Supporting Information

# Polyether-based Waterborne Synergists: Effect of Polymer Topologies on Pigment Dispersion

*Hansol Kang,[1,2‡] Si Eun Kim,[1‡] Young Il Park,[1] Jin Chul Kim,[1] Ji-Eun Jeong,[1] Hyocheol Jung,[1] Hyosun Lee,[3] Sung Yeon Hwang,[4]\* In Woo Cheong,[2]\* Sang-Ho Lee,[1,5]\* and Eunyong Seo[1,6]\**

[1]Center for Advanced Specialty Chemicals, Korea Research Institute of Chemical Technology, Ulsan 44412, Republic of Korea

[2]Department of Applied Chemistry, Kyungpook National University (KNU), Daegu 41566, Republic of Korea

[3]Department of Chemistry and Green-Nano Materials Research Center, Kyungpook National University, 80 Daehakro, Buk-gu, Daegu 41566, Republic of Korea

[4]Department of Plant & Environmental New Resources and Graduate School of Biotechnology, Kyung Hee University, Gyeonggi-do 17104, Republic of Korea

[5]Advanced Materials and Chemical Engineering, University of Science and Technology (UST), Daejeon 34113, Republic of Korea

[6]Department of Chemical Engineering, Ulsan College, Ulsan 44610, Republic of Korea

Supporting Information

E-mail: (E. S.) eyseo@uc.ac.kr; (S.-H. L.) slee@krict.re.kr; (I.W. C.) inwoo@knu.ac.kr; (S.Y. H.) crew75@khu.ac.kr

**KEYWORDS** Waterborne Synergist, Polymer Topology, Polyether, Pigment Dispersion, Dispersibility, Storage Stability.

**EXPERIMENTAL SECTION**

**Preparation of (2-(1,3-dioxo-1,3-dihydro-2H-benzo[f]isoindol-2-yl)acetic acid).** The reactions were carried out in a 250-mL glass reactor with a magnetic stirrer under a nitrogen atmosphere. Naphthalenedicarboxylic anhydride (10 g; 50 mmol) was placed in a 250-mL round-bottom flask and dissolved in 20-mL DMF. Glycine (6.5 g; 87 mmol) was slowly added to the flask under a nitrogen atmosphere. The reaction mixture was then stirred for 12 h at 100 °C. After the reaction mixture was cooled to room temperature, cold distilled water was poured into the flask, and the resulting precipitates were filtered and washed several times with distilled water to obtain the intermediate. The obtained product was dried overnight.

**Preparation of (2-(1,3-dioxo-1H-benzo[de]isoquinolin-2(3H)-yl)acetic acid).** Naphthalic anhydride (1, 8-naphthalic anhydride; 20 g; 101 mmol) was added to a 250-mL round-bottom flask and dissolved in 40-mL DMF. Glycine (9.76 g; 130 mmol) was slowly added to the flask under a nitrogen atmosphere. The reaction mixture was then stirred for 12 h at 100 °C. After the reaction mixture was cooled to room temperature, cold distilled water was poured into the flask, and the resulting precipitates were filtered and washed several times with distilled water to obtain the intermediate. The obtained product was dried overnight.

**Table S1.** Characterization of topology-controlled PGSs

| Entry | Synergist | $M_n{}^a$ | $M_w/M_n{}^a$ | $T_g{}^b$ | Ratio (−OH/BzCl/Anchor) |
|-------|-----------|-----------|---------------|-----------|--------------------------|
| 1 | *hb*-PG | 1800 | 1.9 | −27 | 10/0/0 |
| 2 | *hb*-PG-BzA$_1$ | 570 | 1.4 | −25 | 7/2/1 |
| 3 | *lin*-PG | 4400 | 1.0 | −8 | 10/0/0 |
| 4 | *lin*-PG-BzA$_1$ | 600 | 1.5 | −37 | 7/2/1 |

