

Synthesis of a Branched Poly(phenylene ethylene) with Bromomethyl Groups as an Organosoluble and Functional Parylene

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ABSTRACT: We synthesized a branched poly(phenylene ethylene) (BPPE) with bromomethyl groups from 1,3,5-tris(bromomethyl)benzene derivatives via the Wurtz coupling reaction. In the case of 1,3,5-tris(bromomethyl)-2,4,6-trimethoxybenzene as a monomer, the obtained polymer ($M_n = 6100$, $M_w/M_n = 1.9$) had bromomethyl groups. The $^1\text{H NMR}$ analysis showed that a very large number of unreacted bromomethyl groups ($\text{Ph-CH}_2\text{Br}$) remained in the BPPE; the reaction of this polymer with phenolic

hydroxyl groups proceeded quantitatively. This suggested that BPPEs can be functionalized using unreacted bromomethyl groups, making them a very attractive starting point for the creation of functionalized BPPEs with further enhanced processability. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 2775–2780, 2012

Key words: poly(phenylene ethylene); parylene, Wurtz coupling; branched polymer; functional polymer

INTRODUCTION

Among a large number of currently available hydrocarbon polymers, poly(*p*-xylylene) (PPX),^{1–6} which is commercially known as Parylene, has several attractive material properties, and being the only industrial representative of the poly(*p*-phenylene alkylene)⁷ family, it has attracted significant attention from both the synthetic and the material viewpoints. PPX coatings are usually formed by chemical vapor deposition (CVD) polymerization of *p*-xylylene (Scheme 1)^{1–3} and are known for their good conformality and uniformity in thickness. PPX is hydrophobic and has an attractively low dielectric permittivity. Moreover, PPX has excellent thermal and mechanical stability, good solvent resistance, high crystallinity, and the best bulk barrier properties among organic polymeric coatings.⁸ Fluorinated PPX is also widely used in various applications because of its low dielectric constant.⁹

One significant drawback of PPX is its insolubility in most solvents, even at elevated temperatures. This drawback prevents its use in solvent-based coatings and, further, makes it impossible to cast it into films

or spin it into fibers from solution. Several conceivable approaches to synthesize polymers analogous to PPX [for example, poly(*p*-phenylene ethylene) (PPE)] but with enhanced processability have been proposed and investigated. For example, a random PPX polymer with organosolubility has been reported.¹⁰

It is well known that branched polymers have markedly lower crystallinities and higher solubilities than the corresponding linear polymers of similar molecular weight^{11–13}; hence, these macromolecules can be easily functionalized.^{14,15} However, to the best of our knowledge, successful synthesis of branched poly(phenylene ethylene) (BPPE) has not yet been reported. BPPEs are expected to exhibit outstanding processability as well as unique properties of PPX. Here, we report the syntheses of BPPEs by Wurtz coupling and describe their applicability as functional polymers. To prepare an organosoluble BPPE and to control its polymer structure, polymerization must be carried out under mild conditions. Hence, it becomes difficult to simply adapt the procedures used for the synthesis of PPE, such as chemical vapor deposition (CVD). Here, we show that polymerization via Wurtz coupling is the best possible method for the synthesis of BPPEs (Scheme 2).

