98 (μ/s)/ (V /cm) at a surfactant content of 5 wt%.

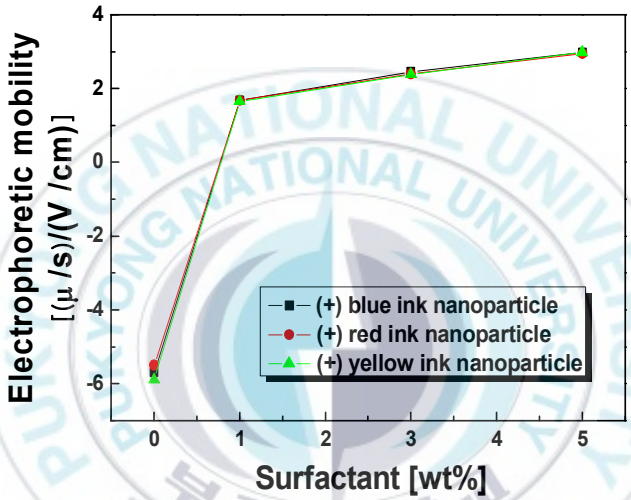
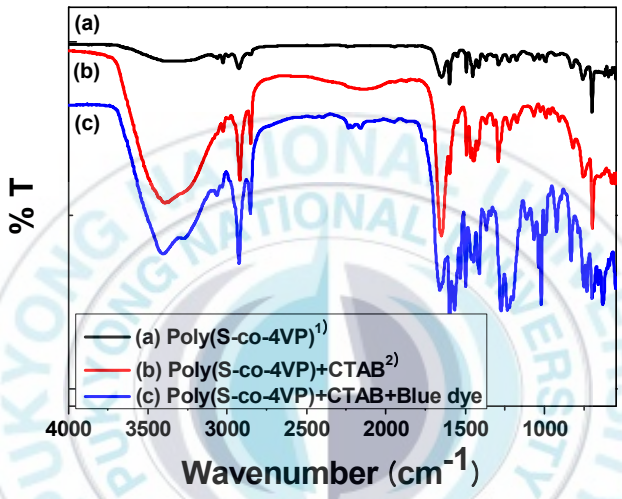


Figure 13. Variation of electrophoretic mobility vs. different CTAB concentrations of blue, red and yellow colors electronic ink particles.

Figure 14 shows the FT-IR spectra of (a) poly (styrene-*co*-4vinyl pyridine), (b) poly (styrene-*co*-4vinyl pyridine) with CTAB and (c) poly (styrene-*co*-4vinyl pyridine) with CTAB and blue dye. In the spectrum of the Figure 14 (a) poly

(styrene-*co*-4vinyl pyridine), it was observed the polystyrene characteristic peak at 1600 and 1475 cm^{-1} belong to C=C bands of phenyl ring. With the addition of CTAB in electrophoretic ink particles, the intensity ratio of peaks at 1360 cm^{-1} - 1310 cm^{-1} increase, suggesting that cationic surfactant CTAB was embedded with styrene and 4-vinyl pyridine. The intensity of the carbonyl peak at 1690 cm^{-1} was increased in Figure 14 (c). This indicates that blue dye was encapsulated with styrene and 4-vinyl pyridine.



[1)] Poly (styrene-co-4vinyl pyridine), [2)] Poly (styrene-co-4vinyl pyridine) with cetyltrimethylammonium bromide

Figure 14. FT-IR spectra of (a) poly(styrene-*co*-4-vinyl pyridine), (b) poly(styrene-*co*-4-vinyl pyridine) with CTAB , (c) poly(styrene-*co*-4-vinyl pyridine) with
CTAB and blue dye.

The intensity of the sulfonate peak at 1330 - 1220 cm^{-1} was increased in Figure 15 (c). This indicates that red dye was (co)polymerized with styrene and 4-vinyl pyridine.