Supporting Information

**Table S2.** Formulation of Red 170 pigment dispersion

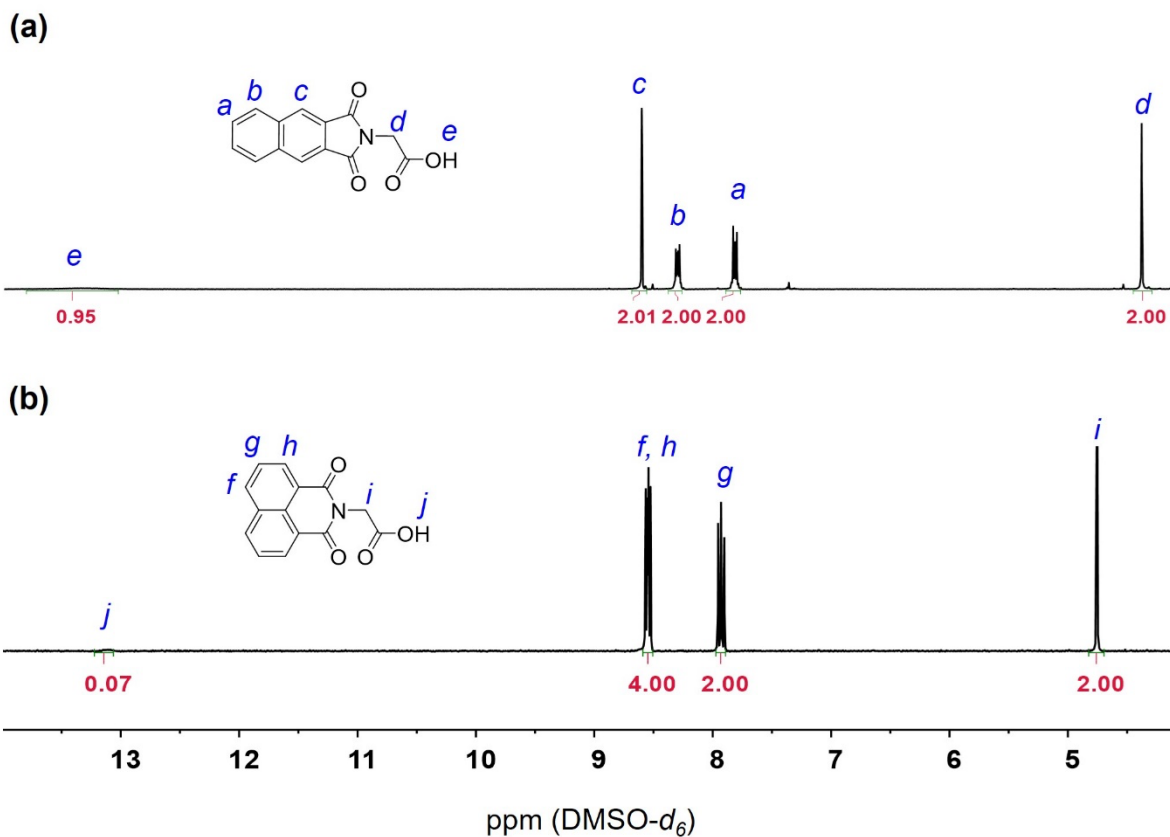| No. | Raw materials | Purpose | Weight (g) | |
|---|---|---|---|---|
| | | | w/o synergist | w/ synergist |
| 1 | Water | Solvent | 30 | 30 |
| 2 | Red 170 (Red F5RK) | Pigment | 25 | 25 |
| 3 | BYK190 | Dispersant | 15 | 15 |
| 4 | PG-based synergist | Synergist | – | 0.75 |
| 5 | CZY 0050 | Bead | 15 | 15 |
| | Total | | 70 | 70.75 |