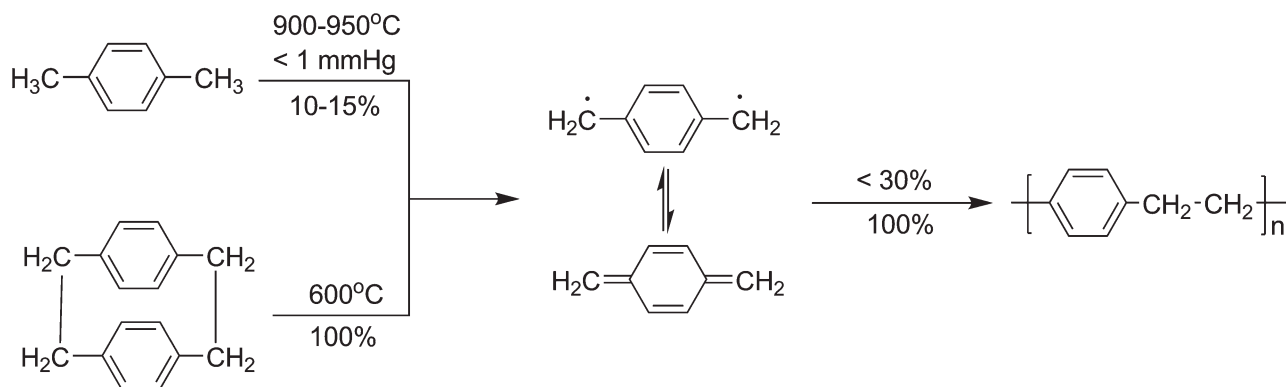
EXPERIMENTAL

General

Unless otherwise noted, all reagents and chemicals were used without further purification. Paraformaldehyde (95%) and magnesium (for Grignard reagent

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Scheme 1 Synthesis of poly(*p*-phenylene ethylene) by chemical vapor deposition (CVD).

grade) were obtained from Nacalai. 1,3,5-Tris(bromomethyl)benzene **1** and 1,3,5-Tris(bromomethyl)-2,4,6-trimethylbenzene **2** were purchased from Aldrich. All the $^1\text{H-NMR}$ spectra (in CDCl_3-d_1) and the $^{13}\text{CNMR}$ spectra (in CDCl_3-d_1) were recorded by a 400 MHz JEOL LNM-EX400 instrument with tetramethylsilane (TMS) as the internal standard. The FT-IR spectra were recorded using a JASCO FT-IR 460 plus spectrometer. Gel permeation chromatography (GPC) was carried out by a JASCO UV-2070 detector and a JASCO RI-2031 detector (TOSOH TSKgel G3000H_{XL} or G4000H_{XL} column) using tetrahydrofuran (THF) as the eluent after calibration with polystyrene standards. The flow rate and column temperature were 1.0 mL/min and 25°C, respectively. Thermogravimetric analysis (TGA) was performed using a SII TG/DTA 6200 (SEIKO) with a heating rate of 10°C/min under a nitrogen atmosphere. Differential scanning calorimetry (DSC) was carried out on a SII DSC 6220 at a heating rate of 5°C/min under a nitrogen atmosphere. The solution property of the polymer in a diluted THF solution was examined by a SEC-VISC-RALLS system (Viscotek). The flow rate and column temperature were 1.0 mL/min and 40°C, respectively.

General procedure of branched polymer (BPPE)

Dry THF and I_2 crystals with magnesium tubing (or sodium solid) were added to a flask under an argon atmosphere at ambient temperature. The dry THF solution of monomer was added dropwise to the mixture. The resulting suspension was refluxed for several hours. After cooling to room temperature, the resulting solution was slowly decomposed by the dropwise addition of 10% aqueous HCl. The mixture was diluted

with chloroform and the organic layer was separated. The obtained solution was concentrated under reduced pressure. The obtained polymer was dissolved in minimum volume of THF and then reprecipitated in methanol. The obtained precipitate was dried *in vacuo* to yield the corresponding branched polymer.