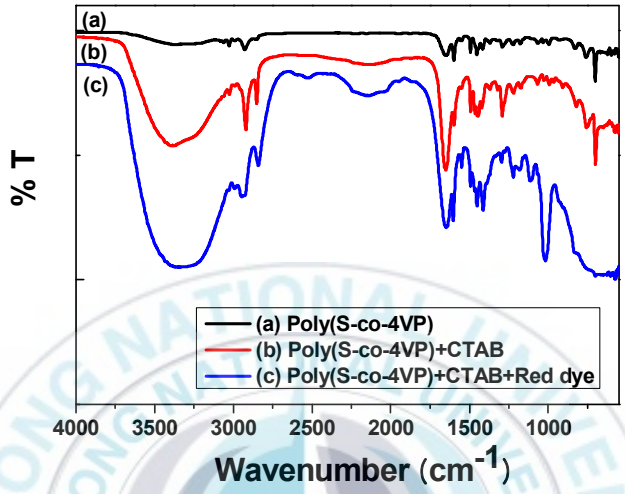


Figure 15. FT-IR spectra of (a) poly(styrene-*co*-4-vinyl pyridine), (b) poly(styrene-*co*-4-vinyl pyridine) with CTAB , (c) poly(styrene-*co*-4-vinyl pyridine) with CTAB and red dye.

The peak at 1490 cm^{-1} belong to N=N stretching band of yellow dye in Figure 16 (c).

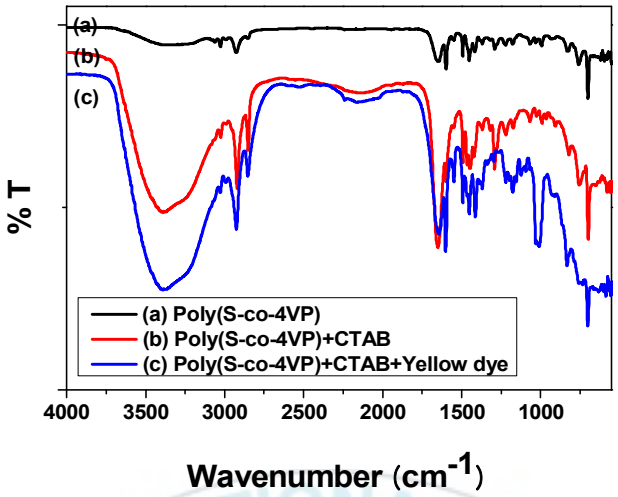


Figure 16. FT-IR spectra of (a) poly(styrene-*co*-4-vinyl pyridine), (b) poly(styrene-*co*-4-vinyl pyridine) with CTAB , (c) poly(styrene-*co*-4-vinyl pyridine) with CTAB and yellow dye.

1.6. Conclusion

The electrophoretic ink nanoparticles were successfully prepared by free-radical polymerization method of styrene and 4-vinyl pyridine in the presence of organic dye acid blue 25 in a methanol and water mixture. The ink particle size was found to decrease with increasing concentration of the surfactant. These ink particles have mobility by ionic surfactant and the electronic charge could be controlled by concentration of surfactant due to the surface charge of electronic ink particles.

2. Application of charged color ink nanoparticles for E-paper

2.1 Materials

Electrophoretic ink nanoparticles of which colors are blue, red, yellow color were prepared and were dispersed in paraffin oil as dielectiric fluid which were purchased from Fluka Chemical Co. Triethanolamine was used as suspension medium and purchased form Sigma-Aldrich Chemicals, USA, and used without purification. Indium-tin-oxide (ITO) coated glass with sheet resistance of 30 Ω/sq was obtained from JM International Co.

2.2 Fabrication of electronic ink display

ITO coated glass with a sheet resistance of 30 Ω/sq was cut into a 4.0 cm × 5.0 cm. It was sequentially cleaned in an ultrasonic bath of distilled water, and methanol, followed by drying it at room temperature. Two ITO-coated glasses were sealed with 100 μm thickness, and electronic ink slurry prepared by mixing charged blue, red, and yellow color ink particles in paraffin oil and triethanolamine was injected through the entry port to give rise to the electrophoretic display.

2.3 Characterization of fabricated electronic ink display

The current-applied voltage characteristics of the E-paper display cell were measured with Current/Voltage Source Meter (KEITHLEY2400).