**Figure S1.** $^1$H NMR spectra (DMSO, room temperature) of anchor molecules (a) (2-(1,3-dioxo-1,3-dihydro-2H-benzo[*f*]isoindol-2-yl)acetic acid) and (b) (2-(1,3-dioxo-1*H*-benzo[*de*]isoquinolin-2(3*H*)-yl)acetic acid). These anchors are denoted by $A_2$ and $A_3$.
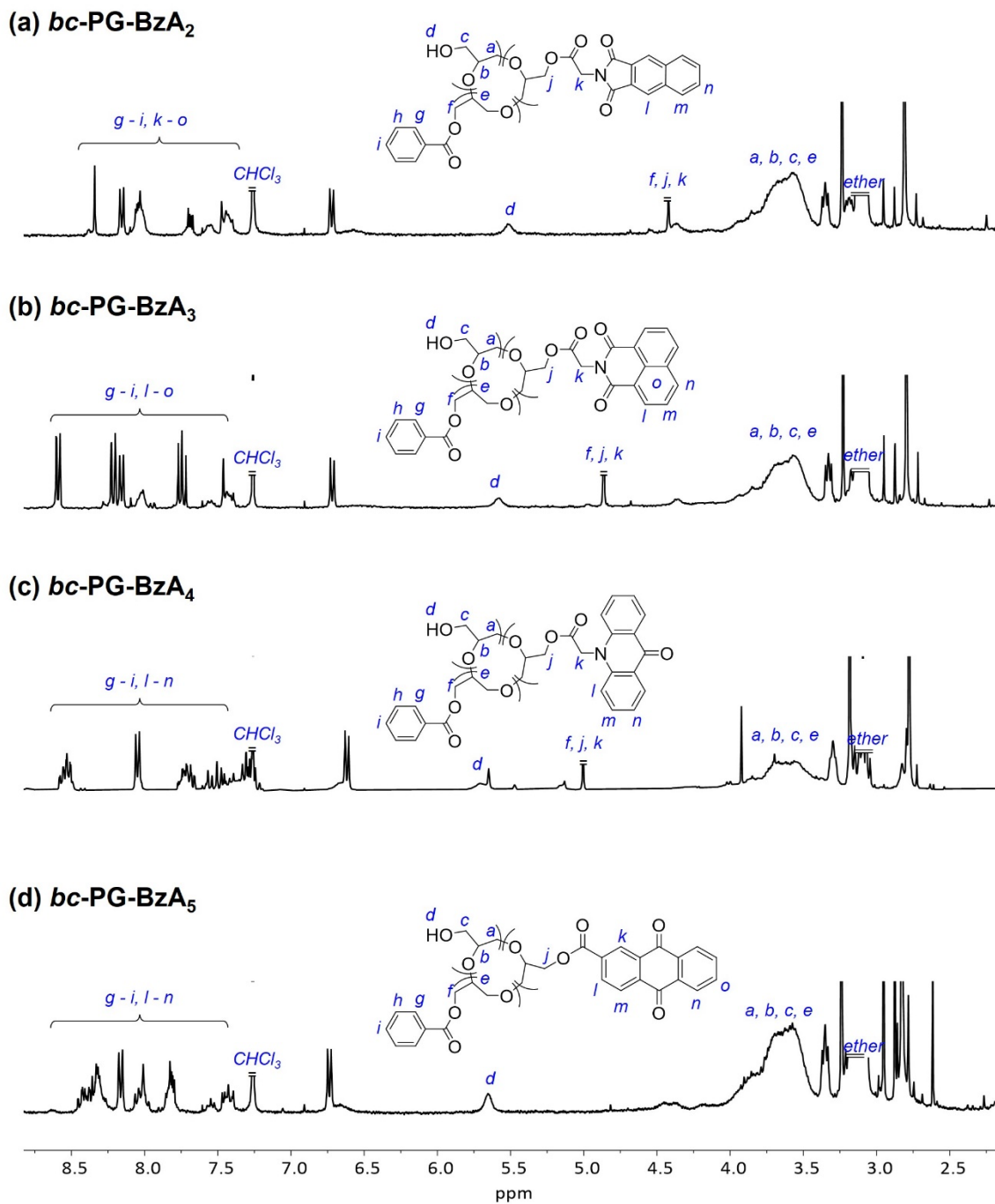
**Figure S2**. $^1$H NMR spectra in CDCl$_3$ of *bc*-PG synergists (a) *bc*-PG-BzA$_2$, (b) *bc*-PG-BzA$_3$, (c) *bc*-PG-BzA$_4$, and (d) *bc*-PG-BzA$_5$. The *bc*-PGSs were identically modified with benzoyl chloride and then functionalized with various anchor molecules.

Supporting Information

**Table S3.** Average size of pigment particles in dispersion[a]

| Entry | Dispersant | Synergist | Milling time[b] (h) | Viscosity (cps) | Average particle size[c] (nm) |
|---|---|---|---|---|---|
| 1 | BYK 190 | none | 12 | 152.4 | 312.9 |
| 2 | BYK 190 | $bc$-PG-BzA$_1$ | 6 | 103.5 | 305.6 |
| 3 | BYK 190 | $bc$-PG-BzA$_2$ | 6 | 171.1 | 320.2 |
| 4 | BYK 190 | $bc$-PG-BzA$_3$ | 6 | 246.6 | 324.1 |

[a]The particle size in dispersion was characterization by dynamic light scattering (DLS). [b]The optimized condition was determined by the milling time of sample with the lowest viscosity. [c]The average particle size was calculated by excluding maximum and minimum values from the experimental results obtained repeatedly.

