

# Hyperbranched Poly(aryl ester)s as Developer Materials for Thermal Printing System

Yeon-Im Jang, Won-Ho Choi, and Byeong-Kwan An\*

Department of Chemistry, The Catholic University of Korea, Gyeonggi-do 420-743, Korea. \*E-mail: bk.an@catholic.ac.kr  
Received December 19, 2012, Accepted January 30, 2013

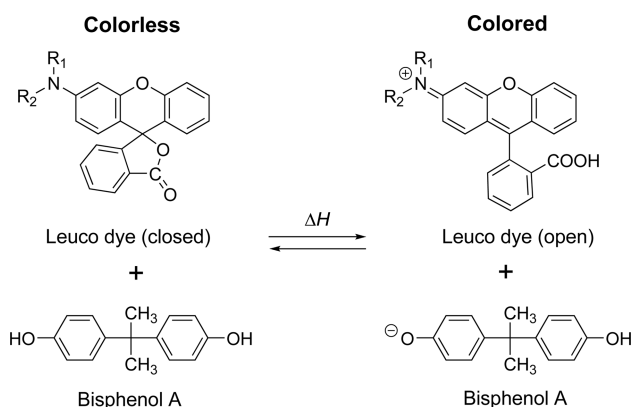
A novel class of hyperbranched polyesters, HPpEP and HPmEP, were prepared via a facile one-pot polymerization of a phloroglucinol (as a B<sub>3</sub> monomer) with a phthaloyl dichloride (as an A<sub>2</sub> monomer) for replacing a problematic BPA developer in thermal printing system. The resulting polymers, HPpEP and HPmEP, had highly branched structures and met well the requirements for high performance developer materials such as colorlessness, easy and inexpensive synthesis, high thermal stability, etc. In addition, these polymers exhibited an efficient reaction with leuco dyes (ODB-2) for a coloring process by releasing protons from linear and terminal phenol groups of polymers when heated.

**Key Words :** Thermal printing papers, Hyperbranched polymers, Leuco dyes, Developers, Bisphenol A

## Introduction

Thermal printing technology has been widely used in commercial applications for information recording paper systems such as point-of-sale receipts, industrial barcodes, faxes and many other types of labels because this technology is simple, rapid, inexpensive and highly reliable.<sup>1,2</sup> Thermal printing papers generally consist of a paper substrate and a color-forming layer which is impregnated with essential chemicals, a leuco dye and a developer, leading to color changes when exposed to heat.<sup>1-3</sup> Leuco dyes (fluoran derivatives) are basically colorless solids, but develop colors in presence of acidic developer materials and heat. This color-forming process involves the ring opening of lactone structure of fluoran on protonation by the weak acid developer and the transformation of colorless neutral fluoran structure to colored cationic fluoran structure accompanying with the extended conjugated double bond system (Figure 1).

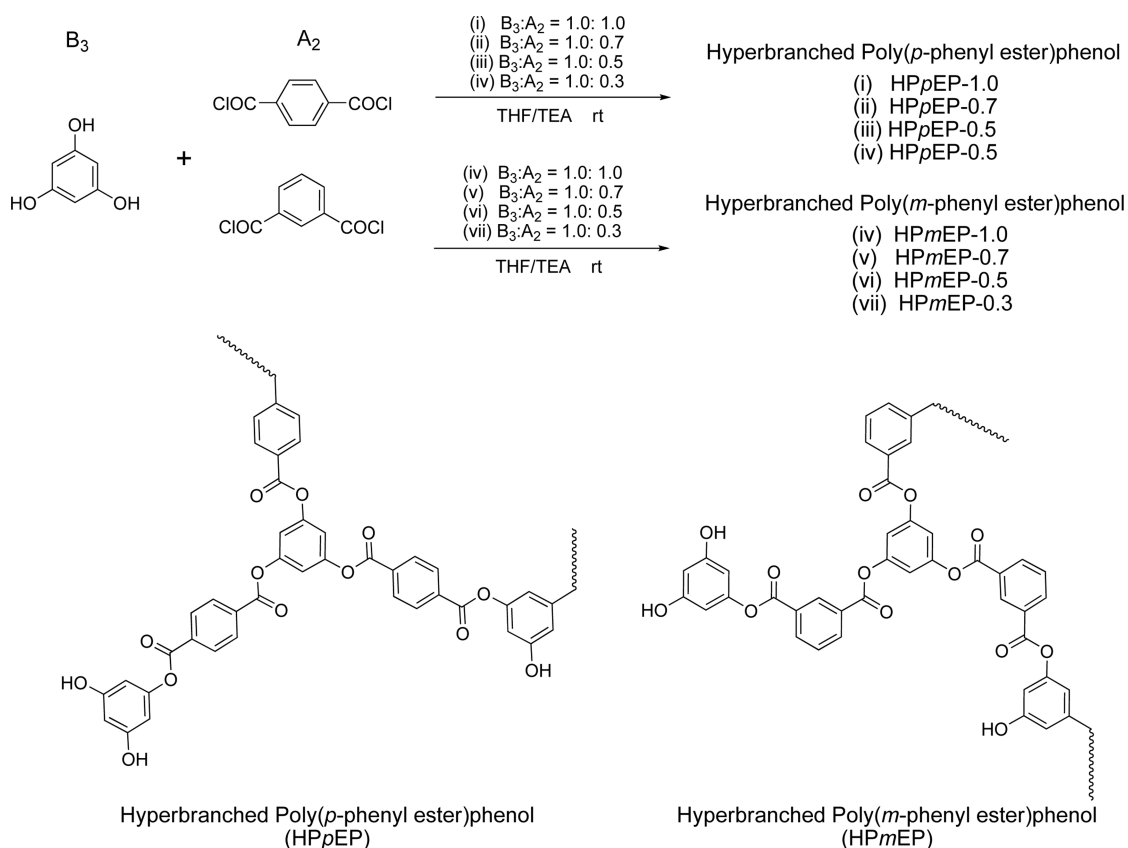
For a developer material which transfer protons to the leuco dye and trigger the color formation, bisphenol A (BPA) has been intensively used because it is available, affordable and efficacious.<sup>1-3</sup> In spite of many versatilities and advantages, however, recently the demands for reducing a BPA usage as a developer material have been considerably growing since the skin penetration/absorption of BPA can reach to 71 mg/day simply by holding thermal printing papers,<sup>4</sup> and BPA exposure can cause a horde of possible health problems such as heart disease, breast cancer, infertility, neuro-developmental disorders, etc.<sup>5</sup> So far several different types of developer materials, such as bisphenol F, bisphenol AP, bisphenol S and their other derivatives, have been introduced and utilized as BPA alternatives for thermal printing papers. But there is still questionable as to whether these BPA alternative materials solve the hazard issues of BPA owing to their structural similarity with BPA and small molecular weight which facilitates their transport into biological membranes.



