Copper Phthalocyanine Pigment의 분산을 위한 (2-Dimethylamino)ethyl Methacrylate와 Oligo(ethylene oxide)methyl Ether Methacrylate를 포함하는 잘 규정된 블록 공중합체형 분산제의 원자 이동 라디칼 중합을 이용한 합성

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Synthesis of Well-Defined Block Copolymer Dispersants with (2-Dimethylamino)ethyl Methacrylate and Oligo(ethylene oxide)methyl Ether Methacrylate via ATRP for Dispersing Copper Phthalocyanine Pigment

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초록: LCD 컬러필터에서 안료의 분산은 컬러 강도를 증가시키는 중요한 요소이므로, 안료를 분산시키기 위한 안료 분산제의 첨가는 필수적이라 할 수 있다. 안료 분산제로서의 고분자는 안료와의 친화성을 가지는 anchoring group과 매체와의 혼화성을 가지는 stabilizing group을 포함하고 있다. 원자 이동 라디칼 중합은 잘 규정된 고분자 합성을 가능하게 하는 중합법으로, 이러한 구조를 포함하는 고분자형 안료 분산제를 얻기 위한 적절한 수단이 될 수 있다. Anchor로서 (2-dimethylamino)ethyl methacrylate를, stabilizer로서 oligo(ethylene oxide)methyl ether methacrylate를 각각 선택해 고분자 분산제를 합성하였다. 고분자의 구조 및 조성이 안료 분산에 미치는 영향을 연구하기 위해 다양한 길이의 stabilizing group을 가지는 diblock copolymer를 합성하여 비교하였다.

Abstract: The dispersion of pigment particles is important because it is capable of increasing the color strength, contrast, and transmittance of color-LCD products. Pigment dispersion properties are very important factors for the quality of LCD color filters. The chemical structure of polymeric dispersants for pigment is important to improve dispersion stability and prevent aggregation or flocculation of pigment in organic or aqueous systems. Polymeric dispersants should contain both anchoring group that interacts with pigment surface and stabilizing group that provides steric stabilization. Moreover, the molecular weight and composition of block copolymer have the an effect on pigment dispersion. In this study, adequate dispersants, block copolymers containing (2-dimethylamino)ethyl methacrylate as anchoring group and oligo(ethylene oxide)methyl ether methacrylate as a stabilizing group were designed and synthesized by atom transfer radical polymerization in order to prepare well-defined structure, molecular weight and composition.

Keywords : LCD color filter, diblock copolymer, dispersants, pigment, ATRP.

Introduction

With increasing demand for flat color displays, the liquid crystal display (LCD) has developed dramatically in recent years. The features such as small outline dimension, thin, light weight, fine resolution and low power consumption have been strongly demanded for LCD.[1] A color filter is a key component for rendering color images in liquid crystal display panels. The color filter layer is fabricated with colorants of red (R), green (G), and blue (B) from either dyes or pigment. These colorants convert white backlight into R, G, B colors. In manufacturing color filters, there are four traditional processes, which include dyeing, pigment dispersion, printing and electrodeposition method. Among these tech-

nologies, the pigment dispersion method has been widely used in mass production of color filter for LCD since it can produce color filters of high durability and good color reproducibility. However, this method has some drawbacks such as decreased transmittance of light and contrast ratio caused by aggregation of pigment particles.[1-7]

Dispersion of pigment particles into smaller size is important because it is capable of increasing the color strength, contrast, and transmittance of color-LCD products. Pigment dispersion properties are very important factor for quality of LCD color filter.[8,9] If aggregates are present, the end-use properties including gloss, opacity, tint strength, color distribution and storage stability will be highly affected. To assist dispersion properties, the dispersion barrier can be greatly improved by addition of a dispersing agent. It is therefore very important to understand the interaction between the pigment particles and dispersing agents with different functionality.[10-12]