Supporting Information

**Table S4.** Analysis of viscosity and particle size of pigment dispersions after storage for 5 days at 50 °C.

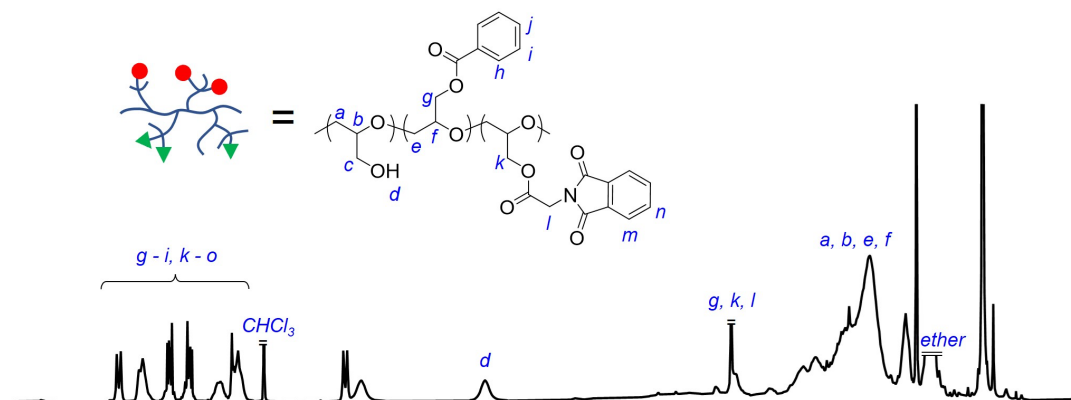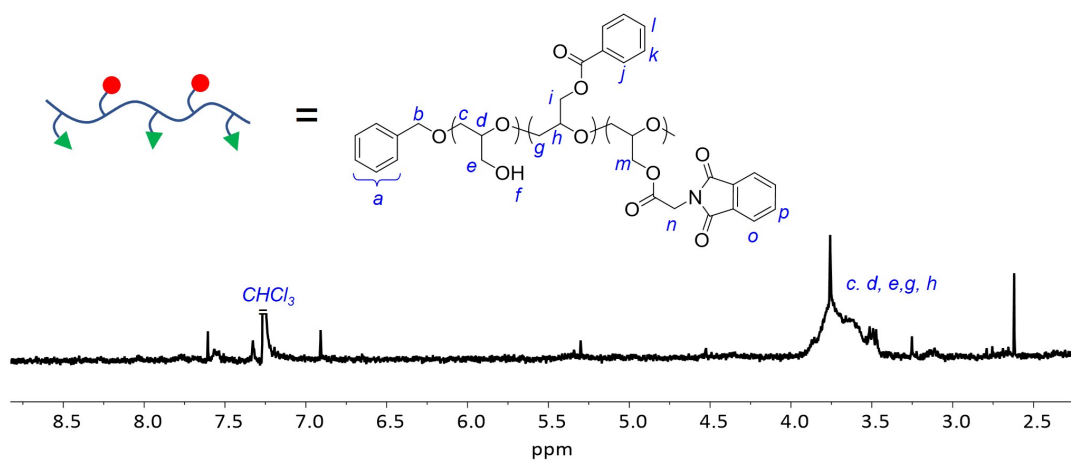| Entry | Dispersant | Synergist | Viscosity (cps) | Average particle size (nm) |
|-------|-----------|-----------|-----------------|----------------------------|
| 1 | BYK190 | None | 242.5 | 341.7 |
| 2 | BYK190 | $bc$-PG-BzA$_1$ | 189.5 | 318.5 |
| 3 | BYK190 | $bc$-PG-BzA$_2$ | 256.8 | 321.7 |
| 4 | BYK190 | $bc$-PG-BzA$_3$ | 153.0 | 319.4 |

**(a) *hb*-PG-BzA$_1$**



**(b) *lin*-PG-BzA$_1$**



**Figure S3.** $^1$H NMR spectra of the synthesized synergists with controlled topology in CDCl$_3$: a) *hb*-PG-BzA$_1$, b) *lin*-PG-BzA$_1$.

Supporting Information

**Table S5.** Analysis of dispersion viscosity at 6 h and after storage for 5 days at 50 °C.

| Entry | Dispersant | Synergist | Viscosity (6 h) (cps) | Viscosity (5 days) (cps) | Average particle size (nm) |
|---|---|---|---|---|---|
| 1 | BYK 190 | $bc$-PG-BzA$_1$ | 103.5 | 189.5 | 318.5 |
| 2 | BYK 190 | $hb$-PG-BzA$_1$ | 98.9 | 91.9 | 287.7 |
| 3 | BYK 190 | $lin$-PG-BzA$_1$ | 378.0 | 152.9 | 352.2 |