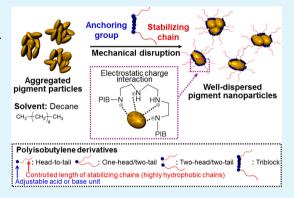


Tailoring Pigment Dispersants with Polyisobutylene Twin-Tail Structures for Electrowetting Display Application

Patricia T.C. Lee, [†] Chih-Wei Chiu,**, [‡] Ling-Yu Chang, [†] Peng-Yi Chou, [‡] Tzong-Ming Lee, [§] Te-Yi Chang, [§] Ming-Tzung Wu, [§] Wei-Yuan Cheng, [†] Shu-Wei Kuo, [†] and Jiang-Jen Lin*, [†]

Supporting Information

ABSTRACT: We have designed a class of highly hydrophobic dispersants for finely dispersing carbon black and organic pigment nanoparticles in apolar mediums. The synthesis involved the use of polyisobutylene-g-succinic anhydride (PIB-SA) and judiciously selected amines by amidation and imidation. The structures were characterized by infrared spectroscopy for anhydride functionalities in the starting materials and amide/imide linkages in the products. These polymeric forms of dispersants were structurally varied with respects to their PIB molecular weight, twin-tails, and linkages. Their relative performance for dispersing six different pigments in decane was evaluated against solution homogeneity, viscosity, stability, and particle size. The fine dispersion was achieved at particle sizes of ca. 100 nm, with the viscosity as low as 2–3 cP. The measurement of zeta potentials, which varied from –39.8 to –5.1 mV with pigment addition, revealed a strong surface-charge



interaction between pigment and PIB dispersant molecules. Examination by TEM (transmission electronic microscope) showed the homogeneous dispersion of the primary structures of pigment particles at ca. 20 nm in diameter. The polymeric dispersants with different PIB tails and imide functionalities could be tailored for pigment stability in the oil phase, which is potentially suitable for the electrowetting devices.

KEYWORDS: pigment, carbon black, poly(isobutylene) dispersant, colorant in oil, electrowetting display

1. INTRODUCTION

In electronic displays the use of organic pigments, instead of conventional dye colorants, offer advantages such as good photosensitivity, transparency, high color saturation, brilliance, and product stability. 1-3 Organic pigments have recently been used in areas such as coatings, 4 inks, 5 color filters, 6 cosmetics, 7 and plastics.8 However, because of their insolubility, the tendency for pigment particles to aggregate in organic mediums is the main technical challenge, as aggregates or crystalline structures affect the pigments' color efficiency and gloss properties. Strong mechanical grinding to reduce the pigment particle size may have an adverse effect. Therefore, the development and optimization of pigment/dispersant/medium triphase dispersions to prevent particle coalescence, sedimentation, and flocculation is imperative. Selection of suitable dispersants is important for balancing pigment aggregating forces, including electrostatic attraction, van der Waals forces, hydrogen bonding, and hydrophobic interactions. In a complementary manner, the dispersant plays a crucial role in forming noncovalent bonding interactions between the pigment surface and solvent molecules. Because pigments of different geometric shapes and sizes are insoluble in any organic solvent, a suitable dispersant is required to be highly soluble in the selected medium. With correctly balanced dispersant/ medium interactions, pigment particles could then be finely dispersed and controlled for the dispersion viscosity and particle dispersion homogeneity. A well-designed dispersant may allow high-quality pigment functions and process/storage stability.

Common surfactants are conventionally employed to prevent pigment aggregation, but these low-molecular-weight surfactants often lack the ability to stabilize insoluble particles in the dispersion. Industrially useful polymeric dispersants are more effective as stabilizers than surfactants because of the presence of polar and nonpolar polymer blocks for anchoring and solvation stabilization. The structural architecture, composition, and molecular weight distribution of well-defined polymeric dispersants are well correlated to their dispersion

Received: June 9, 2014 Accepted: July 21, 2014 Published: July 21, 2014

[†]Institute of Polymer Science and Engineering, National Taiwan University, Taipei 10617, Taiwan

[‡]Department of Materials Science and Engineering, National Taiwan University of Science and Technology, Taipei 10607, Taiwan [§]Material and Chemical Research Laboratories and ^LDisplay Technology Center, Industrial Technology Research Institute, Hsinchu 31040, Taiwan

Figure 1. Chemical structures of pigments.

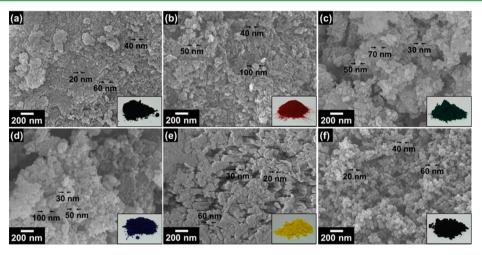


Figure 2. FE-SEM micrographs of (a) Carbon Black MA100, (b) C.I. Pigment Red 254, (c) C.I. Pigment Green 36, (d) C.I. Pigment Blue 15, (e) C.I. Pigment Yellow 138, and (f) C.I. Pigment Violet 23 (inset: their corresponding pigment raw materials).

performance. The use of amphiphilic copolymers as dispersants for inorganic particles is well documented. ^{13,14} For example, polymeric structures such as random, A-B block, comblike copolymers, and other structures ^{15–22} were used for dispersing RGB colored pigments in water ^{12,23,24} and in hydrocarbon mediums. ^{25,26} In more recent studies, poly(oxyethylene)-segmented and amide—imide functionalized surfactants were found to be highly effective for dispersing carbon nanotubes, ²⁷ silver nanoparticles, ²⁸ and platinum crystals, ^{29–33} to enhance the efficiency of dye-sensitized solar cells.