The stabilization of dispersed particles could be achieved by using some proper dispersants in the dispersing process.[9] It is favorable if dispersants contain the surfactant molecules having both pigment- and solvent-affinity ends.[13-15] Polymeric pigment dispersants are copolymers with pigment affinic "anchoring group" and soluble polymeric chains "stabilizing group".[16-19] In the case of polymeric dispersants, however, dispersion stabilization is generally provided by two major mechanisms: electrostatic and steric stabilization. Electrostatic stabilization in organic system involves adsorbed ions building up a charged layer around the pigment, preventing aggregation by electrostatic repulsion. Steric stabilization, on the other hand, is generally described to arise from two factors: a volume restriction component and an entropic or osmotic component.[12-15] Anchoring groups in polymeric dispersants attaches to the pigment surface and stabilizing group prevent reagglomeration by these mechanisms (Figure 1).[12-19]

The benefits of polymeric dispersants can be split into three basic categories:

• Increased productivity through: dispersions of high pigment loading without increased viscosity; reduction in mill time; the manufacture of millbases which can be letdown into a variety of base paints.

• Improved quality, particularly: better coating properties, especially flow and gloss; superior color development.

• "Problem solving" through: enhanced flocculation resistance; improved color stability.[15]

Nowadays, macromolecular engineering of a steadily increased number of polymers is a very instrumental tool for well-defined copolymers, in terms of molecular architecture, chemical composition, weight composition, and molecular weight.[13-23]

Controlled radical polymerization (CRP) is a technology for the synthesis of well-defined functional copolymers. It allows the design of complex polymer architectures such as defined block copolymers. Among various techniques for CRP, atom transfer radical polymerization (ATRP) has proven to be especially suitable to synthesize well-defined block copolymer as pigment dispersants. Well-defined polymer pigment dispersants offer application properties with pigment and improved pigment stabilization.[19]

We synthesized poly[(2-dimethylamino)ethyl methacrylate-*b*-oligo(ethylene oxide)methyl ether methacrylate] by ATRP and tested it as polymeric dispersants for the pigment, copper phthalocyanine blue (CuPc).

Experimental

Materials. The monomers, (2-dimethylamino)ethyl methacrylate (DMAEMA; Aldrich) and oligo(ethylene oxide)methyl ether methacrylate (OEOMA ($M_n = 475$ g/mol); Aldrich) were passed through an alumina column to remove inhibitor, degassed with nitrogen for at least 30 min, and stored in refrigerator. Anisole was degassed with nitrogen for at least 30 min before use. Copper (I) chloride (CuCl; Aldrich) was purified with acetic acid and dried in vacuum oven. 2,2-
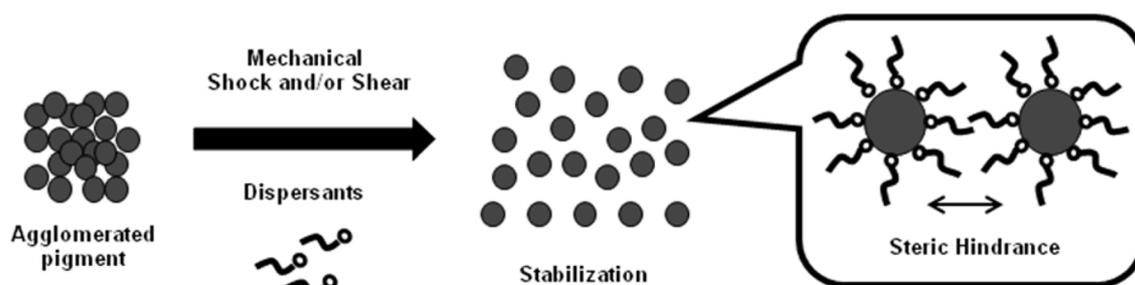

Figure 1. Mechanism of pigment dispersion.

Bipyridine (bpy; Aldrich) was all used as received. Ethyl 2-bromoisobutyrate (EBiB; Aldrich) was distilled, degassed with nitrogen for at least 30 min, and stored in refrigerator.