**Figure 1.** Reversible color-formation reaction between leuco dye and bisphenol A (BPA).

In this regard the polymeric developer materials could be a promising alternative for overcoming the skin absorption problem of small molecular developer materials because high molecular weight molecules tend to be less mobile in biological and environment systems, and restrict their transport through biological membranes. Contrary to the conventional linear polymers, in particular, hyperbranched polymers could provide a better way to develop a new polymer developer material in that large numbers of active groups for reacting with leuco dyes are built three-dimensionally in space owing to their highly branched architectures,<sup>6</sup> which in turn facilitates the color-forming process. To the best of our knowledge, there is no report on hyperbranched polymer developer materials for thermal printing system.

In reality, however, it is challenge to develop new high-performance hyperbranched polymer developer materials for successfully replacing BPA alternatives because it is difficult to meet all the following various requirements; (i) ability to fully react with leuco dye when heated, (ii) colorlessness for no background imaging, (iii) low water solubility and solid morphology for homogeneous high-quality suspension, (iv) thermal stability at end use temperature, (v)



**Scheme 1.** Synthesis of hyperbranched poly(*p*- and *m*-phenyl ester)phenols, HPpEP and HPmEP, and possible molecular structures of HPpEP and HPmEP prepared by the mole ratio of  $A_2:B_3 = 1:1$ .

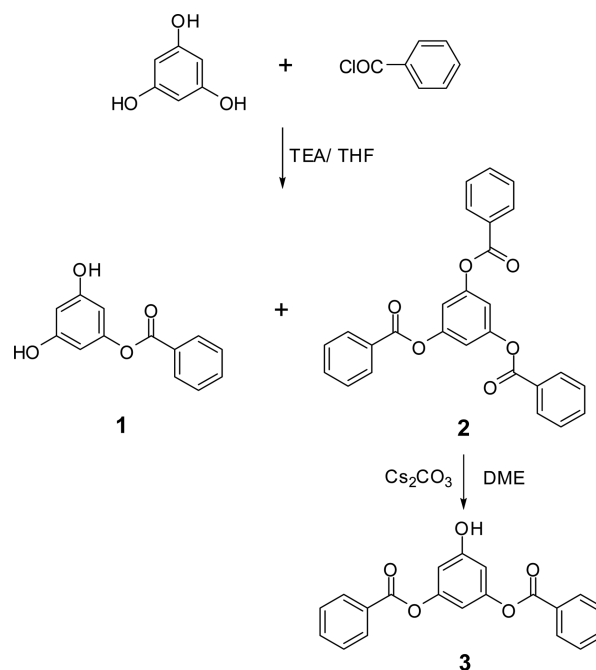
inexpensive synthesis for commercialization and feasibility in large-scale production, and (vi) low bioaccumulation hazard potential.

Herein we report a novel class of hyperbranched poly(phenyl ester)s with phenol groups as linear and terminal units (Scheme 1), HPpEP and HPmEP, prepared from a facile polycondensation reaction of  $A_2$  (*tere*- or *iso*-phthaloyl dichloride) and  $B_3$  (phloroglucinol) monomer. The prepared HPpEP and HPmEP exhibited an efficient reaction with leuco dyes for a coloring process (requirement (i)) and fulfilled all other above-mentioned requirements ((ii)-(vi)) for high-performance developer materials in thermal printing papers.

### Experimental

**Materials.** Phloroglucinol was purchased from Aldrich and was dried in a vacuum oven for 12 h. Cesium carbonate, benzoyl chloride, *tere*-phthaloyl dichloride, *iso*-phthaloyl dichloride, triethylamine and dimethoxyethane were purchased from Aldrich and used as received. Tetrahydrofuran (THF) was purchased from Aldrich, and was distilled from sodium/benzophenone before use. Bisphenol A and 2-anilino-6-dibutylamino-3-methylfluoran (ODB-2) were purchased from Aldrich and ChemPacific, respectively, and used as received.

