

Linear and nonlinear optical properties of linear and hyperbranched conjugated polymers

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ABSTRACT

Azo-functionalized hyperbranched polymers **1** and **2**, and linear polyacetylene **3** are synthesized by palladium-catalyzed coupling of triiodoarenes with a diethynylazobenzene, and post functionalization, respectively. These polymers are soluble, film-forming, and morphologically stable ($T_g > 180$ °C). The poled polymer films of **1** and **2** 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 poled film of polymer **3** shows the trade-off of nonlinearity-transparency-orientation thermal stability. The poled films are all orientationally and thermally stable due to the facile cross-linking of the multiple acetylenic triple bonds in the hyperbranched polymer and the rigid backbone in the linear polyacetylene, respectively.

Keywords: Second-order nonlinear optics, linear and hyperbranched polymers, orientation thermal stability, trade-off.

1. INTRODUCTION

Organic/polymeric second-order nonlinear optical (NLO) materials have attracted much attention for their potential applications in optical communication and modulators. Though high-speed electro-optical (EO) devices with very broad bandwidth (> 200 GHz) and low driving voltage (< 1 V) have been achieved, there are still two main challenges to be well resolved for practical applications.¹⁻⁴ The first challenge is how to efficiently translate the high molecular first hyperpolarizabilities (β) into large macroscopic EO coefficient (r_{33}) or second harmonic generation (SHG) coefficient (d_{33}).^{5,6} The second one is the nonlinearity-transparency-orientation thermal stability trade-off.⁷ Nowadays, great successes have been achieved in enhancing the β values, but the harmony and balance of aforementioned issues are still not trivial tasks.

The involved problem in the first challenge is the anti-parallel aligned chromophores diminish the EO or SHG activities due to the high polarized intramolecular push-pull interactions among the chromophores, which will further decrease the NLO effect in the bulk during device fabrication.⁸ Much work has been done to tackle this aggregation-quenching problem. Recent theoretical analyses suggest that optimization of the molecular shape can bring about a boost in the maximum realizable EO activity.^{9,10} The NLO chromophores in spherically shaped molecules cannot regularly stack in a side-by-side fashion. Dendrimer possesses a spherical shape, and indeed, dendritic molecules containing NLO chromophores have been demonstrated to display large EO coefficients. Dendrimers are, however, tedious to synthesize and are commonly used by doping into film-forming polymer matrices. In sharp contrast, hyperbranched polymers are easy to synthesize and can be used in pure forms without doping into other matrices because of their own good film-forming ability. The three-dimensional spatial separation of the chromophores endows the polymers with favorable site-isolation effect, and their void-rich topological structure helps minimize optical loss in the NLO process.¹¹⁻¹³ The globular macromolecules are thus promising candidates for NLO materials with large bulk EO activities.