Instruments. Molecular weights (M_n) and molecular weight distributions (M_w/M_n) were determined by using gel permeation chromatography (GPC) calibrated with polystyrene standards and equipped with Agilent 1100 pump, RID detector and PSS SDV (5 μm, 105, 103, 102 Å 8.0 × 300.0 mm) columns. ^{1}H NMR spectra were obtained on Varian Unity Plus 300 spectrometer. IR spectra were obtained on Mattson Instruments, InC. 1001 Fourier Drive, Model GL-5060 spectrometer. Transmission electron microscope (TEM) was taken with H-100 HITACHI operating at 120 kV. Samples were prepared at 25 °C by dipping a TEM grid (Carbon coated grid) into the pigment solution. Dynamic light scattering (DLS) analysis was performed on Brookhaven 90Plus Particle Size Analyzer. Relative specific surface area of pigment, CuPc was determined by using BET, Quantachrome Instruments NOVA 4000e Surface Area and Pore Size Analyzer.

Synthesis of Macroinitiator by ATRP. Chloro-end functionalized poly[(2-dimethyl-amino)ethyl methacrylate)] (p(DMAEMA)-Cl) was synthesized according to the following procedure. A dried Schlenk flask containing bpy (0.713 g, 4.565 mmol) was evacuated and refilled with N_2 three times. To the flask, deoxygenated monomer (5 mL DMAEMA, 29.674 mmol) and anisole (50 wt%) were added via syringe. After the flask was degassed by three freeze-pump-thaw cycles, deoxygenated CuCl (0.226 g, 2.283 mmol) was added to the flask, followed by two freeze-pump-thaw cycles. The flask was placed in an oil bath set at 50 °C. Then EBiB initiator (0.335 mL, 2.283 mmol) was added to the flask. After 5 hrs, the polymerization was stopped by cooling to room temperature and opening the flask to air. The mixture was dissolved in THF, passed through a column of neutral alumina, and precipitated into hexane. After filtration and vacuum-drying, slightly yellow powder was collected (yield: 95%). The molecular weight of the obtained polymer was determined by GPC. We confirmed polymer structure from ^{1}H NMR.

Synthesis of Diblock Copolymer by ATRP. Bpy (0.089 g, 0.268 mmol) was added to the Schlenk flask, and then the flask was degassed with N_2. The monomer (5 mL OEOMA, 11.368 mmol) and macroinitiator (0.568 g, 0.284 mmol) dissolved in anisole (50 wt%) were added to the flask. Oxygen was removed by five freeze-pump-thaw cycle and then CuCl (0.028 g, 0.284 mmol) was added under N_2 flow, followed by two freeze-pump-thaw cycles (yield: 90%, entry No. 1 in Table 1). The polymerization was conducted at 50 °C. The reaction aliquots were taken periodically to monitor conversion and molecular weight using and GPC. After 5 hrs, the reaction was stopped by opening the flask to air and the catalyst was removed by passing through the solution a neutral alumina column. The solvent was removed under high vacuum. The molecular weight of the obtained polymer was determined by GPC.

Dispersion Test. The pigment used in test was CuPc. The synthesized polymeric dispersants (0.1 g) were dissolved in THF solvent (3 mL), pigments (0.3 g) were added, shaken for 5-10 min and sonicated for 2 hrs. The pigment dispersion was checked by transmission electron microscopy (TEM) and dynamic light scattering (DLS).

Results and Discussion

The objective of this study was to find out the appropriate structure for pigment dispersants. Dispersants require compatibility between pigment and solvent during dispersion of pigment in solvent. For this reason, the selection of the optimal anchoring and stabilizing groups is the most important factor for dispersion of pigment. The anchoring groups have a key role to bind to the pigment particle and the dispersant. The stabilizing groups have an affinity with the media to prevent flocculation of the pigment.