We report here new oil-soluble polymers for effectively dispersing pigment nanoparticles and enhancing dispersion stability. The polymeric surfactants were prepared through amidation and imidation of polyisobutylene-g-succinic anhydride (PIB-SA) with alkylamine and ethylene polyamine. Different designs of mono- and twin-tailed PIB dispersants with polar-tethering functionalities allowed for fine dispersions of pigments. The presence of PIB polymer chains is essential for providing steric hindrance when dispersing pigments in

decane solvent. The performance metrics such as pigment particle size, viscosity, zeta potential, and stability were correlated with the polymeric surfactant structures. Overall, the goal of this study was to employ a polymeric surfactant to improve the dispersion of pigments for the optimization of colorants in next-generation electrowetting displays (EWD).³⁴

2. EXPERIMENTAL SECTION

Materials. Polyisobutylene-g-succinic anhydride (PIB-SA) with molecular weights $(M_{\rm w})$ of 700 and 1300 g/mol (abbreviated as PIB-700 and PIB-1300, respectively) was obtained from Chevron Corp. A series of primary amines, including n-alkylamines ($C_nH_{2n+1}NH_2$, n=12, 14, and 18), ethylenediamine (EDA, $M_{\rm w}$ 60 g/mol), diethylenetriamine (DETA, $M_{\rm w}$ 103 g/mol), tetraethylenepentamine (TEPA, Mw 189 g/mol), and pentaethylenehexamine (PEHA, Mw 232 g/mol) were purchased from Aldrich Chemical Co. The inorganic pigment carbon black (Carbon Black MA100) was provided by Mitsubishi Chemical Holdings Corp., Japan. Red, green, blue, yellow, and violet organic pigments (commercial C.I. names: Pigment Red 254, Pigment Green 36, Pigment Blue 15, Pigment Yellow 138, Pigment Violet 23,

respectively) were obtained from BASF in powder form, and their chemical structures are provided in Figure 1. The morphology of the powder form of the pigment nanoparticles was characterized by field emission scanning electron microscopy (FE-SEM) (Figure 2).

Preparation of PIB Dispersants. As an example of the dispersant synthesis process, PIB-SA-derived polymeric surfactants were synthesized from the reaction of PIB-SA and EDA at a 2:1 molar ratio (product PIB-EDA-PIB) according to the following experimental procedures. PIB-1300 (42.9 g, 0.033 mol) in tetrahydrofuran (THF, 42.9 g) was added to a 250 mL three-necked, round-bottomed flask equipped with a magnetic stirrer and a thermometer. A solution of EDA (1.0 g, 0.016 mol) in THF (1.0 g) was then added. Under constant stirring, the mixture was maintained at a temperature of 25 °C for 3 h. An aliquot of the reaction mixture was taken and analyzed using Fourier transform infrared spectroscopy (FT-IR). Characteristic absorption peaks at 1556 and 1644 cm⁻¹ were obtained for the amidoacid functionalities. After increasing and maintaining the temperature at 150 °C for 3 h, cyclized imide functionality absorptions of 1713 and 1770 cm⁻¹ appeared as the major absorption peaks. The change of the characteristic peaks indicated a significant conversion from PIB-amidoacid to PIB-imide. The product was recovered by water extraction and rotary evaporation under vacuum to remove the unreacted amines and solvents. PIB-SA of different molecular weights was used to react with EDA using similar procedures.

In a similar process, a reaction of PIB-SA and n-alkylamine of PIB-1300 (13.0 g, 0.01 mol) in decane (13.0 g) and n- $C_{18}H_{37}NH_2$ (2.6 g, 0.01 mol) in decane (2.6 g) generated a PIB-N-alkyl amidoacid and the corresponding imide products at a 1:1 molar ratio of PIB-SA and n-octadecylamine. PIB-SA with various alkylamines ($C_nH_{2n+1}NH_2$, n = 12, 14, and 18) and ethylene polyamines of EDA, DETA, TEPA, and PEHA are abbreviated as PIB-amidoacid-C12, PIB-amidoacid-C14, PIB-amidoacid-C18, PIB-amidoacid-PIB-0, PIB-amidoacid-PIB-1, PIB-amidoacid-PIB-2, PIB-amidoacid-PIB-3, and PIB-amidoacid-PIB-4, respectively.

Evaluation of Dispersants for Homogenizing Pigments under Bead Mill Grinding. The dispersion of pigments in decane was prepared by subjecting the pigment powder to mechanical grinding in a bead mill (zirconium beads with a diameter of 1.5 mm) in the presence of the PIB-derived dispersant at weight ratios of pigment/dispersant of 2:1, 1:1, and 1:2. The pigment homogenizing performance was examined by preparing an aliquot of slurry of 10 wt % dispersant in decane to which pigment was added. At a pigment/ dispersant weight ratio of 1:1, 20 g of pigment dispersion was prepared by mixing the dispersant (1.0 g) in decane (18.0 g), and then the pigment powder (1.0 g) was added in one portion. The slurry was homogenized further using a mechanical vibrator for 10 min and then transferred to a vertical ball mill containing zirconium beads and processed 500 times/min for 60, 90, and 120 min at room temperature. As a control experiment, each pigment (2.0 g) in decane (18.0 g) was homogenized following the same procedure without dispersant. The dispersions were characterized in terms of particle size distribution, viscosity, morphology, and oil/water repulsive property.