2.4 Result and discussion

Figure 17 shows the schematic drawing on the cross sectional structure of a electronic paper display using conductive ink nanoparticles into which negatively charged blue color ink particles are loaded. The sandwith-type cell

structure[56] consists of two indium-tin-oxide (ITO) coated glass plates. The inner surfaces of the ITOs are coated with charge-transport layers (CTLs).[57] The device display color depending on the polarity of the applied voltage. When a positive vias voltage is applied to the upper ITO electrode, the conductive ink particles move to the upper electrode because they are negatively charged. When viewed through the upper electrode, the blue ink particles adhere to the CTL of the upper electrode, and therefore, the indication of "blue" is perceived by the human eye. Even if the device is turned off, the conductive ink remains attached to the CTL by an electrostatic force. The display of blue, red, and yellow can be controlled by swiching the polarity of the applied voltage.

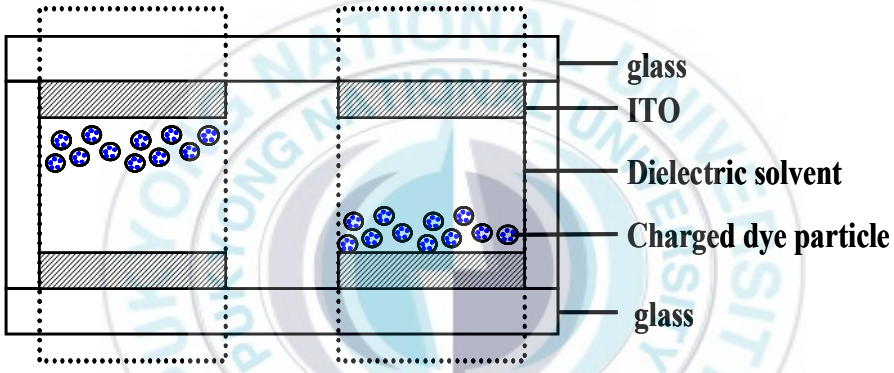


Figure 17. Schematic drawing on the cross sectional structure of an electronic paper display using conductive color ink nanoparticles.

Figure 18 shows current *vs*. applied voltage characteristics of electrophoretic ink particle display cell. The electrophoretic displays with ink particles using organic nanoparticles exhibited relatively good electrical characteristics. Comparing three devices, the cell with ink particles using 5 wt% concentration

of SDS surfactant shows the best electrical characteristics. This is approximately consistent with the result of elecrophoretic mobility.

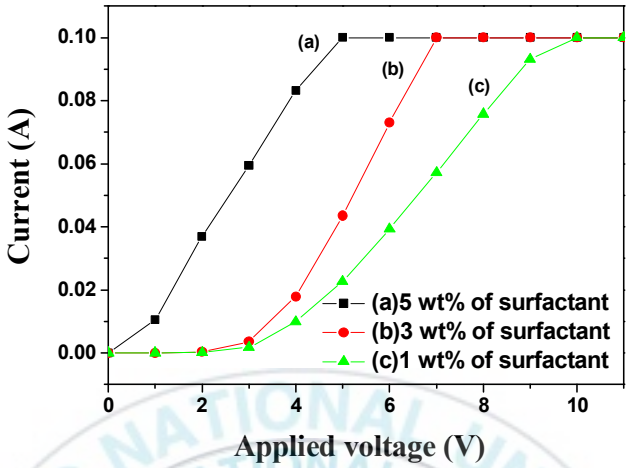


Figure 18. Variation of current vs. applied voltage curves on the SDS surfactant concentration in electrophoretic display.

Electrophoretic slurry was prepared by blending of ink particles with paraffin oil. The electronic paper displays with ink particles using organic nanoparticles exhibited relatively good electrical characteristics. Figure 19 shows current *vs*. applied voltage characteristics of electrophoretic ink particle display cell. In comparing three devices, the cell with CTAB containd ink slurry shows the best electrical characteristics. In only paraffin oil phase, current was not appeared because it is dielectric oil. Therefore paraffin oil is proper one as that using in ink slurry.