We carried out the dispersion test using various kinds of block copolymer containing prenominated two groups with different molecular weight and composition. Pigment dispersion tests were performed in only solvent system.

Polymer Design and Synthesis. Recently, polymers have been researched and can be used as dispersants for

Table 1. Analytical Results of Synthesized Polymers

| Entry No. | Polymer | Degree of polymerization (DP) | | M_n | M_w/M_n |
		p(DMAEMA)	p(OEOMA)		
1	p(DMAEMA)-*b*-p(OEOMA)	13	40	21000	1.107
2	p(DMAEMA)-*b*-p(OEOMA)	13	28	16000	1.147
3	p(DMAEMA)-*b*-p(OEOMA)	13	20	11500	1.135
4	p(DMAEMA)-*b*-p(OEOMA)	13	6	5600	1.102

the pigment in various dispersion systems.[7,11-23] The performance of dispersants strongly depends on the design of the polymer in terms of functional groups, molecular weight distribution, molecular architecture and molecular composition. ATPR provides the opportunity to prepare well-defined copolymers and exact control of polymer structure. For optimal dispersing performance, DMAEMA, was selected as anchors which interact with the pigment-affinic monomer, OEOMA was used as a stabilizer which gives the dispersants compatibility with the media and prevents flocculation of the pigments as giving steric hindrance between the pigments. Both monomers also have solubility in media (Figure 2).

Synthesis of p(DMAEMA)-b-p(OEOMA). The diblock copolymers were synthesized by two steps in Scheme 1.[24,25] In the first step, p(DMAEMA) macroinitiator, M.I. was
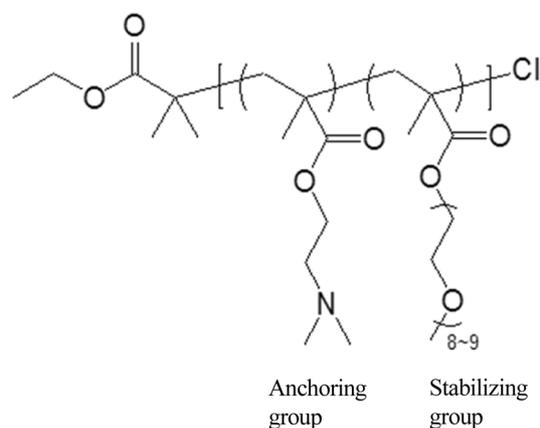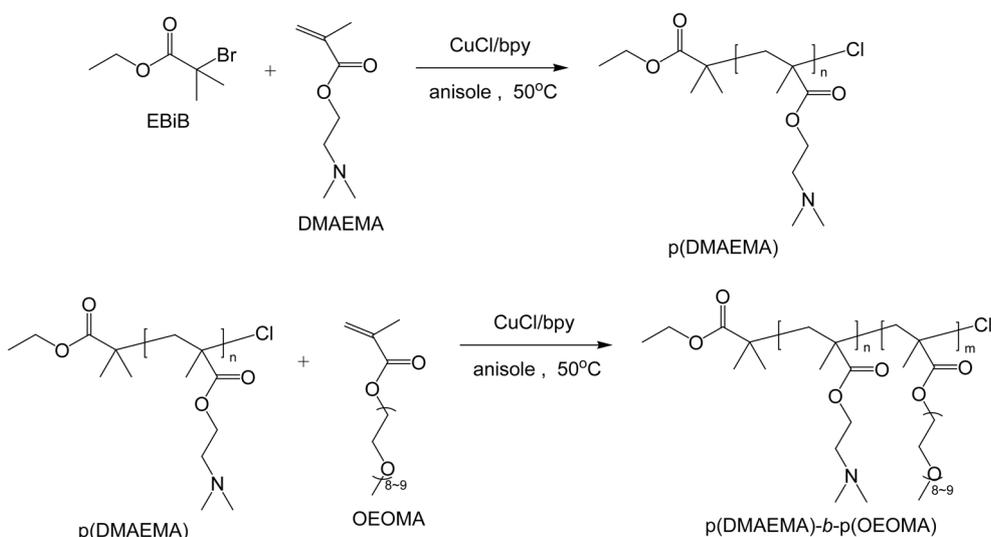
prepared by ATRP. The initiation by EBiB for DMAEMA was slow,[26,27] compared with those by other initiators. In order to increase the efficiency of initiation and reduce the rate of propagation, the halogen exchange method was used.[28-30]