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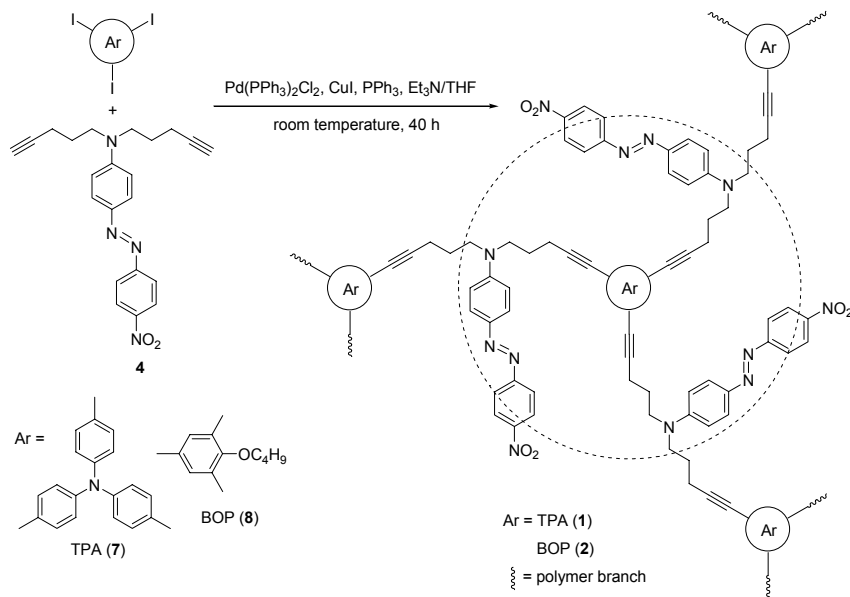
We have previously synthesized a series of hyperbranched polyarylenes through alkyne polycyclotrimerization.¹⁴ Due to their structural rigidity, these polymers enjoy excellent morphological stability, with no glass transition temperatures (T_g) detectable in the measured temperature region (room temperature to 180 °C) of the differential scanning calorimetry (DSC) analysis. In our group, we also systematically investigated mono- and disubstituted polyacetylenes (PAs).¹⁵ It turns out that the disubstituted PAs generally demonstrate much better stability. For example, poly(1-phenyl-1-octyne), a disubstituted PA, strongly resists thermal decomposition (no molecular weight change detectable after annealing in air at 120 °C for 20 hrs).¹⁶⁻¹⁸ Thus, combining with the high glass transition temperature, PAs would surely benefit the polymeric NLO materials as the backbone. Till now, however, there are no reports concerned about the NLO disubstituted polyacetylenes.

On the other hand, indole-based NLO chromophores and polymers containing indole-based NLO chromophores as side groups have shown the trade-off of nonlinearity, relatively good transparency, and high orientation thermal stability.¹⁹ By means of post-functionalization, a series of polymers with indole-based chromophores as side chain are prepared and their properties also confirm the advantages mentioned above.²⁰⁻²² It is notable that those polymers with sulfonyl groups as the acceptor in the structure of their NLO chromophores show even better trade-off properties, such as their UV absorption maxima wavelength shorter than 400 nm. Meanwhile, the polymeric backbones used before, such as polyphosphazenes and polysiloxanes, are not good to the chromophore orientation thermal stability due to their flexible main-chains with relatively low glass transition temperature (T_g). This prompts us to attach the indole-based NLO chromophores to rigid polymeric backbone to obtain NLO polymers with higher T_g and better thermal stabilities.

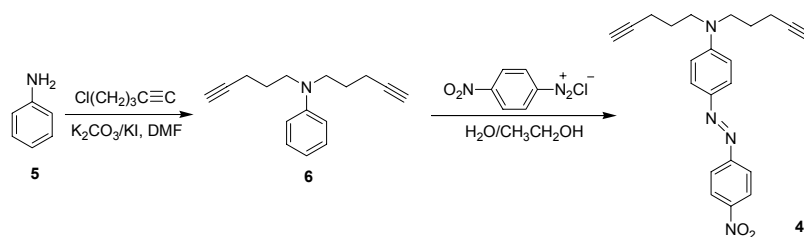
In this contribution, we would like to report our efforts to solve above challenges. Firstly, we synthesized two hyperbranched poly(aryleneethynylene)s (*hb*-PAEs) by Sonogashira coupling reactions (Scheme 1). The *hb*-PAEs are macroscopically processable, thermolytically resistant, and morphologically stable. Polymer **2** exhibits a high SHG coefficient ($d_{33} = 177$ pm/V), outperforming lithium niobate (LiNbO₃), a practical and technologically important inorganic crystal, in terms of EO activity. Then, a disubstituted polyacetylene **3** with sulfonyl groups as acceptor by post-functionalization was synthesized, combining the trade-off of this type NLO chromophore and the thermally stable and relatively rigid disubstituted PAs. Polymer **3** shows the maximum absorption at 393 nm and onset depoling temperature as high as 160 °C.

2. EXPERIMENTAL SECTION

The synthetic routes of hyperbranched polymer **1** and **2** and their diacetylene chromophore are given in Scheme 1 and 2. The synthesis of disubstituted PA **3** containing NLO chromophores is shown in Scheme 3.



