Facile Synthesis, Large Optical Nonlinearity, and Excellent Thermal Stability of Hyperbranched Poly(aryleneethynylene)s Containing Azobenzene Chromophores

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ABSTRACT: Azo-functionalized hyperbranched poly(aryleneethynylene)s (*hb*-PAEs) (**4** and **5**) are synthesized by palladium-catalyzed coupling of triiodoarenes (**1** and **2**) with a diethynylazobenzene (**3**). The *hb*-PAEs are soluble, film-forming, and morphologically stable (T_g > 180 °C). Their poled films exhibit high second-harmonic-generation coefficients (d_{33} up to 177 pm/V) thanks to the chromophore-separation and site-isolation effects of hyperbranched architectural structure of the polymers in the three-dimensional space. The optical nonlinearities of the poled films are thermally stable (no drop in d_{33} when heated to 152 °C) due to the facile cross-linking of the multiple acetylenic triple bonds in the *hb*-PAEs at moderate temperatures (down to 88 °C).

Introduction

Second-order nonlinear optical (NLO) molecules have attracted much attention due to their potential applications in photonics.[1] A major effort in the area has been to efficiently translate large molecular first hyperpolarizability (β) value into high macroscopic second-harmonic-generation (SHG) coefficient (d_{33}). The involved problem here is that chromophoric aggregation often quenches electrooptical (EO) activity.[2] The chromophores of the NLO dyes are usually highly polarized by intramolecular push−pull interactions. During film fabrication, the chromophores with large dipole moments tend to compactly pack in a centrosymmetric manner due to the strong intermolecular electrostatic interactions, resulting in the cancellation of the NLO effects in the bulk.

Much work has been done to tackle the aggregation-quenching problem. Recent theoretical analyses suggest that optimization of molecular shape can bring about a boost in the maximum realizable EO activity. The NLO chromophores in spherically shaped molecules cannot regularly stack in a side-by-side fashion.[3] Dendrimer possesses a spherical shape, and indeed, dendritic molecules containing NLO chromophores have been demonstrated to display large EO coefficients.[4] Dendrimers are, however, tedious to synthesize and are commonly used by doping into film-forming polymer matrixes. In sharp contrast, hyperbranched polymers are easy to synthesize and can be used in pure forms without doping into other matrixes because of their own film-forming ability. The three-dimensional spatial separation of the chromophores endows the polymers with favorable site-isolation effect,[5] and their void-rich topological structure helps minimize optical loss in the NLO process.[4] The globular macromolecules are thus promising candidates for NLO materials with large bulk EO activities.

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We have previously synthesized a series of hyperbranched polyarylenes (*hb*-PAs) through alkyne polycyclotrimerization.[6,7] Because of their structural rigidity, the *hb*-PAs enjoy excellent morphological stability, with no glass transition temperatures (T_g) detectable in the measured temperature region (room temperature to 180 °C) of the differential scanning calorimetry (DSC) analysis. The *hb*-PAs are NLO-active, effectively attenuating the harsh optical pulses. In this work, we synthesized two hyperbranched poly(aryleneethynylene)s (*hb*-PAEs) by simple halide−alkyne coupling reactions (Scheme 1). The *hb*-PAEs are macroscopically processable, thermolytically resistant, and morphologically stable. Polymer **5** exhibits a high SHG coefficient (d_{33} = 177 pm/V), outperforming lithium niobate, a technologically important inorganic crystal, in terms of EO activity.[8]

Experimental Section

Materials. THF was distilled from sodium benzophenone ketyl under nitrogen immediately prior to use. Triethylamine (RdH) was distilled under normal pressure and kept over potassium hydroxide. Copper(I) iodide, dichlorobis(triphenylphosphine)palladium(II), 2,4,6-triiodophenol, 1-bromobutane, 5-chloro-1-pentyne, potassium carbonate, aniline, 4-nitroaniline, potassium iodide, triphenylphosphine, sodium nitrite, 1-pentyne, concentrated hydrochloric acid, ethanol, methanol, DMF, and potassium hydroxide were all purchased from Aldrich and used as received without further purification. Tris(4-iodophenyl)amine (**1**) was prepared according to the published procedures.[9]

Instrumentation. The ^{1}H and ^{13}C NMR spectra were measured on a Bruker ARX 300 spectrometer using tetramethylsilane (TMS; δ = 0 ppm) as internal standard. The FT-IR spectra were taken on a Perkin-Elmer 16 PC spectrometer. The mass spectra were recorded on a Finnigan TSQ 7000 triple quadrupole spectrometer operating in a chemical ionization (CI) mode using methane as carrier gas. The UV−vis absorption spectra were taken on a Milton Roy Spectronic 3000 Array spectrophotometer. The thermal stabilities of the *hb*-PAEs were evaluated on a Perkin-Elmer thermogravimetric analyzer TGA 7 at a heating rate of 20 °C/min under nitrogen, and their thermal transitions were studied using a Setaram DSC92 at a scanning rate of 10 °C/min also under nitrogen. Single