After 5 hrs reaction, product of M.I. was obtained. The obtained product was characterized with GPC (Figure 3). The structure of M.I. was confirmed by ^{1}H NMR analysis (Figure 4). In next step, M.I. was used as a macroinitiator for chain extension with OEOMA via ATRP. The GPC traces for the diblock copolymers were symmetrical and reactions were well-controlled with narrow molecular weight distribution (Figure 3). The diblock copolymers were assigned by ^{1}H NMR in Figure 4 and final compositions of copolymers were determined by GPC molecular weight (Figure 3) and integral
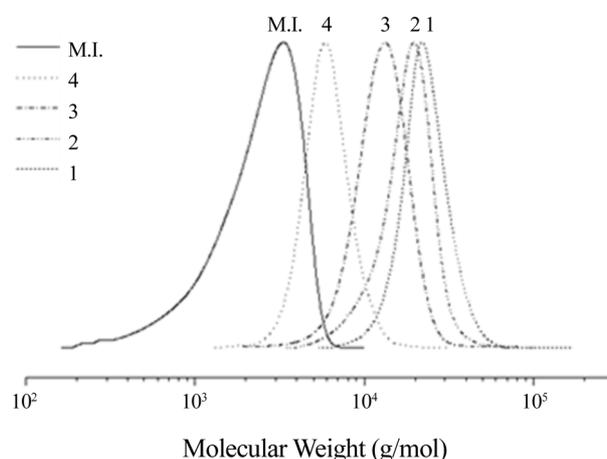

Figure 2. Polymer design for dispersants.

Figure 3. GPC chromatograms of p(DMAEMA) macroinitiator (M.I.) and p(DMAEMA)-b-p(OEOMA) diblock copolymers 1, 2, 3, and 4.