**Characterization.**  $^1\text{H-NMR}$  spectra were recorded on



**Scheme 2.** Synthesis of model compounds (1-3).

Advance 300 (Bruker BioSciences Korea Co. Ltd.). All mass spectra of the model compounds, 1-3, were measured by mass spectrometry (EI method) carried out on a ELAN 6100 (Perkin Elmer (USA)). The UV/vis absorption spectra

were recorded on a Lambda 1050 (Perkin Elmer). Degradation temperatures ( $T_d$ ) and glass transition temperatures ( $T_g$ ) of the polymers were measured by thermogravimetric analysis (TGA) using a TGA 4000 (Perkin Elmer) and differential scanning calorimetry (DSC) using a DSC 4000 (Perkin Elmer), respectively. The characteristic functional groups of polymers were determined from FT-IR spectra (TENSOR27, Bruker).

**General Procedure for the Preparation of Hyperbranched Polymers.** To a mixture solution of dehydrated phloroglucinol ( $B_3$  monomers) and triethylamine (5 equivalent to  $B_3$  monomer) in anhydrous THF (150 mL), a solution of  $A_2$  monomer in anhydrous THF (50 mL) was added dropwise under vigorous stirring at 0 °C. The reaction was allowed to continue for additional 1 h at room temperature. The resulting solution was quenched by adding a diluted HCl (2 M, 30 mL). The precipitates were filtered, washed with water, and dried under vacuum.

**HPpEP-1.0:** white solids. Yield: 86%. FT-IR (ATR,  $\text{cm}^{-1}$ ): 3100 (OH, weak, br) and 1746 (C=O, strong).

**HPpEP-0.7:** white solids. Yield: 78%. FT-IR (ATR,  $\text{cm}^{-1}$ ): 3113 (OH, weak, br) and 1741 (C=O, strong).

**HPpEP-0.5:** white solids. Yield: 71%. FT-IR (ATR,  $\text{cm}^{-1}$ ): 3333 (OH, medium, br) and 1741 (C=O, strong).

**HPpEP-0.3:** white solids. Yield: 61%.  $^1\text{H-NMR}$  (500 MHz,  $\text{DMSO-}d_6$ )  $\delta$  10.16 (d,  $J=9$  Hz, 1H), 9.50 (d,  $J=4$  Hz, 2H), 8.29-8.83 (m, 4H), 7.48-7.51 (m, 3H), 6.73-6.85 (m, 3H), 6.15-6.18 (m, 3H); FT-IR (ATR,  $\text{cm}^{-1}$ ): 3114 (OH, weak, br) and 1736 (C=O, strong).

**HPmEP-1.0:** white solids. Yield: 80%. FT-IR (ATR,  $\text{cm}^{-1}$ ): 3119 (OH, weak, br) and 1741 (C=O, strong).

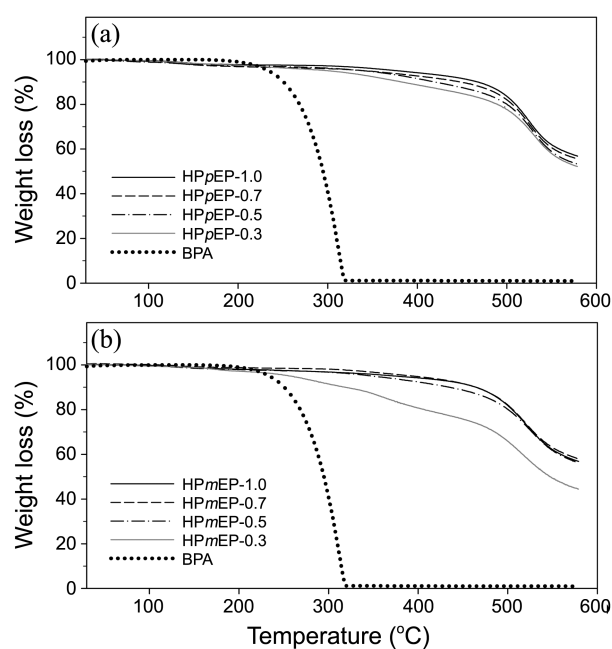
**HPmEP-0.7:** white solids. Yield: 77%. FT-IR (ATR,  $\text{cm}^{-1}$ ): 3115 (OH, weak, br) and 1741 (C=O, strong).

**HPmEP-0.5:** white solids. Yield: 62%. FT-IR (ATR,  $\text{cm}^{-1}$ ): 1746 (C=O, strong).

**HPmEP-0.3:** white solids. Yield: 82%.  $^1\text{H-NMR}$  (300 MHz,  $\text{DMSO-}d_6$ )  $\delta$  10.18 (s, 1H), 9.52 (s, 2H), 8.26-8.38 (m, 4H), 7.47-7.51 (m, 3H), 6.74-6.87 (m, 3H), 6.15-6.18 (m, 3H); FT-IR (ATR,  $\text{cm}^{-1}$ ): 3409 (OH, medium, br) and 1736 (C=O, strong).