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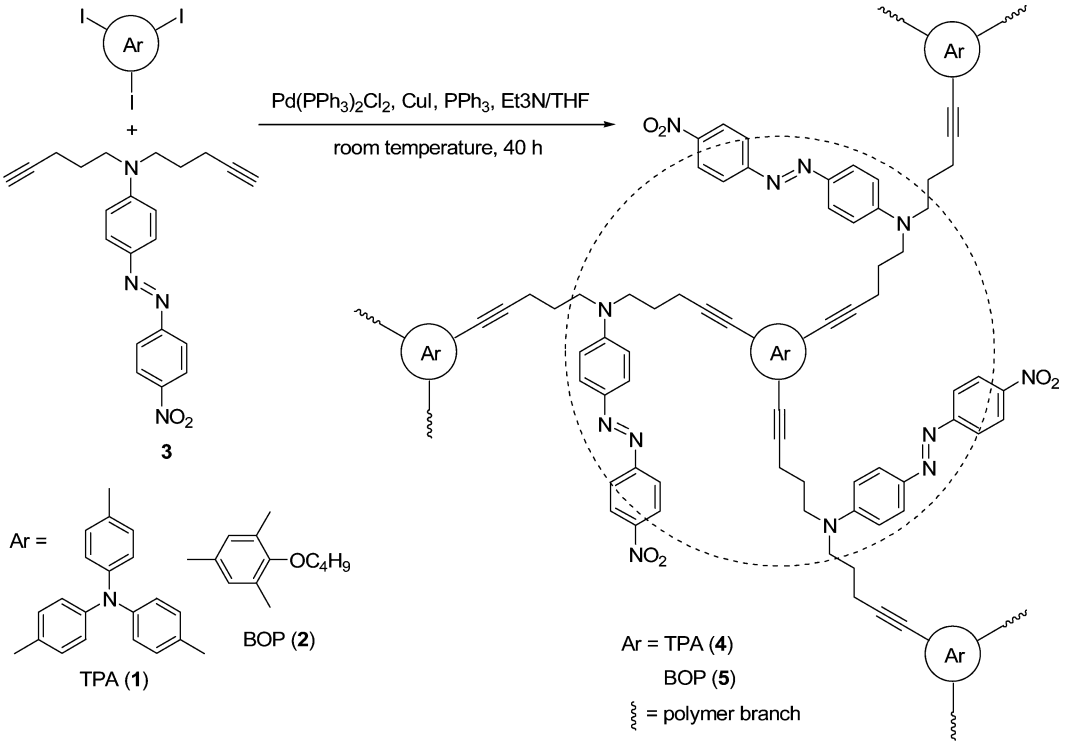
Scheme 1



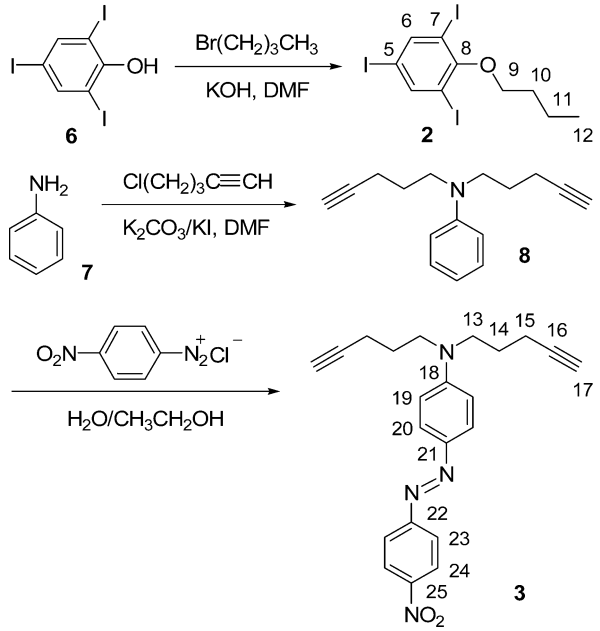
crystals of **1** were grown from acetone (very large crystals of optical quality could be easily obtained). Their X-ray diffraction intensity data were collected at 295 or 100 K on a Bruker-Nonius Smart Apex CCD diffractometer with graphite-monochromated Mo Kα radiation. The intensity data were processed using the SAINT and SADABS routines, and the structure solution and refinement were carried out by the SHELXTL suite of X-ray programs (Version 6.10). The crystal data of **1** collected at 100 K are given in the Supporting Information.