Polymer 4

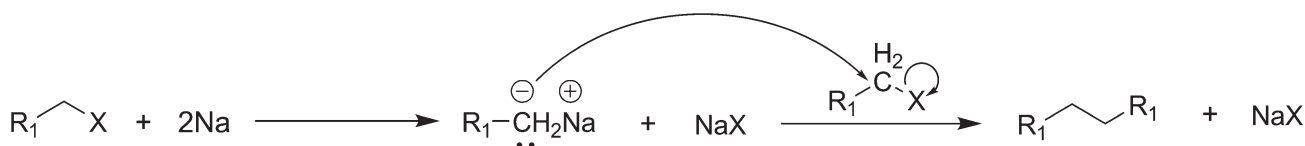
From 1,3,5-Tris(bromomethyl)benzene **1** (0.18 g, 0.50 mmol), Mg (0.036 g, 1.5 mmol), I_2 (30 mg, 0.12 mmol), dry THF (2.5 mL). Yield 31%; $M_n = 2800$, $M_w = 6100$, $M_w/M_n = 2.2$; $^1\text{HNMR}$ (CDCl_3 , 400 MHz, ppm) δ 7.04-6.55 (Ph-H), 4.56-4.20 (Ph- CH_2Br), 2.99-2.58 (Ph- $\text{C}_2\text{H}_4\text{-Ph}$), 2.39-2.02 (Ph- CH_3), peak at 1.5 ppm is water; $^{13}\text{CNMR}$ (CDCl_3 , 100 MHz, ppm) δ 138.1-135.4, 134.0-131.4, 31.5-29.4, 17.5-15.1; IR (KBr, cm^{-1}) $\nu = 3010, 2920, 2860, 1600, 1460, 1210, 1160, 1100$.

Polymer 5

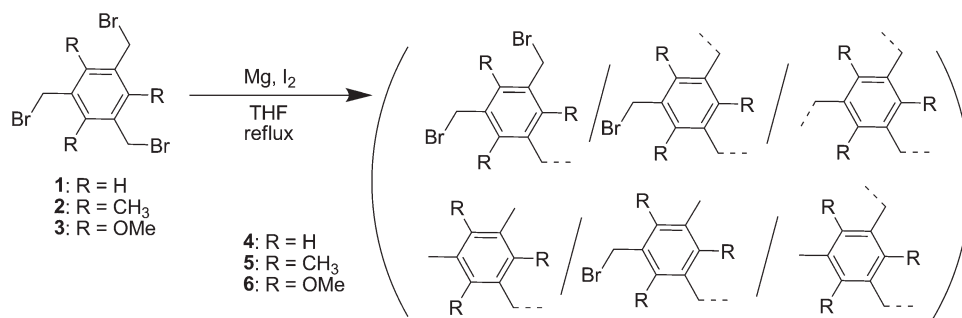
From 1,3,5-Tris(bromomethyl)-2,4,6-trimethylbenzene **2** (0.20 g, 0.50 mmol), Mg (0.036 g, 1.5 mmol), I_2 (30 mg, 0.12 mmol), dry THF (2.5 mL). Yield 37%; $M_n = 2400$, $M_w = 4400$, $M_w/M_n = 1.9$; $^1\text{H-NMR}$ (CDCl_3 , 400 MHz, ppm) δ : 4.68-4.22 (Ph- CH_2Br), 3.10-2.67 (Ph- $\text{C}_2\text{H}_4\text{-Ph}$), 2.67-1.88 (Ph- CH_3); $^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz, ppm) δ 139.8-135.4, 133.8-131.6, 31.3-29.4, 17.5-15.1; IR (NaCl, cm^{-1}) $\nu = 2960, 2920, 1450, 1380, 1150, 1100, 1020$.

1,3,5-Tris(bromomethyl)-2,4,6-trimethoxybenzene 3

HBr was added (33% in HOAc, 12 mL) to a solution of 1,3,5-trimethoxybenzene (1.86 g, 11 mmol), para-formaldehyde (95%) (1.25 g, 42 mmol), and glacial



Scheme 2 Synthesis of poly(*p*-phenylene ethylene) by Wurtz coupling reaction.