#### Synthesis of the Model Compounds.

**Model Compound 1 (3,5-Dihydroxyphenyl benzoate) and 2 (1,3,5-Tribenzoyloxybenzene):** To a mixture solution of dehydrated phloroglucinol (0.50 g, 3.965 mmol) and triethylamine (2.7631 mL, 19.82 mmol) in anhydrous THF (150 mL), a solution of benzoyl chloride (0.46 g, 3.965 mmol) in anhydrous THF (50 mL) was added dropwise under vigorous stirring at 0 °C. The reaction was allowed to continue for additional 1 h at room temperature. The solvents were removed *in vacuo*, and quenched by adding a diluted HCl (2 M, 30 mL). The resulting precipitates were extracted with ethyl acetate (200 mL), washed with water (400 mL), and dried with anhydrous  $\text{MgSO}_4$ . The crude product **1** and **2** were separated and purified by silica column chromatography (ethyl acetate:hexane = 1:10 (v/v)) to give 0.12 g (yield = 25.1%) and 0.11 g (yield = 19.2%) and respectively, as white solids; The compound **1**:  $^1\text{H-NMR}$  (300



**Figure 2.** TGA traces for BPA, HPpEP and HPmEP at heating rate 20 °C/min in nitrogen.

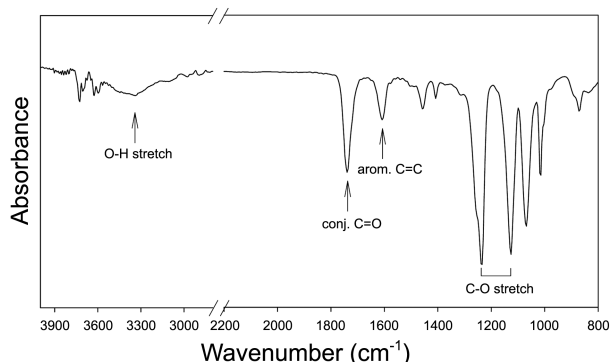
MHz,  $\text{DMSO-}d_6$ )  $\delta$  9.57 (s, 2H), 8.06-8.09 (m, 2H), 7.70-7.76 (m, 1H), 7.56-7.61 (m, 2H), 6.15 (s, 1H), 6.09 (s, 2H). EI-MS  $m/z$  calcd for  $\text{C}_{13}\text{H}_{10}\text{O}_4$  203.22, found: 230. Anal. Calcd. for  $\text{C}_{13}\text{H}_{10}\text{O}_4$ : C, 67.82; H, 4.38. Found: C, 67.76; H, 4.34.

The compound **2**:  $^1\text{H-NMR}$  (300 MHz,  $\text{DMSO-}d_6$ )  $\delta$  8.14-8.15 (m, 6H), 7.74-7.80 (m, 3H), 7.60-7.65 (m, 6H), 7.38 (s, 3H). EI-MS  $m/z$  calcd for  $\text{C}_{27}\text{H}_{18}\text{O}_6$  438.43, found: 438.

**Model Compound 3 (5-Hydroxy-1,3-phenylene dibenzoate).** Cesium carbonate (0.54 g, 1.66 mmol) was added to a solution of the compound **2** (0.45 g, 1.02 mmol) in dimethoxyethane (10 mL). After refluxing for 30 h, the mixture solution was filtered and the filtrate solvent was removed *in vacuo*. The resulting yellow residue was dissolved in diethyl ether (50 mL) and treated with water (50 mL) and an aqueous HCl (2 M, 30 mL). The solution mixture was extracted with diethyl ether (50 mL), washed with water (100 mL), and dried with anhydrous  $\text{MgSO}_4$ . The crude product was purified by silica column chromatography (ethyl acetate:hexane = 1:5 (v/v)) to give 0.086 g (yield = 25.1%) as a colorless liquid;  $^1\text{H-NMR}$  (300 MHz,  $\text{DMSO-}d_6$ )  $\delta$  10.24 (s, 1H), 8.10-8.16 (m, 4H), 7.72-7.78 (m, 2H), 7.58-7.63 (m, 4H), 6.73 (s, 1H), 6.65 (s, 2H). EI-MS  $m/z$  calcd for  $\text{C}_{24}\text{H}_{14}\text{O}_5$  334.32, found 334.

## Results and Discussion

In order to prepare the target polymers, HPpEP and HPmEP,  $A_2 + B_3$  polymerization method was employed because this approach generally provides a facile preparation and a highly branched structure compared to  $AB_2$  monomer system.<sup>6,7</sup> Phloroglucinol was chosen for the  $B_3$  monomer which acts branching units and reaction sites for leuco dyes



**Figure 3.** FT-IR spectrum (ATR mode) of HPpEP-0.5.

by releasing protons. *Tere*-phthaloyl dichloride was selected as  $A_2$  linking monomers reacting with a  $B_3$  monomer, and *iso*-phthaloyl dichloride was also used to probe the effect of molecular backbone position (*para* vs. *meta*) of  $A_2$  linkers on the developing capability of the resulting hyperbranched polymers. It is noteworthy that, unlike other complex hyperbranched polymer systems, the chosen  $A_2$  and  $B_3$  monomers are not only commercially-available cheap chemicals, but also provide a facile one-pot polymerization process owing to the known high reactivity of acyl chloride groups towards esterification with phenols, which could expedite the commercial availability and mass production of the polymers (fulfillment of the requirement for (v) mentioned the above).