The average molecular weights and polydispersity indexes of the *hb*-PAEs were estimated by gel permeation chromatograph (GPC) using a Waters Associates liquid chromatograph equipped with a Waters 515 HPLC pump, a Rheodyne 7725i injector with a stand kit, a set of HT Styragel columns (HT3, HT4, and HT6) covering molecular weight range of 10^2-10^7, a column temperature controller, a Waters 486 wavelength-tunable UV−vis detector, and a Waters 2414 differential refractometer. All the polymer solutions were prepared in THF (∼2 mg/mL) and filtered through 0.45 μm PTFE syringe-type filters before being injected into the GPC system. THF was used as eluent at a flow rate of 1.0 mL/min. The column temperature was maintained at 40 °C, and the working wavelength of the UV−vis detector was set at 254 nm. A set of monodisperse polystyrene standards (Waters) was used for calibration purpose.

Monomer Preparation. 2-Butoxy-1,3,5-triiodobenzene or monomer **2** was prepared by the reaction of 2-hydroxy-1,3,5-triiodobenzene (**6**) with 1-bromobutane following a published procedure,[10] while (*E*)-4-[2-(4-nitrophenyl)diazenyl]-*N*,*N*-di(4-pentynyl)benzenamine or monomer **3** was prepared by a two-step reaction route shown in Scheme 2.

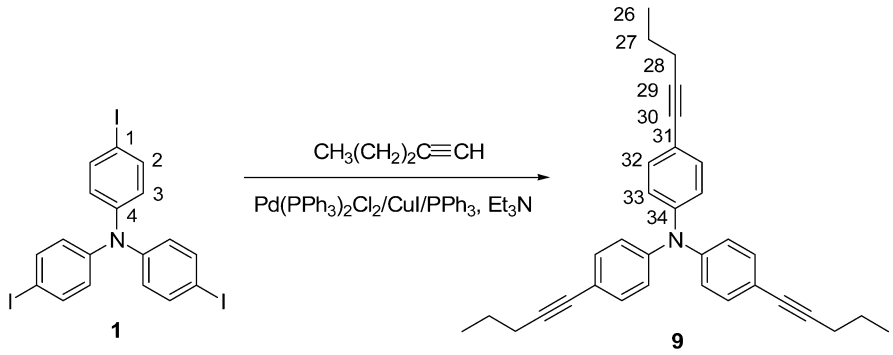
N,*N*-*Di(4-pentynyl)benzenamine* (**8**). Into a dry 100 mL flask were added 1.86 g of aniline (**7**) (20 mmol), 0.7 g of potassium iodide (4.2 mmol), 5.12 g of 5-chloro-1-pentyne (50 mmol), 8.28 g of potassium carbonate (60 mmol), and 200 mL of DMF. The mixture was stirred at 90 °C for 2 days under nitrogen. The suspension was cooled to room temperature and filtered. The filtrate was poured into water (500 mL) and extracted with 200 mL of chloroform four times. The combined organic layers were dried over sodium sulfate and then concentrated. The residue was purified on a silica gel column using chloroform as eluent. Colorless oil of **8** was obtained in 30% yield (1.7 g). ^{1}H NMR (300 MHz, $CDCl_3$), δ (TMS, ppm): 7.28 (m, 2H), 6.77 (m, 3H), 3.46 (m, 4H), 2.28 (m, 4H), 2.05 (s, 2H), 1.87 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$), δ (TMS, ppm): 148.2, 129.7, 116.5, 112.7, 84.1, 69.4, 50.3, 26.2, 16.4.

Scheme 2



(E)-4-[2-(4-Nitrophenyl)diazenyl]-N,N-di(4-pentynyl)benzenamine (**3**). 4-Nitroaniline (0.83 g, 6.0 mmol) was dissolved in a solution of concentrated hydrochloric acid (1 mL) in 10 mL of water. The mixture was cooled to 0 °C in an ice bath. A solution of sodium nitrite (0.42 g, 6.1 mmol) in 3 mL of water was added slowly, and the mixture was stirred in the ice bath for 30 min. While keeping the mixture in the ice bath, a solution of **8** (1.35 g, 6.0 mmol) in ethanol (3 mL) was added. The mixture was agitated below 2 °C for 2 h. The dark red precipitate was filtered, washed with water, and air-dried. Recrystallization from an acetone/methanol mixture gave 1.41 g of pure product of **3** (63% yield). IR (thin film), ν (cm^{-1}): 3200 (≡C−H stretch), 1515, 1337 (NO_2

Scheme 3



1 **9**

stretch), 858 (C−N stretch), 625 (≡C−H bend). ^{1}H NMR (300 MHz, $CDCl_3$), δ (TMS, ppm): 8.24 (d, 2H), 7.86 (m, 4H), 6.78 (d, 2H), 3.55 (m, 4H), 2.26 (m, 4H), 2.04 (s, 2H), 1.85 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$), δ (TMS, ppm): 157.1, 151.7, 147.5, 144.0, 126.7, 125.2, 123.0, 111.7, 83.7, 69.7, 50.2, 26.2, 16.6. MS (CI): *m/e* 375 [$(M + 1)^+$].