Scheme 1. Synthesis of p(DMAEMA) M.I. and p(DMAEMA)-b-p(OEOMA) diblock dopolymers 1, 2, 3, and 4 by ATRP.
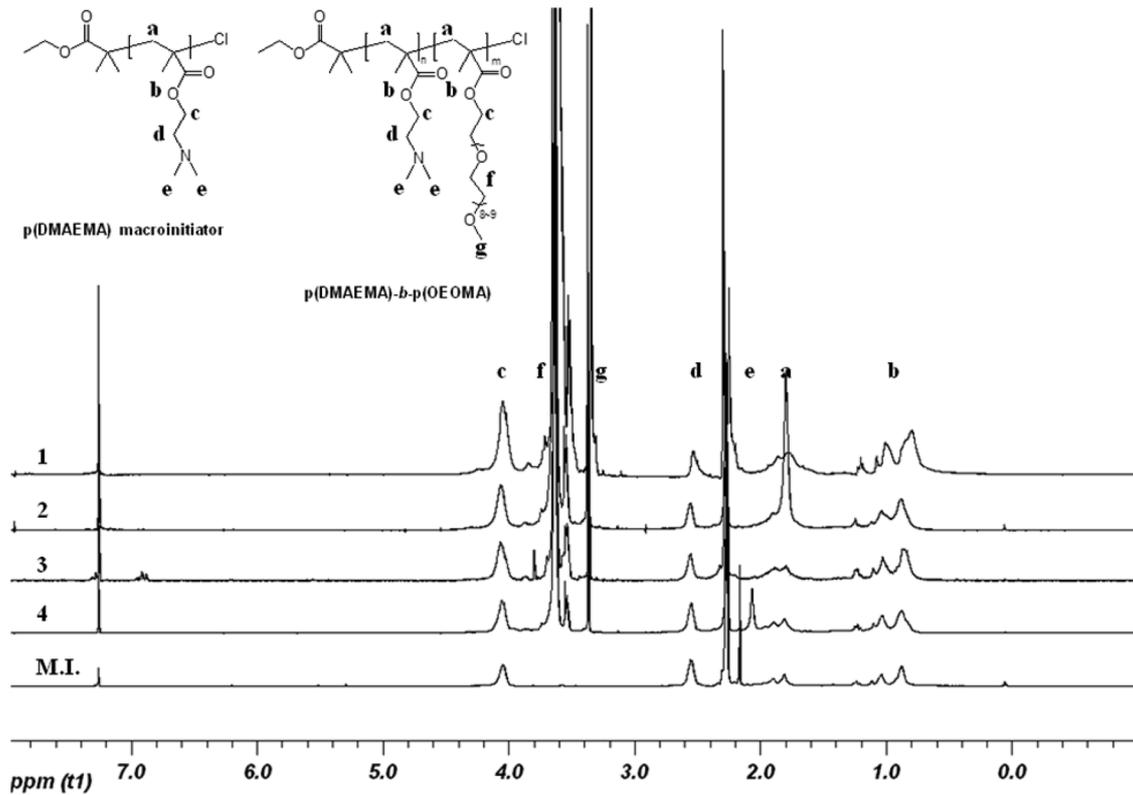
Figure 4. ^{1}H NMR spectra of p(DMAEMA) M.I. and p(DMAEMA)-*b*-p(OEOMA) diblock copolymers 1, 2, 3, and 4.
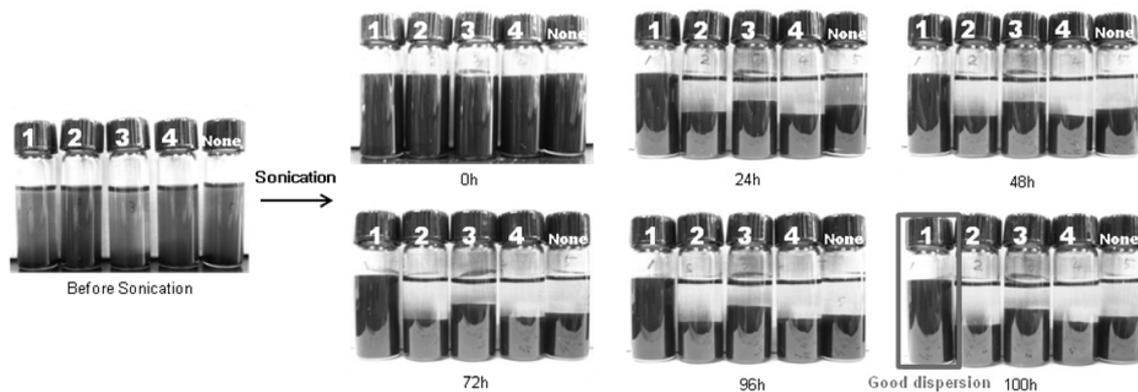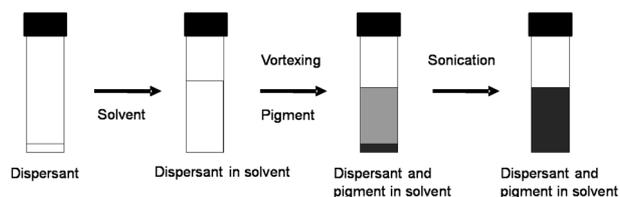

Figure 5. Dispersion test of pigment with diblock copolymer 1, 2, 3, and 4 in THF.

ratio of ^{1}H NMR spectroscopy (Figure 4). The data are summarized in Table 1.