Characterization and Instruments. Field-emission scanning electronic microscopy (FE-SEM) was performed on a Zeiss EM 902A, operated at 80 kV. The samples were prepared by dropping a small amount of the pigment powder on a clean glass surface, followed by dehydration in an oven at 60 °C for 2 h. The samples were then fixed on a FE-SEM holder with conductive carbon paste and coated with a thin layer of Au prior to measurement. Fourier transform infrared spectroscopy (FT-IR) was recorded on a PerkinElmer Spectrum One FT-IR Spectrometer in the range of 4000-400 cm⁻¹. Samples of PIB-derived dispersants were prepared by dissolving in decane and evaporating into a thin film on a KBr plate. The average pigment dispersion particle size was estimated using a laser particle size analyzer (90 Plus Brookhaven Instrument Corp.) equipped with a 15 mW solid-state laser (675 nm). The sample was then recorded for 1 min per measurement and the results of 20 runs were averaged. The results are quoted as average particle size (mean-diameter). Transmission electron microscopy (TEM) was performed on a Zeiss EM 902A, operated at 80 kV. The samples (0.1 wt % in decane) were

deposited onto a carbon-coated copper grid. General viscosity measurements were performed using a DV-II+ PRO Digital Viscometer (Brookfield), spindle number S21. Measurements were performed after 3 min of rotation to ensure equilibration of the reading.

3. RESULTS AND DISCUSSION

Synthesis of PIB-Derived Polymeric Surfactants. The synthesis of the polymeric surfactants involved the reaction of a cyclic anhydride and an amine $(-NH_2)$ to generate the amidoacid and imide linking sites (Schemes 1). The procedure

Scheme 1. Synthetic Scheme for Converting Polyisobutylene-g-succinic Anhydride and Amine to the PIB-Derived Amidoacid and Imide As the Polymeric Dispersants: (a) PIB Mono-Tail and (b) PIB Twin-Tail Structures

(a)
$$CH_3$$
 CH_3 CH_2 $CH_$

$$CH_3 - C + CH_2 - C + CH_2 - CH_2 -$$

for synthesizing the PIB-amidoacid intermediates was confirmed by FT-IR absorption (Figure 3). The compounds have characteristic chemical functionalities, polyisobutylene-block amide and imide linkages. The anhydride ring-opening reaction was selective at 25 °C for 3 h with high conversion. The characteristic peaks for the starting anhydride at 1782 and 1852 cm⁻¹ disappeared during the reaction progression, whereas the amide peaks at 1556 and 1644 cm⁻¹ were predominant in the product, an indication of complete anhydride ring-opening reaction between the anhydride and amine. The PIB-amidoacid underwent a second stage ring-closure conversion into the corresponding imides, PIB-imide, at an elevated temperature of 150 °C for 3 h. The ring closure and formation of the imide functionalities were confirmed by the appearance of a strong

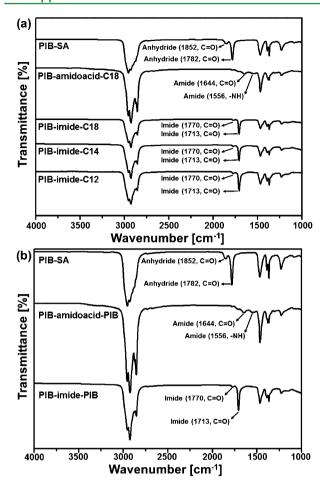


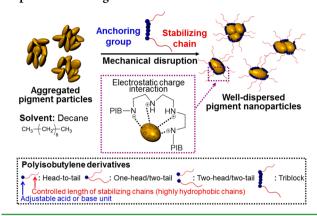
Figure 3. FT-IR spectra of PIB-SA, PIB-derived dispersants of the PIB-amidoacid intermediate, and PIB-imide: (a) PIB monotail and (b) PIB twin-tail structures.

imide absorption at 1713 cm⁻¹ and a weak absorption at 1770 cm⁻¹. Two different molecular weights of PIB-anhydrides and eight amines were used to prepare the series of PIB-imide dispersants.

Homogeneous Dispersion of Pigments in Decane by PIB-Derived Surfactants. Pigments flocculate in water and organic medium on a submicron scale because of insolubility and the strong van der Waals force among the particles. To homogenize the pigment dispersion in a stable manner, mechanical ball milling and addition of a suitable dispersant are required. An oil-soluble dispersant with an optimal balance of noncovalent bonding forces allows homogenization of the pigment dispersion in decane, as conceptually illustrated in Scheme 2. Previously, we developed polymeric surfactants to stabilize various nanoparticles, including platinum and organic pigments.^{27–33} Our findings revealed that by carefully choosing the molar ratio of oxyethylene/oxypropylene in the polymer backbone, the general hydrophilic/hydrophobic balance rendered the dispersant soluble in toluene but insoluble in decane. To achieve homogeneous dispersion, the polymeric dispersants need to be structurally tailored for their solubility in decane and affinity toward pigment particles. The structural design of the dispersants, including head-to-tail, one-head/twotail, two-head/two-tail, and triblock structures, was systematically prepared.