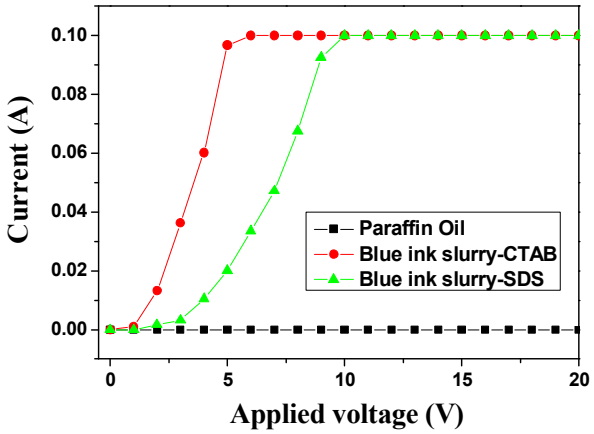


Figure 19. Currnet-voltage curves of blue ink particles with CTAB and SDS in paraffin oil phase.

Electronic ink slurry as prepared by blending of ink particles in paraffin oil was easily separated in a short time. Therefore triethanolamine was added to the ink slurry as dispersant. Figure 20 shows that the applied voltage vs current curve was not appeared without electrophoretic ink particles. In same weight percent of surfactant added into the different color ink particle had similar current vs voltage curves.

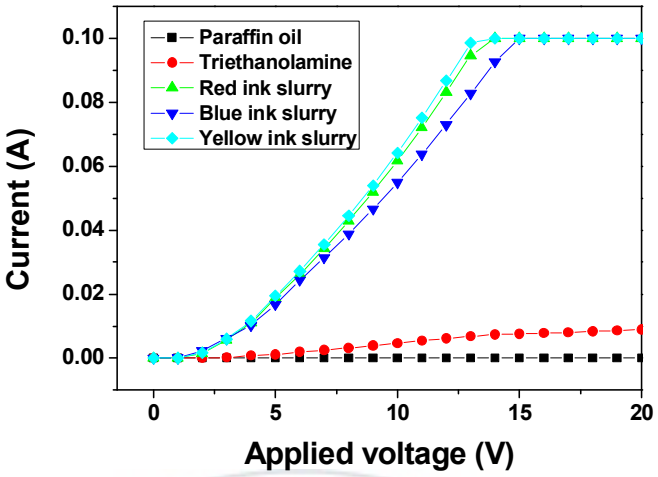


Figure 20. Currnet-voltage curves of blue, red, and yellow colored ink particles in paraffin oil-triethanolamine phase.

Figure 21 presents the photograph of electronic paper display cell (a) before bias voltage applied and (b) after 20 V voltage applied. The cell contains a mixture of negatively charged red color ink nanoparticles and positively charged blue ink nanoparticles in paraffin oil and triethanolamine mixture. After bias voltage applied to 20 V, blue color electronic ink particles moved toward negative electrode of ITO glass (upper side). These figures demonstrate the basis of the image formation process in the electrophoretic display.

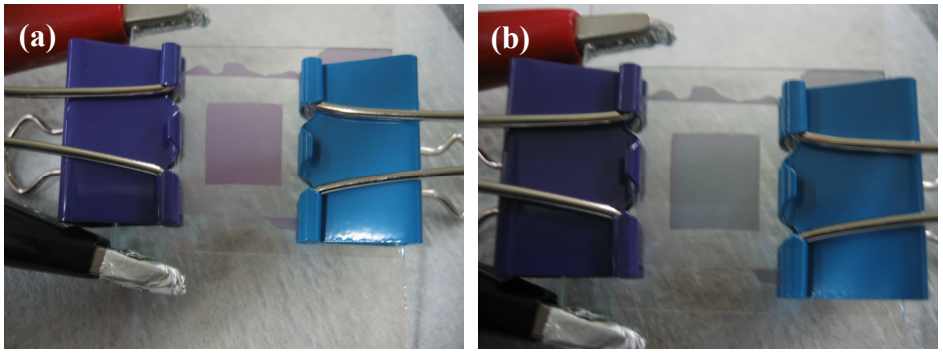


Figure 21. Photographs of blue color electronic paper display in (a) power-off and (b) power-on (20 V).

2.5 Conclusion

Electronic ink nanoparticles were loaded in a sandwich type-cell to color image by applying and switching bias voltages. In the image formation process, the positively charged ink particles moves through the negative side of ITO electrode. Through not shown here, also notable is the fact that our electronic ink nanoparticles can be flexible by the use of flexible ITO plastic sheets. This monodispersed ink particles using organic nanoparticles are expected to be very useful in E-paper displays.