Scheme 1 Construction of hyperbranched polymers by Sonogashira coupling



Scheme 2. Synthesis route of the diacetylene chromophore

2.1 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. Other reagents were all purchased from Aldrich and used as received without further purification. Other solvents were purified before use by standard methods. Tris(4-iodophenyl)amine (**7**) was prepared according to the published procedures.²³

2.2 Instrumentation

The ¹H and ¹³C NMR spectra were measured on a Bruker ARX 300 spectrometer using tetramethylsilane (TMS; $\delta = 0$ 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 polymers were evaluated on a Perkin-Elmer thermogravimetric analyzer TGA 7 at a heating rate of 20 °C/min under nitrogen. Their thermal transitions were studied using a Setaram DSC92 at a scanning rate of 10 °C/min under nitrogen. The average molecular weights (M_w) and polydispersity indices (M_w/M_n) of the polymers were estimated by gel permeation chromatography (GPC) using a Waters Associates liquid chromatography 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 μ m 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.

2.3 Monomer preparation²⁴

N,N-Bis(4-pentynyl)benzenamine (**6**): Into a dry 100 mL flask were added 1.86 g of aniline (**5**) (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 48 h under nitrogen. The suspension was cooled to room temperature and filtered. The filtrate was poured into water (500 mL) and extracted with chloroform (200 mL \times 4). The combined organic phase were washed with water and dried over sodium sulfate and then concentrated. The residue was purified on a silica gel column using chloroform as eluent. Colorless oil of **6** was obtained in 30% yield (1.7 g). ¹H NMR (300 MHz, CDCl₃), 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). ¹³C NMR (75 MHz, CDCl₃), δ (TMS, ppm): 148.2, 129.7, 116.5, 112.7, 84.1, 69.4, 50.3, 26.2, 16.4.

(*E*)-4-[2-(4-Nitrophenyl)diazonyl]-*N,N*-bis(4-pentynyl)benzenamine (**4**): 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 **6** (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 **4** (63% yield). IR (thin film), ν (cm⁻¹): 3200 (\equiv C–H stretch), 1515, 1337 (NO₂ stretch), 858 (C–N stretch), 625 (\equiv C–H bend). ¹H NMR (300 MHz, CDCl₃), 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). ¹³C NMR (75 MHz, CDCl₃), 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).

2.4 Hyperbranched polymer synthesis

Hyperbranched polymers **1** and **2** were synthesized by palladium-catalyzed polycoupling (Sonogashira coupling) of triiodides **7** and **8** with diethynylazobenzene **4**, respectively. A typical experimental procedure for the preparation of polymer **1** is given below as an example.

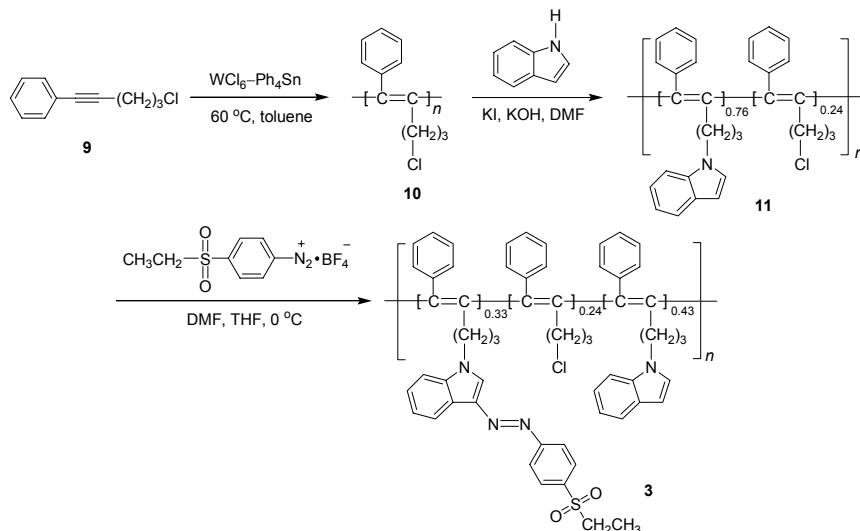
In a dry Schlenk tube were placed 124.6 mg of **7**, 112.2 mg of **4**, 10 mg of PdCl₂(PPh₃)₂, and catalytic amounts of CuI and PPh₃ in a glove box. Dry THF (5 mL) and Et₃N (0.5 mL) were then added. The resultant mixture was stirred at room temperature for 40 h. The mixture was passing through a cotton 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 vacuum at 40 °C to a constant weight.