Here, we report the synthesis and the structural correlation to the performance of pigment dispersion. Various PIB-imide

Scheme 2. Conceptual Illustration of the Dispersion of PIB Dispersants and Pigments in Decane



structures, including the hydrophobic polyisobutylene-segmented tails, and the functionalities of carboxylic acid, amide, and imide were evaluated for their ability to disperse various pigments. In Table 1 and Table S1 in the Supporting

Table 1. Particle Size Distribution of the PIB-Derived Surfactant/Inorganic Carbon Black Dispersions

	viscosity (сР) ^ь			
dispersants ^a	immediately	one week	particle size (nm) ^c	PDI^c	zeta potential (mV)
PIB-1300	gel	gel	3545	0.458	
PIB-amidoacid- C12	8.3	13.7	484.9	0.314	
PIB-amidoacid- C14	4.5	12.3	164.9	0.245	
PIB-amidoacid- C18	2.1	6.4	140.8	0.128	
PIB-imide-C18	4.5	10.4	481.0	0.256	
PIB-amidoacid- PIB-0	2.3	2.6	120.0	0.118	-27.7
PIB-amidoacid- PIB-1	1.8	1.8	117.6	0.118	-20.9
PIB-amidoacid- PIB-2	1.8	1.9	119.3	0.118	-19.0
PIB-amidoacid- PIB-3	2.1	1.9	125.2	0.130	-9.4
PIB-amidoacid- PIB-4	1.8	1.9	119.6	0.124	-7.2

^αPolyisobutylene-g-succinic anhydride (PIB-SA) with various alkylamines (C_nH_{2n+1} NH₂, n=12, 14, and 18) and ethylene polyamines of EDA, DETA, TEPA, and PEHA are abbreviated as PIB-amidoacid-C12, PIB-amidoacid-C14, PIB-amidoacid-C18, PIB-amidoacid-PIB-0, PIB-amidoacid-PIB-1, PIB-amidoacid-PIB-2, PIB-amidoacid-PIB-3, and PIB-amidoacid-PIB-4, respectively. ^bDispersion: 1.0 g of pigment, 1.0 g of dispersant, and 18 g of decane; viscosity was measured (spindle S21; 100 rpm; 25 °C) immediately and after 1 week settling after milling. ^cSamples were diluted to 2 ppm concentrations for particle size analysis (25 °C); particle size was measured immediately after milling.

Information, the particle size, viscosity, and zeta potential of PIB-derived surfactants in the pigment dispersions are compared as a function of chemical structures such as PIB-amidoacid, PIB-imide, PIB-amidoacid-PIB, and PIB-imide-PIB. In comparison, Table 2 and Table S2 in the Supporting Information show the average particle size of organic pigments in decane. It can be clearly seen that for organic pigments without dispersion solutions, the dispersed organic particles are

Table 2. Particle Size Distribution of the PIB-Derived Surfactant/Organic Pigment Dispersions

dispersants ^a immediately one week particle size Yellow 138 PIB-amidoacid-C18 6.6 10.2 315.9 PIB-imide-C18 3.5 8.3 264.3 PIB-imide-PIB-0 2.1 2.1 114.8 PIB-imide-PIB-1 1.8 1.9 112.9 PIB-imide-PIB-2 1.8 1.8 111.9 PIB-imide-PIB-3 1.8 1.8 110.7 PIB-imide-PIB-4 1.8 1.8 110.6 Red 254 PIB-imide-C18 7.2 13.5 334.9/5060 (9) PIB-imide-PIB-4 1.9 2.1 128.1 Green 36 30.2 30.2 30.2	0.167 0.129 0.219 0.219	zeta potential (mV) -39.8
PIB-amidoacid-C18 6.6 10.2 315.9 PIB-imide-C18 3.5 8.3 264.3 PIB-imide-PIB-0 2.1 2.1 114.8 PIB-imide-PIB-1 1.8 1.9 112.9 PIB-imide-PIB-2 1.8 1.8 111.9 PIB-imide-PIB-3 1.8 1.8 110.7 PIB-imide-PIB-4 1.8 1.8 110.6 Red 254 PIB-imide-C18 7.2 13.5 334.9/5060 (9 PIB-imide-PIB-4 1.9 2.1 128.1 Green 36	0.129 0.219 0.219	-39.8
PIB-imide-C18 3.5 8.3 264.3 PIB-imide-PIB-0 2.1 2.1 114.8 PIB-imide-PIB-1 1.8 1.9 112.9 PIB-imide-PIB-2 1.8 1.8 111.9 PIB-imide-PIB-3 1.8 1.8 110.7 PIB-imide-PIB-4 1.8 1.8 110.6 Red 254 PIB-imide-C18 7.2 13.5 334.9/5060 (9 PIB-imide-PIB-4 1.9 2.1 128.1 Green 36	0.129 0.219 0.219	-39.8
PIB-imide-PIB-0 2.1 2.1 114.8 PIB-imide-PIB-1 1.8 1.9 112.9 PIB-imide-PIB-2 1.8 1.8 111.9 PIB-imide-PIB-3 1.8 1.8 110.7 PIB-imide-PIB-4 1.8 1.8 110.6 Red 254 PIB-imide-C18 7.2 13.5 334.9/5060 (9 PIB-imide-PIB-4 1.9 2.1 128.1 Green 36	0.219 0.219	-39.8
PIB-imide-PIB-1 1.8 1.9 112.9 PIB-imide-PIB-2 1.8 1.8 111.9 PIB-imide-PIB-3 1.8 1.8 110.7 PIB-imide-PIB-4 1.8 1.8 110.6 Red 254 PIB-imide-C18 7.2 13.5 334.9/5060 (9 PIB-imide-PIB-4 1.9 2.1 128.1 Green 36	0.219	-39.8
PIB-imide-PIB-2 1.8 1.8 111.9 PIB-imide-PIB-3 1.8 1.8 110.7 PIB-imide-PIB-4 1.8 1.8 110.6 Red 254 PIB-imide-C18 7.2 13.5 334.9/5060 (9 PIB-imide-PIB-4 1.9 2.1 128.1 Green 36		
PIB-imide-PIB-3 1.8 1.8 110.7 PIB-imide-PIB-4 1.8 1.8 110.6 Red 254 PIB-imide-C18 7.2 13.5 334.9/5060 (9 PIB-imide-PIB-4 1.9 2.1 128.1 Green 36		-39.3
PIB-imide-PIB-4 1.8 1.8 110.6 Red 254 PIB-imide-C18 7.2 13.5 334.9/5060 (9 PIB-imide-PIB-4 1.9 2.1 128.1 Green 36	0.224	-36.2
Red 254 PIB-imide-C18 PIB-imide-PIB-4 1.9 2.1 128.1 Green 36	0.218	-19.6
PIB-imide-C18 7.2 13.5 334.9/5060 (9 PIB-imide-PIB-4 1.9 2.1 128.1 Green 36	0.214	-5.1
PIB-imide-PIB-4 1.9 2.1 128.1 Green 36		
Green 36	$(98.6/1.4)^d$ 0.192	
	0.263	-18.3
PVP + +1 G40		
PIB-imide-C18 330.5	0.195	
PIB-imide-PIB-4 2.3 2.6 89.1	0.271	-14.1
Blue 15		
PIB-imide-C18 8.1 13.8 463.7/5163 (9	$(0.221)^d$	
PIB-imide-PIB-4 7.7 12.3 369.9	0.195	-9.6
Violet 23		
PIB-imide-C18 2.6 8.2 192.5	0.159	
PIB-imide-PIB-4 1.9 2.1 110.6		-5.9