Scheme 3 Synthesis of a branched poly(phenylene ethylene).

acetic acid (5 mL) in a sealed tube, and the resulting solution was stirred for 1 h. The solution was then heated at 70°C for 3 h in the sealed tube. After cooling to room temperature, the reaction mixture was poured into water (150 mL) and the obtained precipitate was dissolved in CH₂Cl₂. The organic layer was separated and the aqueous layer was extracted with CH₂Cl₂. All organics were combined and washed sequentially with saturated aqueous solution of NaHCO₃, water, and brine. The obtained solution was concentrated *in vacuo* to obtain the crude product as an orange oil. Further purification was carried out by chromatography on silica gel using hexane/chloroform (2 : 3) to afford **3** (1.22 g, 24%) as a colorless solid. ¹H-NMR (CDCl₃, 400 MHz, ppm) δ 4.15 (s, 9H), 4.60 (s, 6H); ¹³CNMR (CDCl₃, 100 MHz, ppm) δ 160.0, 123.2, 62.6, 22.4; IR (NaCl, cm⁻¹) ν = 3050, 2990, 2950, 2840, 1580, 1460, 1410, 1220, 1150, 1090, 1000.

Polymer 6

From 1,3,5-Tris(bromomethyl)-2,4,6-trimethoxybenzene **3** (0.18 g, 0.41 mmol), Mg (0.030 g, 1.2 mmol), I₂ (24 mg, 0.096 mmol) dry THF (2 mL). Yield 67%; $M_n = 6100$, $M_w = 11700$, $M_w/M_n = 1.9$; ¹HNMR (CDCl₃, 400 MHz, ppm) δ 5.02-4.46 (Ph-CH₂Br), 4.46-3.56 (Ph-OCH₃), 3.32-2.97 (Ph-C₂H₄-Ph), 2.24-2.09 (Ph-CH₃); ¹³CNMR (CDCl₃, 100 MHz, ppm) δ 158.2-155.8, 126.9-124.5, 63.1-59.6, 26.7-24.8, 9.96-9.27; IR (NaCl, cm⁻¹): ν = 3010, 2940, 2830, 1580, 1460, 1410, 1200, 1160, 1010, 994.

Reaction of 6 with phenol

A THF solution (5 mL) of polymer **6** (15 mg, 0.05 mmol), phenol (0.14 g, 1.5 mmol), and K₂CO₃ (0.21 g, 1.5 mmol) was stirred and refluxed for two days. The resulting mixture was filtered to remove the salts. The resulting solution was evaporated under reduced pressure. The obtained residue was dissolved in CH₂Cl₂ and sequentially washed with 10% aqueous NaOH (2 × 50 mL) and water (50 mL). The organic layer was dried over MgSO₄. After the re-

moval of the solvent, the residue was dissolved in a minimum volume of THF and then reprecipitated in methanol (50 mL). The obtained product was dried *in vacuo* to yield the phenyl ether of branched polymer **7**. Yield 16%; $M_n = 7200$, $M_w = 24,100$, $M_w/M_n = 3.3$; ¹HNMR (CDCl₃, 400 MHz, ppm) δ: 7.50-7.28, 7.15-6.83 (Ph-H), 5.34-5.00 (Ph-CH₂-OPh), 4.30-3.55 (Ph-OCH₃), 3.31-2.72 (Ph-C₂H₄-Ph), 2.38-2.13 (Ph-CH₃); ¹³CNMR (CDCl₃, 100 MHz, ppm) δ: 160.9-156.0, 130.1-129.1, 126.6-124.9, 122.1-119.7, 115.3-114.1, 63.4-59.7, 30.2-24.7; IR (KBr, cm⁻¹): ν = 3010, 2940, 2890, 2830, 1590, 1500, 1460, 1410, 1230, 1200, 1160, 1100, 1010.