III. References

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IV. Korean abstract

본 연구에서는 차세대 디스플레이인 전자종이에 이용하기 위한 유기 전자잉크입자를 고분자 중합법에 기초를 두고 합성되었다. 칼라 디스플레이를 구현하기 위하여 빨강, 파랑, 노랑색의 상용화 되는 유기염료를 이용하여 styrene과 4-vinyl pyridine으로 입자화하였다. 전기영동성을 부여하기 위한 charge control addictive로서 이온성 계면활성제를 사용하였는데 음이온성 계면활성제인 SDS(sodium dodecyl sulfate)를 이용하여 (-)표면 전하를 부여하였고 양이온성 계면활성제인 CTAB(cetyltrimethylammonium bromide)이용하여 (+)표면전하를 부여하였다. 그리고 계면활성제 농도 조절에 따라 입자 크기조절과 분산성 향상을 실현하고 높은 계면활성제의 농도에서 더 많은 전하를 가지게 되는 것을 확인하였다. 합성된 유기전자잉크입자를 이용하여 ITO glass로 간단한 디스플레이 셀을 제작하고 전하를 걸어 입자의 이동을 확인 해 봄으로써 합성된 입자의 전자종이로의 적용 가능성을 확인 하였다.

이러한 유기 전자잉크입자는 혼합 용매의 극성, 다양한 계면활성제의 첨가 및 투입양의 조절, 온도 등을 조절하여 입자의 크기 및 크기 분포를 조절하여 높은 해상도를 가지는 전기영동입자 제조의 최적의 조건을 검토하였다. 유기 합성의 경로를 통해 새로운 입자합성 방법을 고안하였으며 간단한 계면활성제의 특성을 이용하여 입자표면에 전하를 부여하였다. 고분자 중합법을 이용한 유기 전자잉크입자 제조 및 그 물성 연구는 유기나노 화학의 학문적 발전에도 큰 기여를 할 것이다. 본 연구의 수행과정에서 유기 합성, 계면 화학, 분광학적 기기 사용법의 습득으로 매우 큰 학문적 성과를 얻게 될 것으로 기대한다.

Epilogue (감사의 글)

2 여년의 석사과정과 본 논문을 완성하기까지 많은 지도와 격려하여주신 강영수 지도교수님께 진심으로 감사드립니다.

부족한 논문의 심사를 맡으셔서 조언과 지도 해 주신 문성두, 이동재 교수님께도 감사드립니다.

실험 조언뿐만이 아니라 생활 상담까지 항상 든든한 조언을 해주신 오선화 선생님, 큰 목소리 반면 따뜻한 마음으로 측정을 도와주신 강순배 선생님, 마음편히 기기를 사용할 수 있도록 항상 배려해주신 이태훈 박사님께도 감사드립니다.

2 년간 가족보다 더 많은 시간을 함께 보낸 실험실 식구들... 실험에서 업무처리까지 꼼꼼히 살펴주신 영환선배, 항상 냉철한 시각으로 완벽한 업무처리를 추구하는 말썽꾸러기 창우선배, 말과는 다르게 정이 많은 따뜻한 남자 현길선배, 힘들 때 찾을 수 있는 옥상 아지트와 실험실 생활 지침서를 알려준 송이선배, 멋진 여성상의 표본을 보여준 효심선배, 2 년새 너무 부지런해진 매너남 진국이 오빠, 4 년간 같은 공간에서 지내 친구 같은 영철이 오빠, 업무처리에서 인생상담까지 언변의 마술사 은선이 언니, 친구지만 친동생만큼 귀여운 향이, 대학과 대학원 생활의 전부를 함께 보내며 나보다 나를 더 잘 아는 베스트 프렌드 미나에게 고맙다는 말을 전하고 싶습니다.

마지막으로 자신의 공부를 하면서 나의 대학원 생활을 뒷바라지 해준 하나뿐인 동생 현진이와 딸이 공부하겠다고 했을 때 따뜻한 가정아래에 든든한 지원해주신 사랑하는 부모님께 감사드립니다.