"Polyisobutylene-g-succinic anhydride (PIB-SA) with *n*-octadecylamine and various ethylene polyamines of EDA, DETA, TEPA, and PEHA are abbreviated as PIB-imide-PIB-18, PIB-imide-PIB-19, PIB-imide-PIB-29, PIB-imide-PIB-39, and PIB-imide-PIB-49, respectively. Dispersion: 1.0 g of pigment, 1.0 g of dispersant, and 18 g of decane; viscosity was measured (spindle S21; 100 rpm; 25 °C) immediately and after 1 week settling after milling. Samples were diluted to 2 ppm concentration for particle size analysis (25 °C); particle size was measured immediately after milling. Particle size (nm) and distribution (%; bimodal peaks).

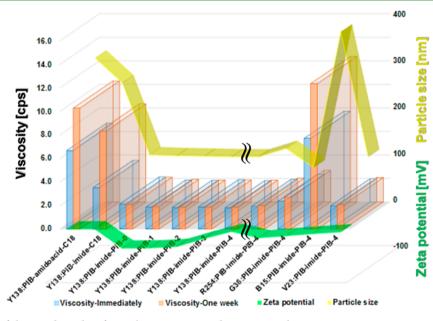


Figure 4. Characteristics of the PIB-derived surfactant/organic pigment dispersions in decane.

stacked because of aggregation, resulting in average particle sizes of 110.6, 128.1, 89.1, 369.9, and 110.6 nm for C.I. Pigment Yellow 138, C.I. Pigment Red 254, C.I. Pigment Green 36, C.I. Pigment Blue 15 and C.I. Pigment Violet 23, respectively. The PIB-derived polymeric surfactants were employed to form a steric structure for the stabilization of dispersed organic particles in solution at room temperature and atmospheric pressure. As observed from Table 2, dispersed organic nanoparticles with PIB-derived polymeric surfactants were remarkably stable. For the dispersion of carbon black, the

noncovalent interactions between the inorganic pigment and noncyclized PIB-amidoacid-PIB produced a powerful anchoring force and stabilized the solution in nonpolar decane through hydrophobic interactions between the PIB and the alkyl chain segments. In contrast to the case for the PIB-imide-PIB dispersant, a weak anchoring force due to noncovalent bonding results in less effective pigment dispersion. On the other hand, the noncyclized amidoacids had a weaker anchoring force and were thus less effective for homogenizing the organic pigment particle size than the corresponding PIB-imide analogs.

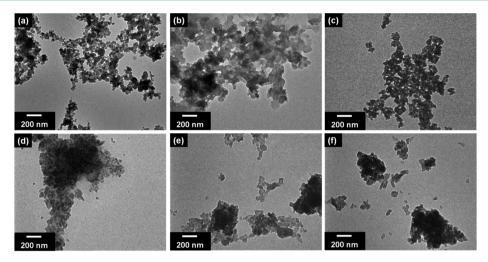


Figure 5. TEM micrographs of (a) Carbon Black MA100, (b) C.I. Pigment Red 254, (c) C.I. Pigment Green 36, (d) C.I. Pigment Blue 15, (e) C.I. Pigment Yellow 138, and (f) C.I. Pigment Violet 23 solutions without dispersant in decane.