RESULTS AND DISCUSSION

Synthesis and characterization

We synthesized BPPEs from 1,3,5-tris(bromomethyl)benzene derivatives via Wurtz coupling in the manner shown in Scheme 3. We also identified the appropriate catalyst for the synthesis of an organo-soluble BPPE. The synthesis procedure is described as follows. Under argon atmosphere, a catalytic amount of crystalline I₂ was added to magnesium turnings (3 eq.) in dry tetrahydrofuran (THF) at room temperature. Then, a suspension of **1** (1 eq.) in dry THF was added dropwise to the abovementioned mixture, and the resulting suspension was refluxed. The crude product was purified by reprecipitation in methanol to yield the corresponding branched polymer **4** in 31% yield as a soluble part in organic solvents. Polymerization of 1,3,5-tris(bromomethyl)-2,4,6-trimethylbenzene **2** and 1,3,5-tris(bromomethyl)-2,4,6-trimethoxybenzene **3** carried out in a manner similar to that aforementioned afforded the corresponding polymers **5** and **6** in 37 and 67% yields, respectively. The obtained polymers were well-soluble in THF, chloroform, toluene, and DMF, but insoluble in methanol and water. From gel-permeation chromatography (GPC) analysis (eluent: THF; equivalent linear molecular weights based on polystyrene standards), it was found that the number-average molecular weights (M_n) of **4**, **5**, and **6**

TABLE I
Properties of Hyperbranched Polymers

Run	Product	Cat. (mmol) ^a	Time (h)	Yield (%) ^b	M_n ^c	M_w/M_n ^c
1	4	Mg (3)	21	31	2800	2.2
2		Mg (6)	21	13	2200	2.5
3		Mg (3)	49	27	— ^d	— ^d
4		Na (excess)	21	11	2600	3.2
5	5	Mg (3)	21	37	2400	1.9
6		Mg (6)	21	36	2000	2.6
7		Mg (3)	49	12	— ^d	— ^d
8		Na (excess)	21	7.4	1400	2.6
9	6	Mg (3)	15	67	6100	1.9
10		Mg (6)	15	47	5500	1.9
11		Na (excess)	15	12	2400	2.7

^a I_2 was used as initiator in all reactions.

^b Soluble part in organic solvents.

^c Determined by GPC (eluent THF, polystyrene standards).

^d Not determined. Products were insoluble in various solvents.

were 2800, 2400, and 6100 (polydispersity index (PDI) 2.2, 1.9, and 1.9), respectively. Using excess amount of magnesium (6 eq.), the molecular weight of the polymer (runs 2, 6, and 10) were not changing.

The results of polymerization are summarized in Table I. Products 4 and 5 were less organosoluble than 6, and it was difficult to obtain them in high yields and also ensure that they had high molecular weights and good organosolubility. In contrast, 6 was obtained in high yield and had a high molecular weight. This was because 6 is more organosoluble than 4 and 5, because of the high flexibility of the methoxy groups.^{16–25} Alkoxy groups can add good solubility to aromatic polymer such as poly(phenylenemethylene).^{26,27} Because branched polymers have better organosolubility than their linear analogs with similar molecular weights, polymers obtained under appropriate polymerization conditions were highly soluble in common organic solvents such as THF and chloroform (cf. poly(*p*-phenylene ethylene) was insoluble in these solvents).

The products obtained after prolonged reaction times were found to be crosslinked gels that were insoluble in common organic solvents such as THF and chloroform. In addition, the yields decreased markedly when sodium was used instead of magnesium, because the polymerization reaction was inefficient in the presence of the former compound (runs 4, 8, and 11).

The ¹HNMR spectra of 4, 5, and 6 (Fig. 1) reveal peaks at around 4.6 ppm, suggesting that these polymers possess unreacted terminal bromomethyl groups (Ph-CH₂Br). Under the reaction conditions used in this study, it was difficult to ensure that all the bromomethyl groups participated in the polymerization reaction, because the resulting polymers were converted into insoluble gels before the complete consumption of these groups. The Ph-CH₃

groups were obtained by the reaction of Grignard reagent (Ph-CH₂-MgBr) with methanol in reprecipitation process. In addition, the oxidative addition of Mg to bromomethyl group incompletely proceeded; therefore, both bromomethyl and methyl group were remained after purification.