Tris[4-(1-pentynyl)phenyl]amine (**9**). This amine was prepared as a model compound according to Scheme 3 for the purpose of characterizing *hb*-PAE **4**. To a 250 mL flask were added 0.3 g of **1** (0.48 mmol), 10 mg of copper(I) iodide, 10 mg of triphenylphosphine, and 30 mg of dichlorobis(triphenylphosphine)palladium in the glovebox. Triethylamine (100 mL) and 0.3 g of 1-pentyne (4.4 mmol) were then injected. The resultant mixture was stirred at room temperature for 2 days. The precipitate was removed by filtration. After removing the solvent, the crude product was purified on a silica gel column using a mixture of hexane/chloroform (2:1 by volume) as eluent. White solid of **9** was obtained in 79% yield (0.17 g). ^{1}H NMR (300 MHz, $CDCl_3$), δ (TMS, ppm): 7.24 (d, 6H), 6.96 (d, 6H), 2.36 (m, 6H), 1.59 (m, 6H), 1.03 (t, 9H). ^{13}C NMR (75 MHz, $CDCl_3$), δ (TMS, ppm): 146.9, 133.5, 124.6, 119.3, 90.7, 81.0, 23.1, 22.0, 14.6.

Polymer Synthesis. *hb*-PAEs **4** and **5** were synthesized by the palladium-catalyzed polycoupling of triiodides **1** and **2** with diethynylazobenzene **3**, respectively. A typical experimental procedure for the preparation of *hb*-PAE **4** is given below as an example.

In a dry Schlenk tube were placed 124.6 mg of **1**, 112.2 mg of **3**, 10 mg of $PdCl_2(PPh_3)_2$, and catalytic amounts of CuI and PPh_3 in a glovebox. Dry THF (5 mL) and Et_3N (0.5 mL) were then added. The resultant mixture was stirred at room temperature for 40 h. The mixture was passing through a cotton filter and dropped into 500 mL of acetone. The precipitate was collected, further purified by several precipitations of its THF solution into acetone, and dried in a vacuum at 40 °C to a constant weight.

Characterization Data for hb-PAE **4**. Red powder, 46.5% yield (110 mg). $M_w = 8600$, $M_w/M_n = 1.89$ (GPC, polystyrene calibration). IR (thin film), ν (cm^{-1}): 1516, 1337 (NO_2 stretch), 856 (C−N stretch). ^{1}H NMR (300 MHz, $CDCl_3$), δ (TMS, ppm): 8.22, 7.80, 7.49, 7.25, 6.91, 6.78, 3.58, 2.46, 2.33, 1.90. ^{13}C NMR (75 MHz, $CDCl_3$), δ (TMS, ppm): 157.1, 151.9, 147.7, 146.6, 144.0, 139.0, 133.3, 132.4, 128.9, 126.5, 125.0, 123.9, 123.0, 118.9, 111.9, 89.1, 86.9, 81.7, 50.7, 26.6, 17.7. UV−vis (THF, 28 μg/mL), λ_{max} (nm): 238, 325, 485.

hb-PAE **5**. Red powder, 49.3% yield (107 mg). $M_w = 11\,300$, $M_w/M_n = 1.96$ (GPC, polystyrene calibration). IR (thin film), ν (cm^{-1}): 1514, 1337 (NO_2 stretch), 856 (C−N stretch). ^{1}H NMR (300 MHz, $CDCl_3$), δ (TMS, ppm): 8.22, 7.80, 7.38, 6.77, 4.06, 3.90, 3.54, 2.42, 1.80, 1.49, 0.91. UV−vis (THF, 28 μg/mL), λ_{max} (nm): 240, 484.

Film Fabrication. The *hb*-PAEs were dissolved in THF (concentration ~4 wt %), and the solutions were filtered through syringe filters. The polymer solutions were spin-coated onto indium−tin oxide (ITO)-coated glass substrates, which were carefully precleaned by DMF, acetone, distilled water, and THF sequentially in an ultrasonic bath. Residual solvent was removed by heating the polymer films in a vacuum oven at 40 °C for 2 days. The film thickness was measured by a TENCOR 500 surface profiler.

Table 1. Syntheses[a] and Optical Properties of *hb*-PAEs 4 and 5

hb-PAE	yield (%)	M_w[b]	M_w/M_n[b]	λ_{max}[c]	l_s (μm)[d]	d_{33} (pm/V)[e]
4	46.5	8600	1.89	483	0.42	55
5	49.3	11300	1.96	482	0.14	177

[a] Carried out in a THF/Et_3N mixture at room temperature for 40 h. [b] Determined by GPC in THF on the basis of a polystyrene calibration. [c] Absorption maximum of polymer solution in THF. [d] Thickness of solid film. [e] Second-harmonic-generation coefficient.