Characterization Data for polymer **1**: Red powder: yield 110 mg (46.5%). *M_w* 8600; *M_w/M_n* 1.9 (GPC, polystyrene calibration). IR (thin film), ν (cm⁻¹): 1516, 1337 (NO₂ stretch), 856 (C–N stretch). ¹H NMR (300 MHz, CDCl₃), δ (TMS, ppm): 8.22, 7.80, 7.49, 7.25, 6.91, 6.78, 3.58, 2.46, 2.33, 1.90. ¹³C NMR (75 MHz, CDCl₃), 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 μ g/mL), λ_{max} (nm): 238, 325, 485.

Polymer **2**: Red powder: yield 107 mg (49.3%). *M_w* 11300; *M_w/M_n* 2.0 (GPC, polystyrene calibration). IR (thin film), ν (cm⁻¹): 1514, 1337 (NO₂ stretch), 856 (C–N stretch). ¹H NMR (300 MHz, CDCl₃), 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 μ g/mL), λ_{max} (nm): 240, 484.

2.5 Polyacetylene synthesis by postfunctionalization²⁵

Monomer 5-chloro-1-phenyl-1-pentyne **9** and polymers **10** and **11** were synthesized followed the reported procedures according the routes in Scheme 3. The procedures for preparation of polymer **3** are shown below.



Scheme 3. Synthesis of second-order nonlinear polyacetylenes by post-functionalization.

Polymer **11** (90 mg) was dissolved in the mixture of DMF/THF (0.8/0.4 mL). Then 40 mg *p*-ethylsulfonylbenzenediazonium fluoroborate was added under cooling with an ice bath. The color of the solution changed to red immediately. After stirring for 8 h at 0 °C, excessive anhydrous potassium carbonate was added and the mixture was stirred for another one hour. After filtration, the residue was washed with THF. The filtrates were collected and THF was removed under reduced pressure. The polymer was then precipitated into methanol. After several precipitations from THF into methanol, the solid was dried in vacuum at 40 °C to give 98 mg of orange red product. *M_w* 20300; *M_w/M_n* 2.8 (GPC, polystyrene calibration). IR (thin film), ν (cm⁻¹): 3056 (Ar-H stretching), 2960, 2876 (CH₂ stretching), 1132 (SO₂ stretch). ¹H NMR (300 MHz, CDCl₃), δ (TMS, ppm): 8.37, 7.98, 7.26, 7.00, 6.40, 3.59, 2.11, 1.77, 1.12. UV-Vis (THF, 0.036 mg/mL): λ_{max} : 393 nm.

2.6 Film fabrication

The polymers were dissolved in THF (concentration ~4 wt %) and the solutions were filtered through 0.45 μm PTFE filters. The polymer solutions were spin coated onto indium-tin oxide (ITO)-coated glass substrates, which were carefully pre-cleaned by DMF, acetone, distilled water, and THF sequentially in ultrasonic bath. The polymer films were dried in a vacuum oven at 40 $^{\circ}\text{C}$ for two days to remove residual solvent. The film thickness was measured by a TENCOR 500 Surface Profiler.