6 may have a crosslinked structure with branched units, but it is impossible to estimate a contamination of crosslinked structure by spectroscopic analysis such as NMR and FT-IR spectra. Therefore, it is difficult to determine its exact structure. However, we succeeded in calculating of ration of bromomethyl group. From the ¹HNMR analysis of 6, it was found that the integral ratio of the protons of the bromomethyl groups to those of the trimethoxy groups was ~ 1.3 : 9. This suggests that for every repeating unit in 6, there were 0.65 eq. of unreacted bromomethyl groups. The integral ratio obtained in the case of 6 was bromomethyl groups (A):methoxy groups (B):ethylene groups (C):Ph-CH₃ units (D) =

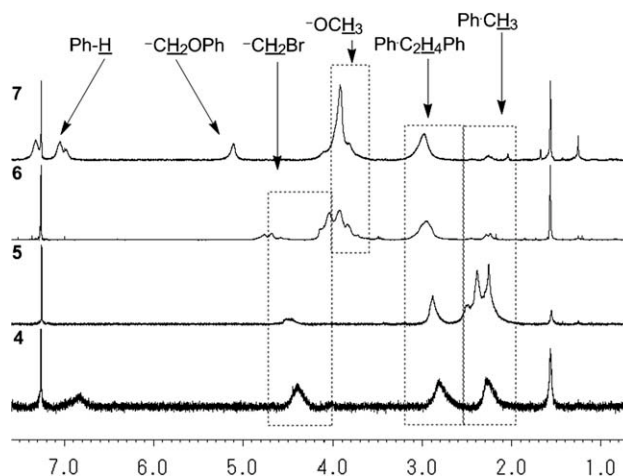
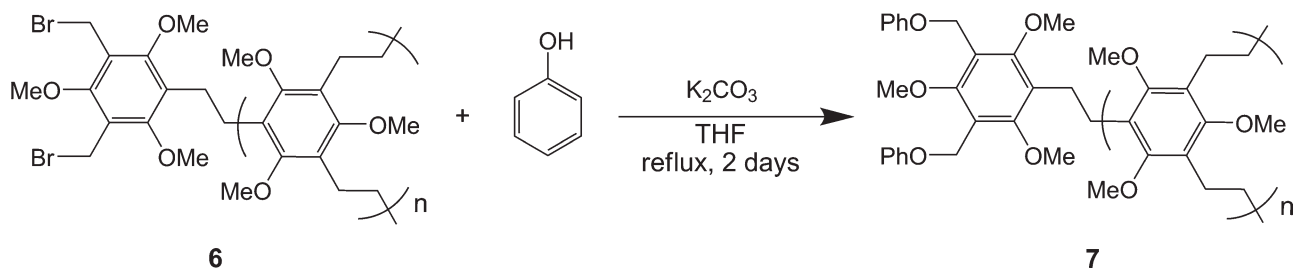


Figure 1 ¹HNMR spectra of branched poly(phenylene ethylene).



Scheme 4 Functionalization of a branched poly(phenylene ethylene).

1.2 : 9.0 : 4.9 : 0.62. However, the exact ratio of degree of branching can not be determined because the obtained polymer is not a branched polymer with perfect structure but a complex branched polymer with inner cyclic structure derived from intramolecular cyclization.

Polymer functionalization

The fact that BPPEs possess a very large number of unreacted Ph-CH₂Br groups^{26–35} is of particular interest in the study of functional polymers. To confirm whether **6** can be made functional, we carried out a simple polymerization reaction and attempted to improve the thermal stability and processability of the obtained polymer. In concrete terms, we prepared the corresponding phenyl ether of **6** according to Scheme 4. We found that the peak attributed to the bromomethyl groups completely disappeared in the ¹HNMR spectrum of the obtained polymer **7** (Fig. 1). The yield of **7** was low (16%) because of the small-scale reaction and purification.