NLO Measurement. The second-order optical nonlinearity of the *hb*-PAEs was determined by in-situ SHG experiments using a closed temperature-controlled oven with optical windows and three needle electrodes. The films were kept at 45° to the incident beam and poled inside the oven, with the SHG intensity monitored simultaneously. Poling conditions were as follows: temperature: 180 °C for **4** and 160 °C for **5**; voltage: 7.6 kV at the needle point; gap distance: 0.8 cm. The SHG measurements were carried out with a Nd:YAG laser operating at a repetition rate of 10 Hz and a pulse width of 8 ns at 1064 nm. A Y-cut quartz crystal was used as reference.

Results and Discussion

Polymer Synthesis. To synthesize the *hb*-PAEs by palladium-catalyzed halide−acetylene coupling, we prepared three monomers, i.e., two aryl triiodides (**1** and **2**) and one azodiyne (**3**). The reactions proceeded smoothly, and the monomers were obtained in good yields. Single crystals of monomer **1** suitable for X-ray diffraction analysis were obtained from acetone, whose crystallographic data are given in the Supporting Information. Whereas monomer **2** is a known compound,[10] monomer **3** is a new one, whose molecular structure was characterized by standard spectroscopic methods (see Experimental Section for its detailed analysis data).

The coupling reactions were carried out in THF/Et_3N using $PdCl_2(PPh_3)_2$ as catalyst (Scheme 1). We initially worried that the reactions might run out of control to yield insoluble networks, as what occurred in some of our previously studied alkyne polymerization systems.[6,7,11] We cautiously monitored the reactions by precipitating small fractions of the reaction mixtures into acetone from time to time but found with delightfulness that the reactions proceeded in moderate rates, with the products remained soluble after 40 h reaction. The products were purified by repeated precipitations of their THF solutions into acetone, and the purified products were obtained in good yields (Table 1). GPC analyses proved the polymeric nature of the products, although their M_w values were only moderate. It should, however, point out that the GPC analysis using linear polystyrenes as calibration standards often underestimates the molecular weights of hyperbranched polymers,

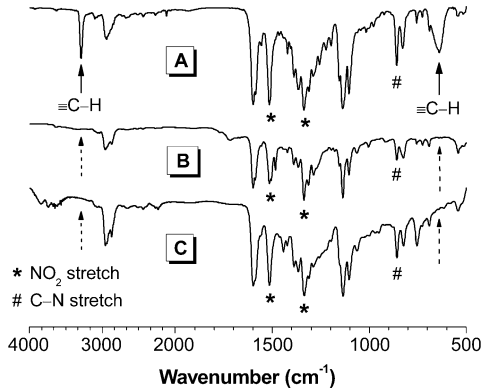


Figure 1. IR spectra of monomer **3** (A) and polymers **4** (B) and **5** (C).

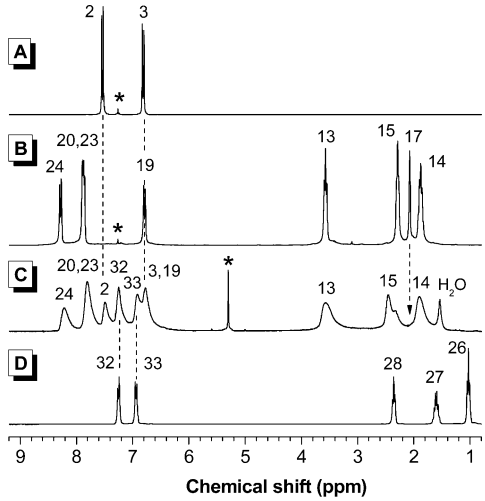


Figure 2. ^{1}H NMR spectra of monomers **1** (A) and **3** (B) in chloroform-*d*, polymer **4** (C) in dichloromethane-d_2, and model compound **9** (D) in chloroform-*d*. The labels of the peaks of the protons correspond to those given in Schemes 2 and 3 and Chart 1. The solvent peaks are marked with asterisks.

with difference as big as ~40 times being reported in the literarture.[12] The actual or true molecular weights of the *hb*-PAEs thus could be much higher than the values given in Table 1.

Structural Characterization. The *hb*-PAEs were characterized spectroscopically, and satisfactory spectral data were obtained. Figure 1 shows the IR spectra of polymers **4** and **5**; the spectrum of one of their monomers, i.e., **3**, is also shown for the purpose of comparison. The ≡C−H stretching and bending vibrations of **3** occur at 3200 and 625 cm^{-1}, respectively, while the absorption bands associated with the nitro groups appear at 1515, 1337, and 858 cm^{-1} (Figure 1A). In the spectra of the *hb*-PAEs, the absorption bands of the terminal acetylene groups disappear but those of the nitro groups remain, thus spectroscopically proving that the alkyne polycoupling has propagated and that the NLO chromophore has been incorporated into the polymer structure.