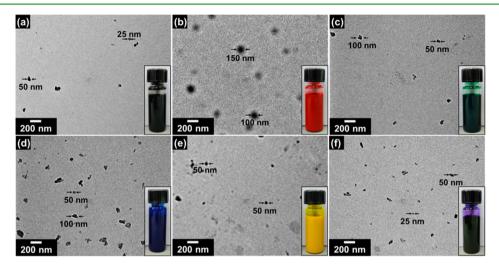


Figure 6. TEM micrographs of (a) Carbon Black MA100, (b) C.I. Pigment Red 254, (c) C.I. Pigment Green 36, (d) C.I. Pigment Blue 15, (e) C.I. Pigment Yellow 138, and (f) C.I. Pigment Violet 23 dispersions in decane (weight ratio of dispersant/pigment = 1/1). The inset pictures show the good dispersion after 6 months of undisturbed suspension.

Performance of the PIB-Derived Surfactants. The viscosities of the inorganic carbon black pigment dispersed in PIB-amidoacid-C18, PIB-amidoacid-PIB-0, PIB-amidoacid-PIB-1, PIB-amidoacid-PIB-2, PIB-amidoacid-PIB-3, and PIB-amidoacid-PIB-4 dispersants in decane after being allowed to settle for 1 week were measured to be 6.48, 2.69, 1.88, 1.92, 1.97, and 1.93 cP, respectively. A considerably low viscosity was achieved by the PIB-amidoacid-PIB-4. Generally, the pigment/dispersant/solvent interaction disperses the particles as a continuous phase but the particles are still interconnected via the polymer chains and consequently caused a flocculation or increased viscosity after settling. Hence, changes in viscosity for pigment-dispersed solutions are informative for probing the dispersant behaviors

The performance of the PIB-derived surfactants in terms of enabling the dispersion of the six pigments was examined by a Zeta-Plus zetameter. After being added to the PIB-derived surfactants and subsequently milled, the pigments were homogeneously dispersed in decane. The zeta potential of inorganic carbon black decreased significantly from -27.7 mV for PIB-amidoacid-PIB-0 to -7.2 mV for PIB-amidoacid-PIB-4 (Figure 4 and Table 1). The zeta potential of the PIB-imide-

PIB-4/pigment hybrid solutions ranged from -5.15 mV for C.I. Pigment Yellow 138 to -18.1 mV for C.I. Pigment Red 23. The six pigments exhibited a low positive charge in zeta potential due to the strong interaction between the pigments and the PIB-derived surfactants. The organic pigment stabilization provided by various PIB derivatives depends on the PIB and alkyl molecular lengths and the amidoacid and imide anchoring forces in the following order: PIB-imide-PIB-4 > PIB-imide-PIB-3 > PIB-imide-PIB-2 > PIB-imide-PIB-1 > PIB-imide-PIB-0 > PIB-imide-C18 > PIB-amidoacid-C18. Therefore, the performance in terms of pigment particle size, viscosity, zeta potential, and stability was correlated with the PIB derivative structures.

Fine Dispersion of Pigment Nanoparticles in Decane Observed by TEM. The six pigments were finely dispersed in decane and characterized by transmission electron microscopy (TEM), as shown in Figures 5 and 6. To observe the particle size and morphologies, the samples had to be diluted in a solvent. Comparative experiments without dispersant yielded large pigment particles of ca. 1000 nm in decane (Figure 5). When the PIB-derived dispersant was added and pulverized, the pigment dispersion was stabilized with particles smaller than

100 nm in the medium (Figure 6). The primary units of the pigment particles were 25–50 nm, with secondary aggregates or clusters over 100 nm. It was noted that the dispersions may maintain their homogeneity for a long periods of time (standing for several months).

Oil/Water Repulsive Properties of Pigment Dispersion. Figure 7 and Movie S1 in the Supporting Information

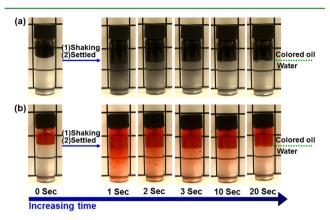


Figure 7. Oil/water repulsive property of PIB-derived pigment dispersion: (a) Carbon Black MA100 and (b) C.I. Pigment R256. After vigorous shaking, the dispersion settled into two layers.

show the oil/water repulsive properties of the PIB-derivative inorganic carbon black and organic pigment dispersions. The pigment was first dispersed in decane and then water was added. After shaking, the dispersions settled into two layers with increasing time from 1 to 20 s. The electrowetting device structural information is listed in Table S3 and Figure S1 in the Supporting Information, where a 5 cm × 5 cm single-layered monochromatic EWD is shown. The display panel was operated with an applied AC voltage of 0-20 V and a frequency of 60 Hz. Furthermore, it is shown that the operation demonstrated of polymeric surfactants for dispersing C.I. Pigment Violet 23 in decane and the ability of exhibiting the colored oil and water phase movement in the EWD device (see Movie S1 in the Supporting Information). In summary, the goal of this study is to employ polymeric surfactants to improve the dispersion of six pigments for use as colorant in EWD.