The synthesis of the HPpEP and HPmEP was simply carried out by a one-pot polycondensation reaction of  $A_2$  and  $B_3$  monomers in the mixture solution of triethylamine (TEA) and tetrahydrofuran (THF) at varying the feed ratio of  $A_2$  monomers without any catalysts and heating. In addition, the polymerization was conducted under the slow monomer addition in order to avoid the statistically inevitable gelation of an  $A_2 + B_3$  system due to cross-linking.<sup>6,7</sup>

All polymers were obtained with high yields (61-86%) in the form of white powders and were insoluble in water (fulfillment of the requirement for (ii) and (iii), respectively). In terms of  $pK_a$  (proton dissociation), it is assumed that HPpEP and HPmEP have lower  $pK_a$  values compared to BPA because the phenol units in polymers are linked with electron-withdrawing carbonyl groups (-OOC-) which enhance the acidity (or decrease of  $pK_a$ ) due to the induction and mesomeric effects.

Owing to the rigid aromatic macromolecular backbones, the obtained polymers had superior thermal properties to BPA. Figure 2 shows that both HPpEP and HPmEP have a high thermal decomposition temperature ( $T_d$ ) (5% weight loss) in the range of 257-394 °C (Table 1) (fulfillment of the requirement for (iv)). Interestingly it was seen that the de-

composition temperature of both polymers are gradually decreased as the portion of  $A_2$  monomers decrease (1.0  $\rightarrow$  0.7  $\rightarrow$  0.5  $\rightarrow$  0.3). This is mainly attributed to the molecular weights of polymers, that is, higher molecular weight polymers exhibit a better thermal property. As the ratio of  $A_2$  monomer decreases, the molecular weight of polymers should be decreased owing to the short supply of  $A_2$  monomers in the system of  $A_2 + B_3$  hyperbranched polymers. In addition, no glass transition temperature ( $T_g$ ) and other thermal transitions were observed in DSC measurements of HPpEP and HPmEP due to the chain stiffness.

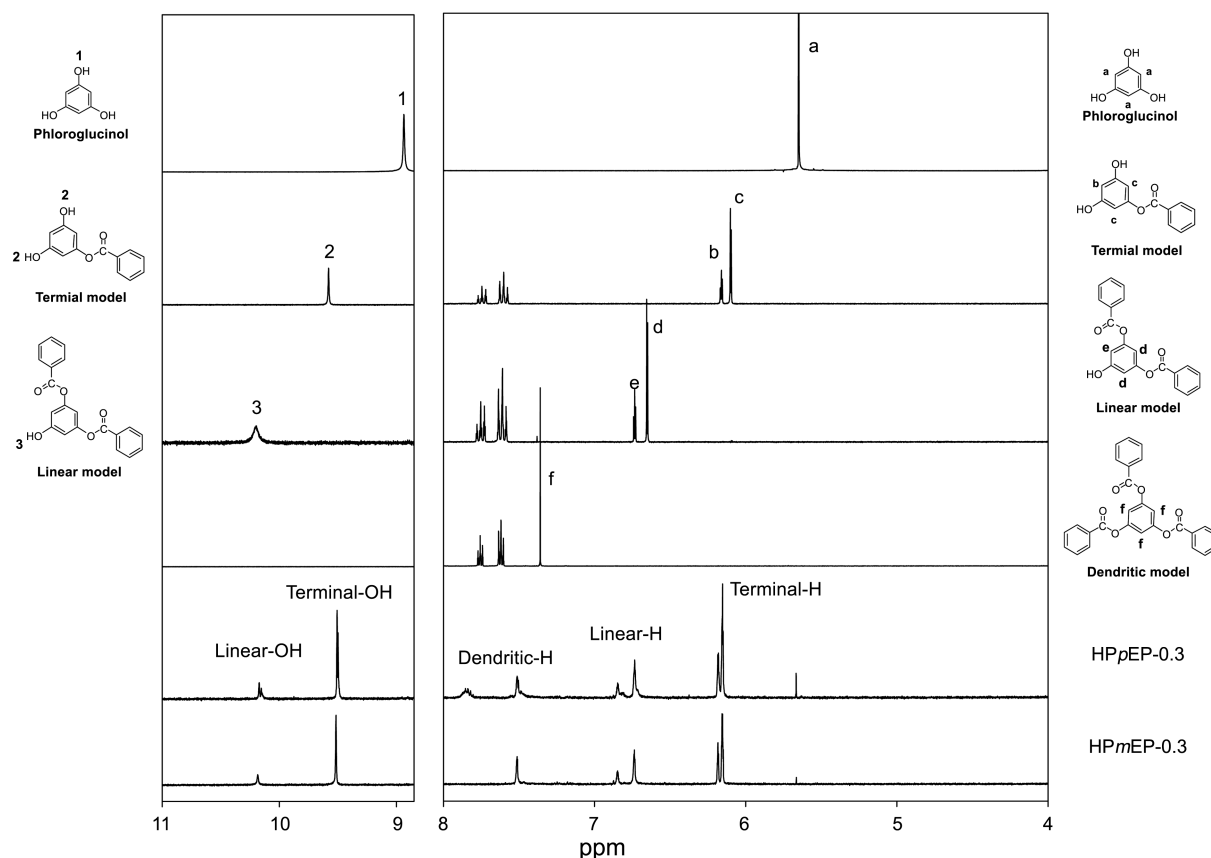
The resulting polymers exhibited a poor solubility in common organic solvents such as ethanol, *n*-hexane, chloroform, and *N,N'*-dimethylformamide (DMF), probably because of the rigid backbone and partial cross-linking, which limits the measurement for molecular weights by gel permeation chromatography (GPC). However, the poor solubility of the polymers in organic solvents brings about no problems against practical applications for thermal printing papers since the developer polymer powders are to be grinded with very fine particles without a dissolving process, and then suspended in water together with leuco dyes, binders and other ingredients for coating on the paper substrates. Instead, this poor solubility both in water and organic solvents could decrease a bioaccumulation potential of polymers upon contacting thermal printing papers because the conglomerate particles consisting of insoluble large size polymer chains cause the difficult transportation through biological membranes (fulfillment of the requirement for (vi)).