2.7 NLO measurement

The prepared polymer films were poled by corona poling at elevated temperature. The second-order NLO coefficient d_{33} of the films was measured by an in situ SHG technique with a Q-switch Nd:YAG laser at 1064 nm fundamental wavelength as described before.²⁶ A closed temperature-controlled oven with optical windows and three needle electrodes was used. The film was poled inside the oven, and the intensities of the SHG signal were determined simultaneously. The film was laid 0.8 cm from the points of the needle and at 45 $^{\circ}$ to the incident beam. A Y-cut quartz crystal was used as a reference. The SHG signals were collected by PMT. The NLO coefficient d_{33} was deduced by comparing the intensities of the SHG signals of the poled film with that of the quartz crystal. The dependence of the poling-induced orientation stability temperature (i.e., the depoling curve of the poled film) was also examined with this apparatus.

3. RESULTS AND DISCUSSION

3.1 Polymer synthesis

To synthesize the *hb*-PAEs by palladium-catalyzed halide-acetylene coupling, we first prepared three monomers, i.e., two aryltriiodides (**7** and **8**) and one azo-diyne (**4**). All the reactions proceed smoothly and the monomers are obtained in good yields. Whereas monomer **8** is a known compound,²⁷ and monomer **4** is a new one (Scheme 2). The coupling reactions of the triiodides and the diynes are carried out in THF/ Et_3N using $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ as catalyst (Scheme 1). We initially worried that the reactions may run out of control to yield insoluble networks, as in some of our previously studied alkyne polymerization systems.²⁸⁻³¹ We cautiously monitored the reactions by precipitating small fractions of the reaction mixtures into acetone from time to time. Delightfully, the polymerizations proceed in moderate rates with no precipitates being formed during the whole course of the reactions. The products are purified by repeated precipitations of their THF solutions into acetone and obtained in good yields (Table 1). GPC analyses prove their polymeric nature, although their M_w values are only moderate. It should, however, point out that the GPC analysis using linear polystyrenes as calibration standards often underestimates the M_w of hyperbranched polymers with difference as big as ~40 times.^{32,33} The actual or true molecular weights of the *hb*-PAEs thus could be much higher than the values given in Table 1.

Table 1. Syntheses and Optical Properties of polymers **1**, **2**, and **3**

polymer	yield (%)	M_w^a	M_w/M_n^a	λ_{max}^b	d_{33} (pm/V) ^c	T_d ($^{\circ}\text{C}$) ^e
1	46.5	8 600	1.9	483	55	152
2	49.3	11 300	2.0	482	177	133
3	70.3 ^d	20 300	2.8	393	17.9	160

^a Determined by GPC in THF on the basis of a polystyrene calibration. ^b Absorption maximum of the polymer solutions in THF. ^c Second-harmonic generation coefficient. ^d Yield of polymer **10**. ^e The onset depoling temperature.

We have successfully prepared the disubstituted polyacetylenes containing carbazole moieties by polymerization of their monomers directly.³⁴ As the indole appends in polymer **3** are structural resemble to carbazole moieties, we thus first attempted to polymerize 1-phenyl-1-pentyne containing indole functionality. Polymerizations catalyzed by $\text{WCl}_6\text{-Ph}_4\text{Sn}$ in toluene at 60 $^{\circ}\text{C}$, give no or only low molecular weight products. Thus, we redesigned the synthetic procedures to polymer **3** (Scheme 3) and adopted a post-functionalization method to attach the NLO chromophores to the disubstituted PA mainchains. Polymer **10** can prepared with ease from the polymerization of its monomer, the chlorine atoms in **10**

could be substituted by indole rings at the presence of base. Reaction of *p*-ethylsulfonylbenzenediazonium fluoroborate with the indole ring finally affords the indole-azo chromophore-functionalized polyacetylene **3**. The synthetic procedures are very simple and only monomer **9** needs to be purified by silica gel chromatography. All the polymers are purified by simply precipitations of their THF solutions into methanol. The advantage of this synthetic route is that it can be used to prepare polymer with very polar functional groups, which are inaccessible directly from their monomers.