4. CONCLUSION

A novel class of PIB-based dispersants were designed, synthesized, and evaluated for homogenizing pigment particles in decane. The apolar PIB tails in the structure provide the hydrophobic groups in combination with the polar moieties including succinic imides. In decane, the polar groups in the PIB-derived molecules serve as strong chelating sites toward the pigment surface. This results in the stability of the pigment nanoparticles in solution with low viscosity (2–3 cP), fine particle size distribution (ca. 100 nm in diameter), a narrow polydispersity index (0.144), and long-term storage stability. The zeta potential shows the dispersion stability by the presence of a strong surface-charge attraction. The homogeneity of pigment particles in oil and the distinct separation of oil/water phases indicate the advantages of applying pigments for fabricating electrowetting displays.

ASSOCIATED CONTENT

S Supporting Information

Particle size distribution and viscosity of the PIB- derived surfactant/pigment dispersions. A movie shows the pigment-in-oil/water repulsive property and EWD panel. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Authors

*E-mail: cwchiu@mail.ntust.edu.tw. Tel: +886-2-2737-6521. Fax: +886-2-2737-6544.

*E-mail: jianglin@ntu.edu.tw. Tel: +886-2-3366-5312. Fax: +886-2-8369-1384.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We acknowledge financial support from the Ministry of Economic Affairs (101-EC-17-A-08-S1-205) and the Ministry of Science and Technology (NSC 102-2218-E-011-006-) of Taiwan. We thank Dr. Jang-Lin Chen (Display Technology Center, ITRI) for useful discussions.

REFERENCES

- (1) Meng, X.; Qiang, L.; Su, X.; Ren, J.; Tang, F. Synthesis of Black Magnetic Electrophoretic Particles for Magnetic-Electric Dual-Driven Electronic Paper. ACS Appl. Mater. Interfaces 2013, 5, 622–629.
- (2) Meng, X.; Wen, T.; Qiang, L.; Ren, J.; Tang, F. Luminescent Electrophoretic Particles via Miniemulsion Polymerization for Night-Vision Electrophoretic Displays. *ACS Appl. Mater. Interfaces* **2013**, *5*, 3638–3642.
- (3) Bieleman, J.; Heilen, W.; Silber, S.; Ortelt, M.; Scholz, W. Surface-Active Agents. In *Additives for Coatings*; Wiley-VCH: Weinheim, Germany, 2007.
- (4) Baez, E.; Quazi, N.; Ivanov, I.; Bhattacharya, S. N. Stability Study of Nanopigment Dispersions. *Adv. Powder Technol.* **2009**, *20*, 267–272.
- (5) Van, S. T.; Velamakanni, B. V.; Adkins, R. R. About Coatings and Cathodic Protection: Electrochemical Features of Coatings Used on Pipelines. *J. Coat. Technol.* **2001**, *73*, 61–65.
- (6) Carotenuto, G.; Her, Y. S.; Matijevic, E. Preparation and Characterization of Nanocomposite Thin Films for Optical Devices. *Ind. Eng. Chem. Res.* **1996**, 35, 2929–2932.
- (7) Qu, D.; Duncan, J. W. A Study on Pigment Dispersion in Color Cosmetics: Milling Process and Scale-Up. *J. Cosmet. Sci.* **2000**, *51*, 324–325.
- (8) Hao, Z. M.; Iqbal, A. Some Aspects of Organic Pigments. *Chem. Soc. Rev.* **1997**, *26*, 203–213.
- (9) Spinelli, H. J. Polymeric Dispersants in Ink Jet Technology. *Adv. Mater.* **1998**, *10*, 1215–1218.
- (10) Kelley, A. T.; Alessi, P. J.; Fornalik, J. E.; Minter, J. R.; Bessey, P. G.; Garno, J. C.; Royster, T. L., Jr. Investigation and Application of Nanoparticle Dispersions of Pigment Yellow 185 Using Organic Solvents. ACS Appl. Mater. Interfaces 2010, 2, 61–68.
- (11) Marcincin, A. Modification of Fiber-Forming Polymers by Additives. *Prog. Polym. Sci.* **2002**, 27, 853–913.
- (12) Lan, Y. F.; Lin, J. J. Clay-Assisted Dispersion of Organic Pigments in Water. *Dyes Pigm.* **2011**, *90*, 21–27.
- (13) Burke, N. A. D.; Stover, H. D. H.; Dawson, F. P. Magnetic Nanocomposites: Preparation and Characterization of Polymer-Coated Iron Nanoparticles. *Chem. Mater.* **2002**, *14*, 4752–4761.
- (14) Creutz, S.; Jerome, R. Effectiveness of Poly(vinylpyridine) Block Copolymers as Stabilizers of Aqueous Titanium Dioxide Dispersions of a High Solid Content. *Langmuir* 1999, 15, 7145–7156.
- (15) In, I.; La, Y.; Park, S.; Nealey, P. F.; Gopalan, P. Side-Chain-Grafted Random Copolymer Brushes as Neutral Surfaces for