The structure of the HPpEP and HPmEP was characterized by Fourier transform infrared (FT-IR) and  $^1H$  NMR measurements. From FT-IR spectrum analysis, the characteristic absorption bands of the polymers were found at around 3340 and 1740  $cm^{-1}$  from hydroxyl (-OH) groups of phenols and ester (-COO-) groups of linkers, respectively (Figure 3). In order to verify the hyperbranched structure, the model compounds, **1-3**, for terminal, dendritic, and linear units of hyperbranched polymer structures, respectively, were newly synthesized (Scheme 2) and  $^1H$  NMR peaks of the model compounds were investigated with those of HPpEP and HPmEP. For this purpose,  $^1H$ -NMR spectra of HPpEP-0.3 and HPmEP-0.3 were characterized in detail because these polymers were very soluble in dimethyl sulfoxide (DMSO) contrary to the other polymers, and could provide an insight into the information on the degree of branching (DB) for the initial state of HPpEP and HPmEP.

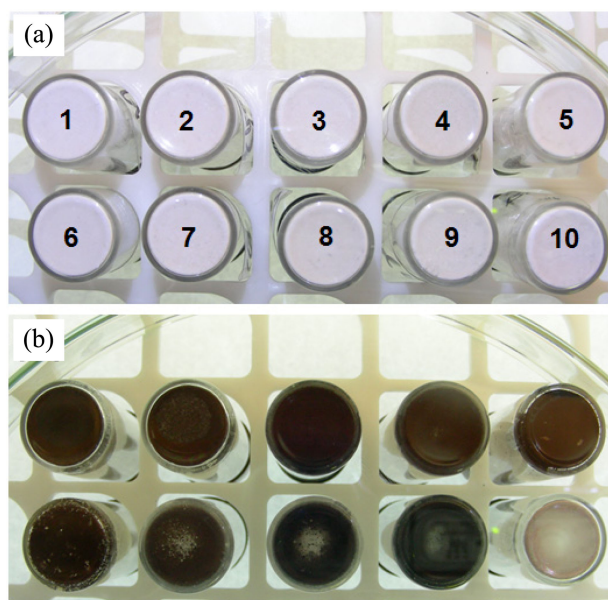
Figure 4 shows the assignment of  $^1H$ -NMR resonances of hydrogens in terminal, linear, and dendritic units of HPpEP-0.3 and HPmEP-0.3. On the basis of  $^1H$ -NMR peaks for model compounds, the proton peaks at around 7.53, 6.86-

**Table 1.** Thermal properties of HPpEP and HPmEP

	BPA	HPpEP				HPmEP			
		1.0	0.7	0.5	0.3	1.0	0.7	0.5	0.3
Temperature of 5% decomposition (°C)	234	379	342	340	301	375	394	349	257



**Figure 4.**  $^1\text{H-NMR}$  spectra of hyperbranched poly(phenyl ester)phenols (HPpEP-0.3 and HPmEP-0.3), phloroglucinol and model compounds as a terminal units (compound 1), a dendritic unit (compound 3), and a linear unit (compound 2) in DMSO- $d_6$ .



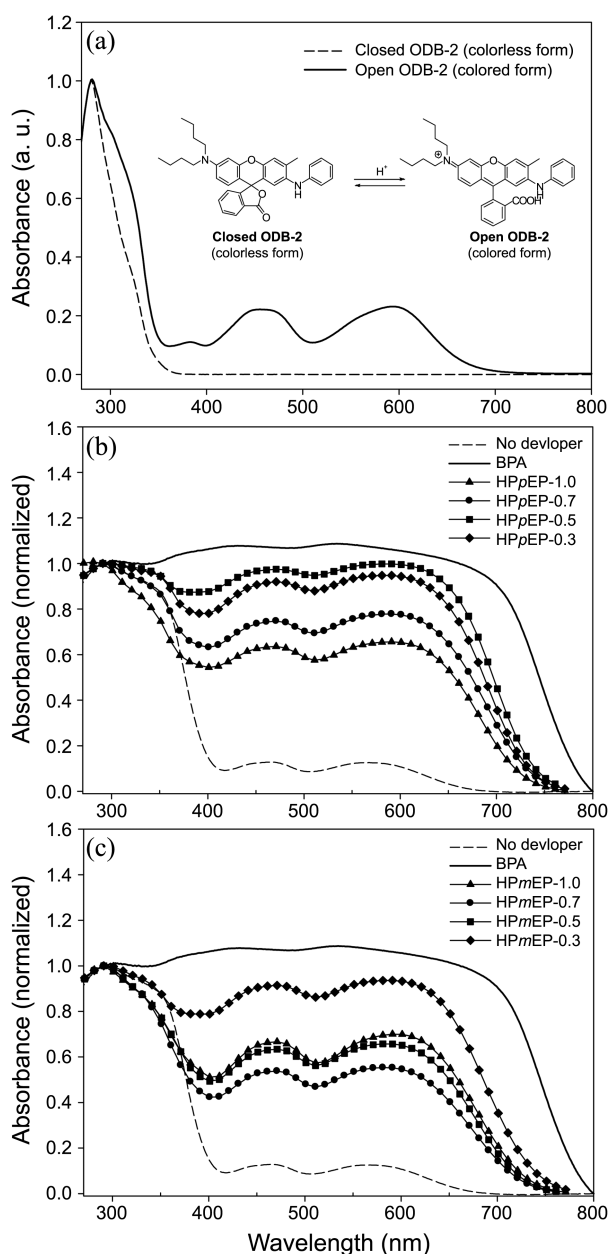
**Figure 5.** Photos of (a) mixtures of octadecanol (binder, 100 mg), leuco dye (ODB-2) (10 mg), and developer compounds (20 mg) in vial bottle and (b) their molten mixtures after heating treatment at 80 °C for 15 sec. The sample 1-4 contain HPpEP-1.0, HPpEP-0.7, HPpEP-0.5, HPpEP-0.3 as developer materials, respectively, and the sample 6-9 contain HPmEP-1.0, HPmEP-0.7, HPmEP-0.5, HPmEP-0.3 as developer materials, respectively. In the sample 5, BPA is added for a developer material, whereas there is no developer material in the sample 10.