In the ^{1}H NMR spectrum of monomer **3**, the resonance peak of its acetylene protons (17) is observed at δ 2.04 (Figure 2B). This peak disappears after polymerization: no acetylene resonance is seen in the spectrum of polymer **4** (Figure 2C). Comparison with the spectra of monomers **1** and **3** reveals that there exist two new resonance peaks (32 and 33) at δ 7.24 and 6.92 in the spectrum of polymer **4**. To identify of the origins of these new peaks, a model compound, namely, tris[4-(1-pentynyl)phenyl]amine (**9**), is synthesized by a model reaction,

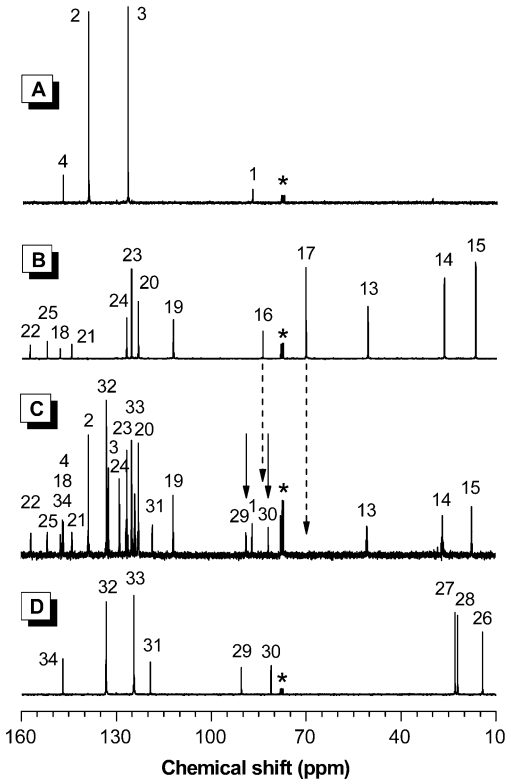


Figure 3. ^{13}C NMR spectra of chloroform-*d* solutions of monomers **1** (A) and **3** (B), polymer **4** (C), and model compound **9** (D). The labels of the resonance peaks of the carbon atoms correspond to those given in Schemes 2 and 3 and Chart 1. The solvent peaks are marked with asterisks.

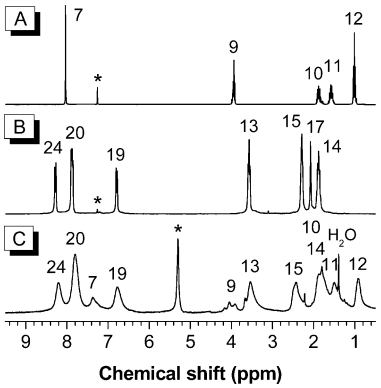
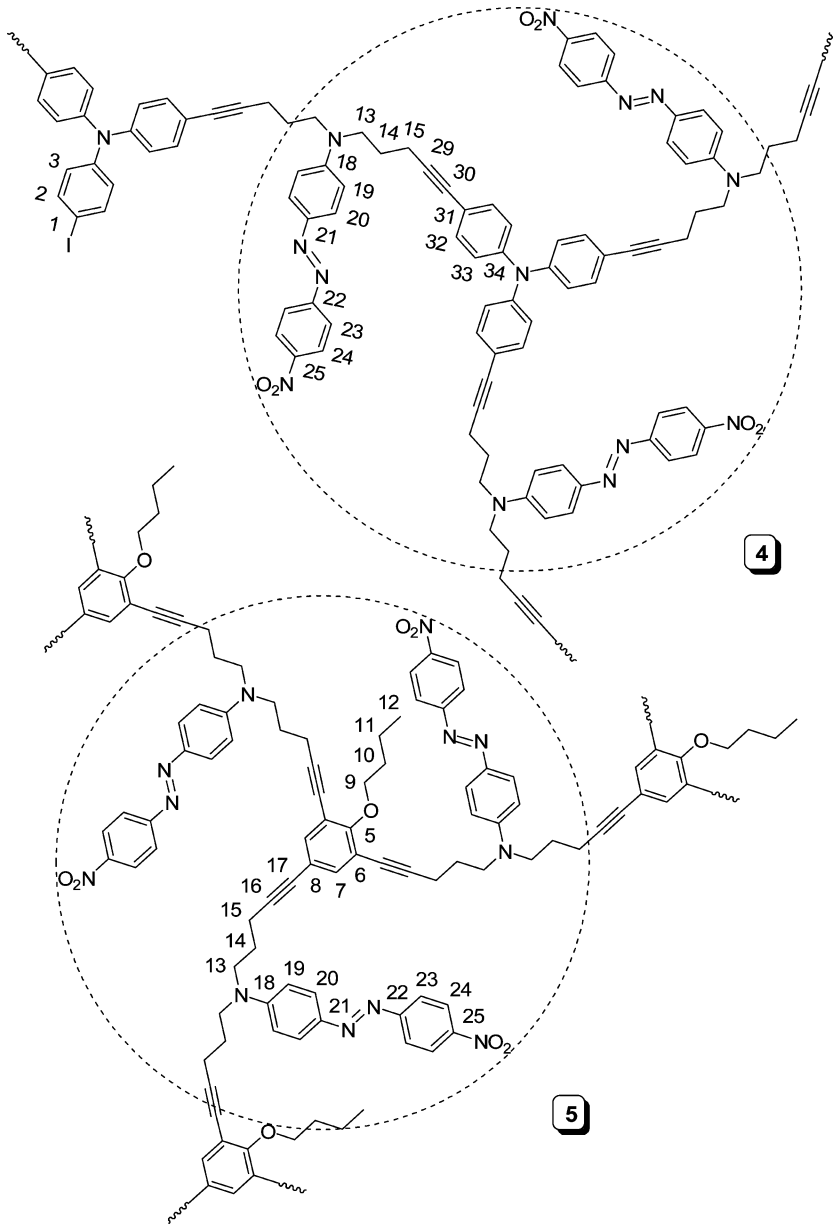