Testing of Polymers as Pigment Dispersants. Dispersion test was carried out in an organic solvent, THF according to the procedure in Scheme 2.[17] The different block copolymers of Table 1 were tested as dispersants for the organic pigment, CuPc. The small particle size of the pigment makes this pigment difficult to disperse and to stabilize. Figure 5 shows the results of dispersion test. To find effect of stabilizing block composition on pigment dispersability, diblock copolymer with different stabilizing blocks was prepared (entry No. 1-4 in Table 1) and used as dispersants for the pigment. The pigment was not flocculated with 1 compared with the pigment with the others (Figure 5). The pigment dispersion was confirmed by TEM and DLS (Figure 6).
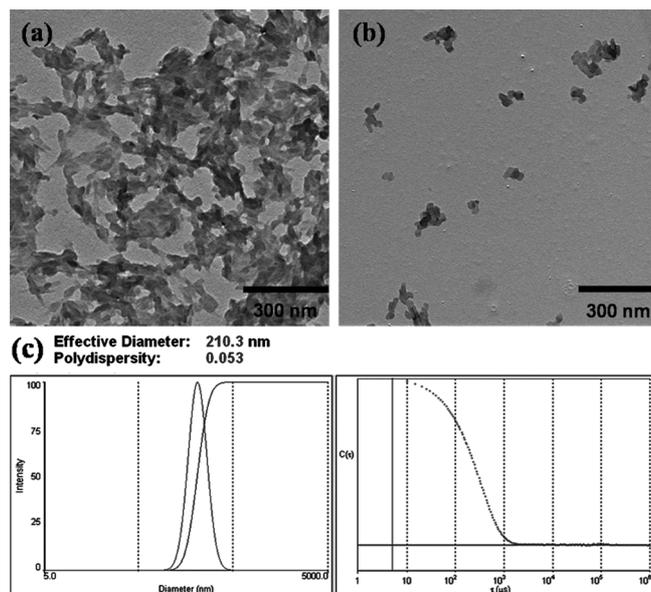
Scheme 2. Dispersion test procedure.

Figure 6. TEM images from the pigment (a) aggregated without dispersants; (b) dispersed with diblock copolymer 1; (c) particle size analysis of dispersed pigment with diblock copolymer 1 by DLS.

Composition Effect on Pigment Dispersability. The molecular composition of the diblock copolymer which has to be optimized for imparting the best stability to dispersion has been shown both theoretically and experimentally.[16] In this study, only stabilizing block composition in diblock copolymer was considered. As far as the diblock copolymers which have different molecular weight of the stabilizing block are compared, the dispersion stability seems to be quite comparable.

The low stabilizing block composition cannot give polymeric dispersants the sufficient steric stability to well-dispersing pigment and, thus, poor stability or flocculation was caused. The observation of well-dispersed pigment could result from the higher molecular weight of the stabilizing block in this diblock copolymer. In this case, the effective volume fraction of the pigment must accordingly be higher. The pigment distance should increase and their mutual interactions decrease. With the comparatively high content of the stabilizing block,

there is indication in favor of the prevention of pigment flocculation.

As a result of comparison between 1, 2, 3, and 4 diblock copolymers, it is obvious that the copolymer composition is very important factor of polymeric dispersants required for imparting stability to the pigment dispersion.

Conclusions

In this study, ATRP was used to prepare well-defined polymeric dispersants with the control of molecular architecture and composition. The molecular weight and molecular weight distribution of polymers were analyzed by GPC and the molecular composition was confirmed by ^{1}H NMR.

The diblock copolymer dispersants containing aminic anchors, p(DMAEMA)-*b*-p(OEOMA) were tested as dispersants for the pigment, CuPc in an organic solvent, THF system. The effect of molecular architectures on pigment was studied by comparing with the results of dispersion test using these two random and diblock copolymers.

The performance of the dispersants with pigment could be optimized by proper design of the block copolymer. The pigment shows best performance with high molecular weight p(DMAEMA)-*b*-p(OEOMA). It is found that the pigment requires the sufficient length of stabilizing group for efficient steric stabilization.

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