6.74, and 6.18-6.14 ppm in HPpEP-0.3 and HPmEP-0.3 were assigned to dendritic, linear, and terminal units of hyperbranched polymers, respectively. More importantly, phenolic protons of the linear and terminal units were shown at 10.24 and 9.60 ppm, respectively, whereas the characteristic peak of phenolic protons from phloroglucinol ( $B_3$ ) monomers was not observed in the  $^1\text{H-NMR}$  spectrum of HPpEP-0.3 and HPmEP-0.3.

To better define the branching structures of HPpEP-0.3 and HPmEP-0.3, the degree of branching (DB) of these polymers were calculated using the following Eq. (1).<sup>8</sup>

$$\text{DB} = \frac{(D + T)}{(D + T + L)} \quad (1)$$

where D, T, and L refer to the numbers of dendritic, terminal, and linear units in the hyperbranched polymers, respectively. The DB is often used as an indicator of the amount of branching, where linear polymers have a DB = 0 and dendrimers have a DB = 1. It was found that the calculated DB of HPpEP-0.3 and HPmEP-0.3 are 0.72 and 0.69, respectively, which is relatively high value compared to the DB (around 0.5-0.6) for general hyperbranched polymers prepared by a one-pot procedure.<sup>9,10</sup> Taken all together, it is concluded that highly branched structures having linear and terminal units of phenols are constructed *via* an esterification reaction between phloroglucinol ( $B_3$ ) and *tere-/iso*-phthaloyl dichloride ( $A_2$ ) monomers from the early stage of polymeri-



**Figure 6.** UV/vis absorption spectra. (a) Closed-ring and opening ODB-2 dye in DMF solution. The lactone ring of ODB-2 is open by adding of a drop of HCl (2M). (b) and (c) The molten mixtures of octadecanol (100 mg), ODB-2 dye (10 mg), and various developer compounds (20 mg) (BPA, HPpEP, and HPmEP) onto the glass substrates after heating treatment at 80 °C for 10 sec.

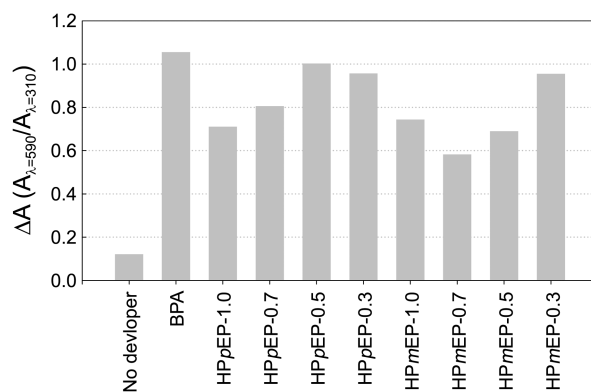
zation.

In order to test a color-formation reaction of the resulting hyperbranched polymers with leuco dye, the mixture samples containing 20 mg of each hyperbranched polymers, 10 mg of leuco dye (2-anilino-6-dibutylamino-3-methylfluoran (ODB-2)), and 100 mg of octadecanol as a binder, were prepared and their optical property changes upon heating treatments were investigated by UV/vis absorption and FT-IR spectroscopy. At the same time the developing capability of hyperbranched polymers were also compared with that of

conventional BPA developers. The prepared mixtures showed white color, but their color was immediately changed into black upon heating at 80 °C for 15 sec (Figure 5), which indicates that the ODB-2 dyes undergo a structural change from closed-lactone form to open-lactone form to produce a black color by releasing protons from developer materials when heated (Figure 1 and 6(a) inset). This color forming reaction was clearly determined by UV/vis absorption study.