Figure 4. ^{1}H NMR spectra of monomers **2** (A) and **3** (B) in chloroform-*d* and polymer **5** (C) in dichloromethane-d_2. The labels of the resonance peaks of the protons correspond to those given in Scheme 2 and Chart 1. The solvent peaks are marked with asterisks.

that is, coupling of **1** with 1-pentyne (Scheme 3). The spectrum of the model compound helps the structural elucidation: peaks 32 and 33 can now be readily assigned to the resonances of the protons of the aromatic rings of the aryleneethynylene units of *hb*-PAE **4** (Chart 1). The existence of peak 2 at δ 7.49 indicates that the polymer contains iodide residues in the form of linear monoiodide and terminal diiodide units.

The ^{13}C NMR analyses offer the similar structural information. As can be seen from the spectra shown in Figure 3, all the resonance peaks can be assigned. Polymer **4** displays no resonance peaks of the carbon atoms of terminal acetylene (16 and 17) but those of internal acetylene (29 and 30; Figure 3C), again verifying the proceeding of the coupling reaction. Similarly, the spectral data of polymer **5** (Figure 4) well

Chart 1



correspond to its expected molecular structure (Chart 1), with no unexpected or strange signals observed.

Optical Properties. Figure 5 shows the UV−vis spectra of the THF solutions of *hb*-PAEs **4** and **5**. Polymer **4** absorbs at 238 (K band), 325 (B band) and 485 nm due to the $\pi-\pi^*$ transitions of its benzene, triphenylamine, and azobenzene chromophores, while polymer **5** absorbs at 240 and 484 nm, owing to the electronic transitions of its benzene and azobenzene chromophores, respectively. The absorbance of **5** at 484 nm is higher than that of **4** at 485 nm, suggesting that the former possesses a higher density of NLO unit than the latter. This is understandable because the comonomer repeat unit of **5** has a lower molar mass than that of **4**.

Both **4** and **5** are soluble in common organic solvents such as chloroform, THF, DMF, and DMSO. Their solutions can be spin-coated into thin solid films. The *hb*-PAEs are thermolytically resistant: **4** and **5** lose 5% of their original weights at temperatures as high as 265 and 258 °C, respectively. No glass transitions are detectable when they are heated to 180 °C (the highest temperature allowable for the DSC measurements at our instrumentation center); that is, the polymers possess high T_g values. The *hb*-PAEs are thus macroscopically processable, thermolytically resistant, and morphologically stable.

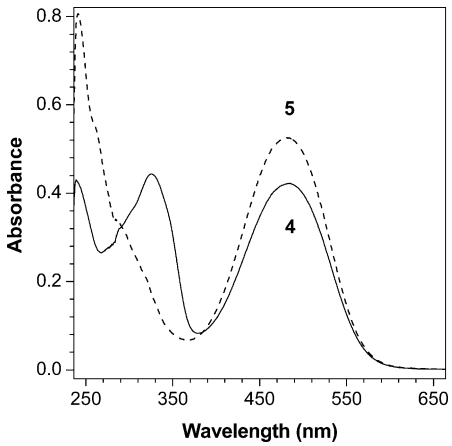


Figure 5. UV−vis absorption spectra of THF solutions of polymers **4** and **5** (concentration: 28 μg/mL).

To evaluate the optical nonlinearity of the azobenzene-containing *hb*-PAEs, their poled thin solid films are fabricated. The most convenient technique for measuring the second-order NLO activity is to investigate the SHG processes characterized by d_{33}. The d_{33} value for a poled film can be calculated from the equation[8,13]

$$\frac{d_{33,s}}{d_{11,q}} = \sqrt{\frac{I_s}{I_q}} \frac{l_{c,q}}{l_s} F \quad (1)$$

where $d_{11,q}$ is the d_{11} of the quartz crystal (0.45 pm/V), I_s and I_q are the respective SHG intensities of the sample (polymer film) and the quartz crystal, $l_{c,q}$ is the coherent length of the quartz crystal (20.6 μm), l_s is the thickness of the sample, and F is the correction factor of the apparatus (1.2 when $l_c \gg l_s$).