The results of GPC analysis showed that M_n of **7** was 7100 (PDI = 3.2), suggesting that **7** was obtained without degradation of the original polymer chain (in this reaction, M_n and PDI of **6** were 4400 and 2.7, respectively). This suggests that BPPEs are highly reactive functional polymers.^{26–31}

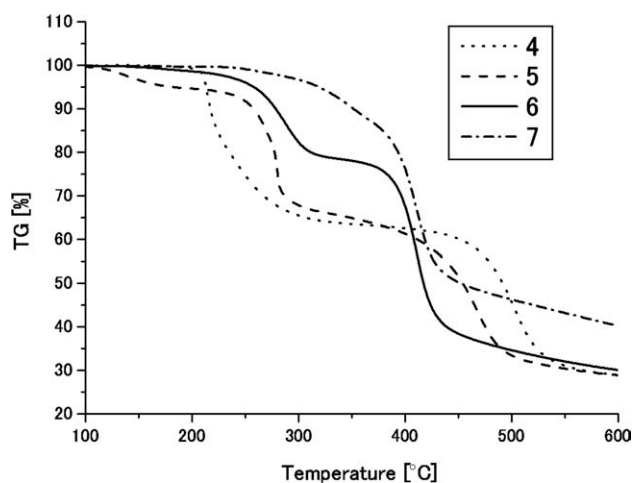


Figure 2 TGA graph for branched poly(phenylene ethylene).

Solution properties

The solution properties of the polymers were estimated on a SEC-VISC-RALLS system (Viscotek), which is equipped with an on-line viscometer (VISC) and a right-angle laser light-scattering (RALLS) detector ($\lambda = 670$ nm), using a diluted THF solution of the polymers.^{40–43} The M_w values of polymer **6** and **7** were estimated to be 25,000 and 52,000, respectively. Further, **6** and **7** had low Mark-Houwink-Sakurada a -values (0.34 and 0.47, respectively), which suggests that they have a spherical structure with a branched three-dimensional topology in solution, as expected.⁴⁴ **7** is less compact morphology than its precursor.

Thermal properties

Differential scanning calorimetry (DSC) and thermogravimetric analyses (TGA) were carried out to determine the thermal transition and degradation behavior of the BPPEs. DSC revealed that these polymers showed neither a sharp glass-transition temperature (T_g) nor a sharp melting temperature (T_m), although poly(*p*-phenylene ethylene) had a well-defined T_g and T_m .^{8,35} The TG curves of the BPPEs revealed two thermal decomposition temperatures (Fig. 2). In the case of **6**, the weight loss at the first thermal decomposition stage was approximately 20%, which is approximately consistent with the molecular weight of Br in **6**. In addition, **7**, which was obtained by reacting **6** with phenol, was found to be more thermally stable. This supports the hypothesis that the aforementioned first thermal decomposition resulted from the loss of Br. During the TG analyses of **4**, **5**, **6**, and **7**, the T_{d10} values (10% loss in weight) were found to be 217, 258, 278, and 352°C, respectively.

CONCLUSIONS

We synthesized highly reactive, organosoluble branched poly(phenylene ethylene)s (BPPEs) by Wurtz coupling polymerization. Although the ratio of the branched unit was ~ 0.2 (/all benzene ring), **6** showed a low Mark-Houwink-Sakurada a -value

(0.34), which suggested that it had a spherical structure with a compactly branched three-dimensional topology in dilute THF solution. In addition, ^1H NMR analysis showed that a very large number of unreacted bromomethyl groups ($\text{Ph-CH}_2\text{Br}$) remained in the BPPes; the reaction of **6** with phenolic hydroxyl groups proceeded quantitatively. This suggested that all of them are reactive and all that sites may be functionalized, making them a very attractive starting point for the creation of functionalized BPPes with further enhanced processability for solution-processing of films, adjustment of optical properties such as refractive index, and creation of polymer blends.

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