Figure 6(a) shows UV/vis absorption spectra of closed and open ODB-2 dyes in DMF. The open ODB-2 dyes developed by HCl exhibited new absorption bands at 450 and 590 nm, enabling black color formation, which are resulted from an extension of the conjugated double bond and charge-transfer band between the electron-donor ( $-\text{NH}-\text{ph}$ ) and electron-acceptor ( $=\text{N}^+$ ), respectively. It was shown that these new strong absorption bands are also observed in the molten mixtures with developers (HPpEP, HPmEP, and BPA) after heating (Figure 6(b) and (c)), however, the molten mixtures without a developer have very weak absorption bands at 450 and 590 nm. This result indicates that the developer materials efficiently transfer protons from phenol units to the ODB-2 dyes upon heating and trigger lactone ring opening of ODB-2 dye molecules leading to the corresponding color formation. Lactone ring opening of ODB-2 dyes was further confirmed by the FT-IR spectrum. A sharp lactone absorption band around  $1747\text{ cm}^{-1}$  was disappeared in the IR spectrum of the molten ODB-2 mixtures with developer materials.

The black color-forming capability of various developer polymers including a BPA was examined by monitoring the absorbance ratio ( $\Delta A$ ) of  $\lambda_{\text{max}} = 590\text{ nm}$  (charge-transfer band (CT)) to  $\lambda_{\text{max}} = 310\text{ nm}$  ( $\pi-\pi^*$  transition band) for the molten mixtures of octadecanol (100 mg), ODB-2 dye (10 mg), and various developer compounds (20 mg) onto the glass substrates after heating treatment at 80 °C for 10 sec (Figure 7). It is implied that, as the value of  $\Delta A_{590\text{nm}/310\text{nm}}$  increases, the color formation reaction is increased because the CT absorption band at 590 nm is generated only the formation of the black-colored ODB-2 structures by releasing protons from developer materials. As expected, the



**Figure 7.** The absorbance ratio ( $\Delta A$ ) of  $\lambda_{\text{max}} = 590\text{ nm}$  to  $\lambda_{\text{max}} = 310\text{ nm}$  for the molten mixtures of octadecanol (100 mg), ODB-2 dye (10 mg), and various developer compounds (20 mg) onto the glass substrates after heating treatment at 80 °C for 10 sec.

molten mixture with a BPA had a very high value of  $\Delta A_{590\text{nm}/310\text{nm}}$  (1.06), but not the molten mixture without a developer ( $\Delta A_{590\text{nm}/310\text{nm}} = 0.12$ ). Importantly, the prepared all polymers exhibited a value of  $\Delta A_{590\text{nm}/310\text{nm}}$  in the range of 0.58-1.00 regardless of *para* and *meta*-positioned structures. Especially, HP*p*EP-0.5, HP*p*EP-0.3 and HP*m*EP-0.3 had much higher values of  $\Delta A_{590\text{nm}/310\text{nm}}$  (0.96-1.00), which is almost compatible with the value of BPA, than other polymers probably because these polymers had lower molecular weights, and therefore, exhibited a better solubility in octadecanol upon heating which leads to the enhanced proton transfer to the adjacent Leuco dye molecules in the molten mixtures.

### Conclusion

We report herein a novel class of hyperbranched polymer developers, HP*p*EP and HP*m*EP, for thermal printing papers in order to replace the conventional BPA developers. A series of HP*p*EP and HP*m*EP were synthesized without a gelation *via* a one-pot polymerization of phloroglucinol (as a B<sub>3</sub> monomer) and phthaloyl dichloride (as an A<sub>2</sub> monomer). <sup>1</sup>H-NMR study of model compounds and polymers revealed that highly branched structures (DB  $\approx$  0.70) were constructed from the early stage of polymerization. The different linking position (*p*- and *m*-) of hyperbranched polymers has a little effect on the structural, thermal and developing properties of

HP*p*EP and HP*m*EP. All the prepared polymers met well the requirements for high performance developer materials such as colorlessness, easy and inexpensive synthesis, high thermal stability, *etc.* Especially, HP*p*EP-0.5, HP*p*EP-0.3 and HP*m*EP-0.3 exhibited a compatible developing capability with BPA.

**Acknowledgments.** This research was supported by the research fund from Small & Medium Business Administration (SA113254). This work was supported by the Catholic University of Korea, Research Fund (M-2010-B0002-00163), 2010.

### References

1. Muthyala, R. *Chemistry of Applications of Leuco Dyes*; Plenum Press: New York, U.S.A., 1997.
2. Zollinger, H. *Color Chemistry*; Wiley-VCH: Weinheim, Germany, 2003.
3. Endo, K.; Fujita, I.; Kobayasi, N. *Anal. Sci.* **1991**, *7*, 785.
4. Biedermann, S.; Tschudin, P.; Grob, K. *Anal. Bioanal. Chem.* **2010**, *398*, 571.
5. Myers, J. P. *et al. Environ Health Perspect.* **2009**, *117*, 309.
6. Gao, C.; Yan, D. *Prog. Polym. Sci.* **2004**, *29*, 183-275.
7. Zhang, X. *Prog. Org. Coat.* **2010**, *69*, 295.
8. Lin, Q.; Long, T. E. *Macromolecules* **2003**, *36*, 9809.
9. Hult, A.; Johansson, M.; Malmstrom, E. *Adv. Polym. Sci.* **1999**, *143*, 1.
10. Murali, M.; Samui, A. B. *J. Polym. Sci. Part A: Polym. Chem.* **2006**, *44*, 53.