From the experimental data, the d_{33} values of *hb*-PAEs **4** and **5** are calculated to be 55 and 177 pm/V, respectively, at the fundamental wavelength of 1064 nm (Table 1). The measurements were repeated three times, which gave similar results within experimental errors, verifying the data reproducibility. Various d_{33} values have been reported for different polymers containing similar azo dye moieties, with the highest value of 169 pm/V being reported by Yu et al.[14] The d_{33} value of an NLO polymer can be different when measured by different methods or even by different testing systems, which makes direct data comparison difficult. However, compared with the d_{33} values of the polymers carrying the similar azobenzene chromophores calculated by the same method using the experimental data obtained from the same apparatus, the d_{33} values of the polymers, especially the data for **5**, are outstandingly high.[15] Most of the NLO polymers prepared so far possess linear molecular structures. The impressively high d_{33} values of *hb*-PAEs **4** and **5** suggest that the 3D architectural structure of the hyperbranched polymers and the spatial chromophore isolation in the macromolecular spheres have helped enhance their optical nonlinearities.

The difference between the d_{33} values of *hb*-PAEs **4** and **5** may mainly stem from their structural difference. According to the one-dimensional rigid orientation gas model[16]

$$d_{33} = \frac{1}{2} N\beta f^{2\omega} (f^{\omega})^2 \langle \cos^3 \theta \rangle \quad (2)$$

where N is the number density of the chromophore, β is its first hyperpolarizability, f is the local field factor, 2ω is the double frequency of the laser, ω is its fundamental frequency, and $\langle \cos^3 \theta \rangle$ is the average orientation factor of the poled film. Obviously, under identical experimental conditions, d_{33} is proportional to the number density of the chromophore. As discussed above, **5** possesses a relatively small comonomer unit and hence a relatively high azo-dye density, in comparison to **4**. Assuming a same poling efficiency and according eq 2, **5** should exhibit a higher d_{33} value.

The dynamic thermal stabilities of the NLO activities of the *hb*-PAEs are investigated by depoling experiments, in which the real time decays of their SHG signals are monitored as the poled films are heated from 35 to 180 °C in air at a rate of 5 °C/min without electrical field. The onset temperatures for decays (T_d) in the d_{33} values of **4** and **5** are found to be as high as 152 and 133 °C, respectively (Figure 6). These high T_d values are partially due to the high T_g values of the *hb*-PAEs thanks to their rigid molecular structures. The thermal curing of the polymers may have also played an important role in boosting their resistance against the thermal depoling. It is well-known that acetylenic triple bonds readily undergo thermal polymerization by moderate heating.[11,17] Indeed, *hb*-PAEs **4** and **5** display large exothermic peaks starting from 88 and 120 °C, respectively, in their DSC thermograms due to the cross-linking reactions accompanying the thermally induced acetylene polymerization. The resultant thermosetting networks impede the depoling relaxation processes, hence shifting the T_d values to the high-temperature region.

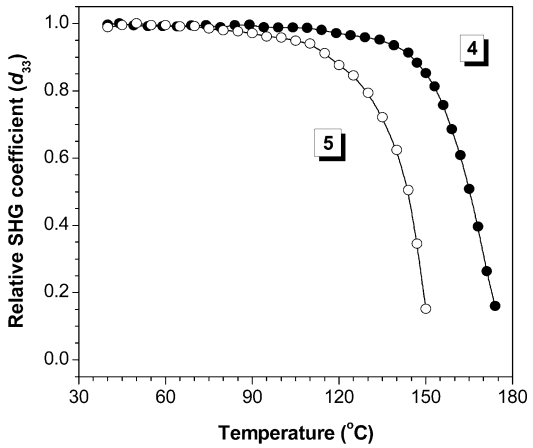


Figure 6. Decays of SHG coefficients of polymers **4** and **5** as a function of temperature.

Concluding Remarks

In summary, in this work, we prepared azobenzene-containing *hb*-PAEs through a simple coupling synthetic route. We demonstrated the beneficial effects of the spherical shape of, and site isolation in, the *hb*-PAEs on their optical nonlinearities. The high d_{33} and T_d values prove that the *hb*-PAEs are efficient and stable NLO materials, which may find technological applications in photonic systems.[1,18]

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Supporting Information Available: Figure S1 showing the molecular structure of crystal **1** with an atom-labeling scheme; Tables S1−S5 listing the crystal data, structure solution and refinement, atomic coordinates, bond lengths/angles, and anisotropic displacement parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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