- Controlling the Orientation of Block Copolymer Microdomains in Thin Films. *Langmuir* **2006**, 22, 7855–7860.
- (16) Kang, Y.; Taton, T. A. Controlling Shell Thickness in Core-Shell Gold Nanoparticles via Surface-Templated Adsorption of Block Copolymer Surfactants. *Macromolecules* **2005**, 38, 6115–6121.
- (17) Nuopponen, M.; Tenhu, H. Gold Nanoparticles Protected with pH and Temperature-Sensitive Diblock Copolymers. *Langmuir* **2007**, 23, 5352–5357.
- (18) Chen, Y. M.; Hsu, R. S.; Lin, H. C.; Chang, S. J.; Chen, S. C.; Lin, J. J. Synthesis of Acrylic Copolymers Consisting of Multiple Amine Pendants for Dispersing Pigment. *J. Colloid Interface Sci.* **2009**, 334, 42–49.
- (19) Wen, Z. Q.; Feng, Y. Q.; Li, X. G.; Bai, Y.; Li, X. X.; An, J.; Lu, M. Surface Modification of Organic Pigment Particles for Microencapsulated Electrophoretic Displays. *Dyes Pigm.* **2011**, *92*, 554–562.
- (20) Tsubokawa, N.; Kobayashi, M.; Ogasawara, T. Graft Polymerization of Vinyl Monomers Initiated by Azo Groups Introduced onto Organic Pigment Surface. *Prog. Org. Coat.* **1999**, *36*, 39–44.
- (21) Daescu, C. Dispersability of Organic Pigments. *Dyes Pigm.* **1998**, 38, 173–180.
- (22) Tsubokawa, N. Functionalization of Carbon Black by Surface Grafting of Polymers. *Prog. Polym. Sci.* **1992**, *17*, 417–470.
- (23) Winnik, F. M.; Keoshkerian, B.; Fuller, J. R.; Hofstra, P. G. New Water-Dispersible Silica-Based Pigments: Synthesis and Characterization. *Dyes Pigm.* **1990**, *14*, 101–112.
- (24) Pugh, S. L.; Guthrie, J. T. Some Characteristics of Pigments that Affect the Kinetics of Fading of Prints Made from Water-Based Liquid Ink Formulations. *Dyes Pigm.* **2002**, *55*, 109–121.
- (25) Hauptman, N.; Vesel, A.; Ivanovski, V.; Gunde, M. K. Electrical Conductivity of Carbon Black Pigments. *Dyes Pigm.* **2012**, *95*, 1–7.
- (26) Christie, R. M.; Chugtai, I.; Mather, R. R. The Influence of Synthesis Conditions on the Crystal and Aggregate Properties of Calcium Salt Azo Pigment CI Pigment Red 48:2. *Dyes Pigm.* **2009**, *80*, 264–270.
- (27) Wang, Y. C.; Huang, K. C.; Dong, R. X.; Liu, C. T.; Wang, C. C.; Ho, K. C.; Lin, J. J. Polymer-Dispersed MWCNT Gel Electrolytes for High Performance of Dye-Sensitized Solar Cells. *J. Mater. Chem.* **2012**, 22, 6982–6989.
- (28) Dong, R. X.; Liu, C. T.; Huang, K. C.; Chiu, W. Y.; Ho, K. C.; Lin, J. J. Controlling Formation of Silver/Carbon Nanotube Networks for Highly Conductive Film Surface. *ACS Appl. Mater. Interfaces* **2012**, *4*, 1449–1455.
- (29) Huang, K. C.; Wang, Y. C.; Dong, R. X.; Tsai, W. C.; Tsai, K. W.; Wang, C. C.; Chen, Y. H.; Vittal, R.; Lin, J. J.; Ho, K. C. A High Performance Dye-Sensitized Solar Cell with a Novel Nanocomposite Film of PtNP/MWCNT on the Counter Electrode. *J. Mater. Chem.* **2010**, 20, 4067–4073.
- (30) Chang, L. Y.; Lee, C. P.; Huang, K. C.; Wang, Y. C.; Yeh, M. H.; Lin, J. J.; Ho, K. C. Facile Fabrication of PtNP/MWCNT Nanohybrid Films for Flexible Counter Electrode in Dye-Sensitized Solar Cells. *J. Mater. Chem.* **2012**, 22, 3185–3191.
- (31) Chang, L. Y.; Lee, C. P.; Vittal, R.; Lin, J. J.; Ho, K. C. Control of Morphology and Size of Platinum Crystals through Amphiphilic Polymer-Assisted Microemulsions and Their Uses in Dye-Sensitized Solar Cells. *J. Mater. Chem.* **2012**, *22*, 12305–12312.
- (32) Liu, C. T.; Wang, Y. C.; Dong, R. X.; Wang, C. C.; Huang, K. C.; Vittal, R.; Ho, K. C.; Lin, J. J. A Dual-Functional Pt/CNT TCO-Free Counter Electrode for Dye-Sensitized Solar Cell. *J. Mater. Chem.* **2012**, 22, 25311–25315.
- (33) Huang, K. C.; Wang, Y. C.; Chen, P. Y.; Lai, Y. H.; Huang, J. H.; Chen, Y. H.; Dong, R. X.; Chu, C. W.; Lin, J. J.; Ho, K. C. High Performance Dye-Sensitized Solar Cells Based on Platinum Nanoparticle/Multi-Wall Carbon Nanotube Counter Electrodes: The Role of Annealing. *J. Power Sources* **2012**, 203, 274–281.
- (34) Lee, P. T. C.; Chiu, C. W.; Lee, T. M.; Chang, T. Y.; Wu, M. T.; Cheng, W. Y.; Kuo, S. W.; Lin, J. J. First Fabrication of Electrowetting Display by Using Pigment-in-Oil Driving Pixels. *ACS Appl. Mater. Interfaces* **2013**, *5*, 5914–5920.

(35) Arts, T. J. C.; Laven, J.; Vader van Voorst, F.; Kwaaitaal, Th. Zeta Potentials of Tristearoylglycerol Crystals in Olive Oil. *Colloids Surf., A* **1994**, 85, 149–158.