3.2 Structural characterization

The polymers are characterized spectroscopically and satisfactory spectral data corresponding to their molecular structures are obtained. Figure 1 shows the IR spectra of polymers **1** and **2**. The spectrum of monomer **4** is also shown for comparison. Whereas $\equiv\text{C-H}$ stretching and bending vibrations of **4** absorb at 3200 and 625 cm^{-1} , respectively, the absorption bands associated with the nitro groups appear at 1515 , 1337 , and 858 cm^{-1} (Figure 1A). After polymerization, the spectra of the *hb*-PAEs show no peaks at 3200 and 625 cm^{-1} . The resonances of the nitro functionalities are still observed, thus spectroscopically proving that the alkyne polycoupling has propagated and the NLO chromophore has been successfully incorporated into the polymer structures.

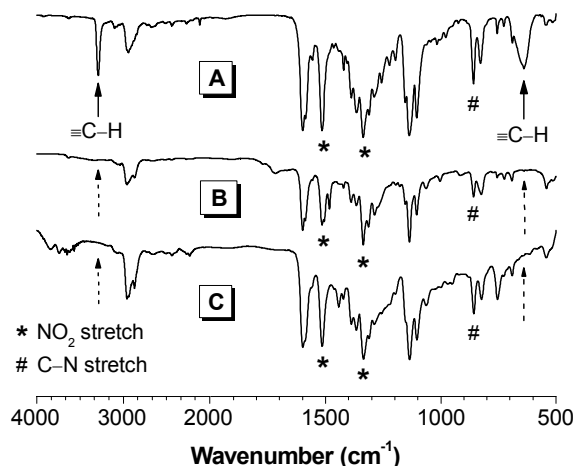


Figure 1. IR spectra of monomer **4** (A) and polymers **1** (B) and **2** (C)

Figure 2 shows the IR spectra of polymers **11** and **3**. An apparent new strong absorption band assigned to the absorption of the sulfonyl groups appears at 1134 cm^{-1} , revealing that the *p*-ethylsulfonylbenzenediazonium fluoroborate does react with the indole ring and furnishing polymers with sulfonyl pendant groups.

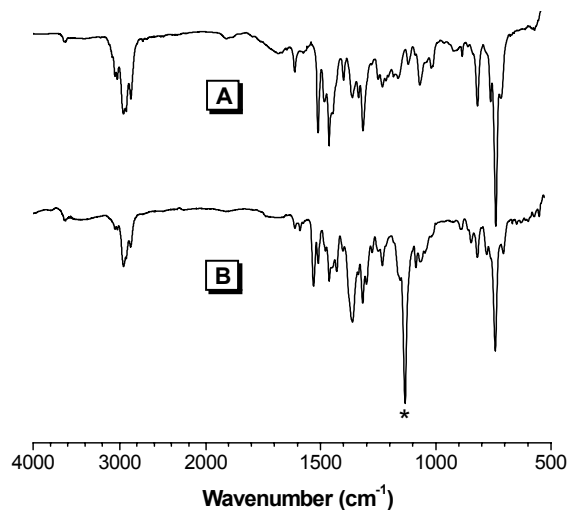


Figure 2. IR spectra of polymers **11** (A) and **3** (B). The absorption band of sulfonyl group is marked with an asterisk (*).

The ^1H NMR spectrum of monomer **4** shows a characterized acetylene protons (9) resonance at δ 2.04 (Figure 3B), which completely disappeared in the spectrum of polymer **1** (Figure 3C). Compare with monomers **7** and **4**, two new resonance peaks (30 and 31) at δ 7.24 and 6.92 in **1** are emerged. To identify the origins of these new resonances, a model compound, namely, tris[4-(1-pentynyl)phenyl]amine (**12**), is synthesized by coupling of **7** with 1-pentyne. The spectrum of the model compound helps the structural elucidation: peaks 30 and 31 can now be readily assigned to the resonances of the protons of the aromatic rings of the aryleneethynylene units of polymer **1** (right of Figure 3). The appearance of peak 2 at δ 7.49 indicates that the polymer contains iodide residues in the form of linear monoiodide and terminal diiodide units.

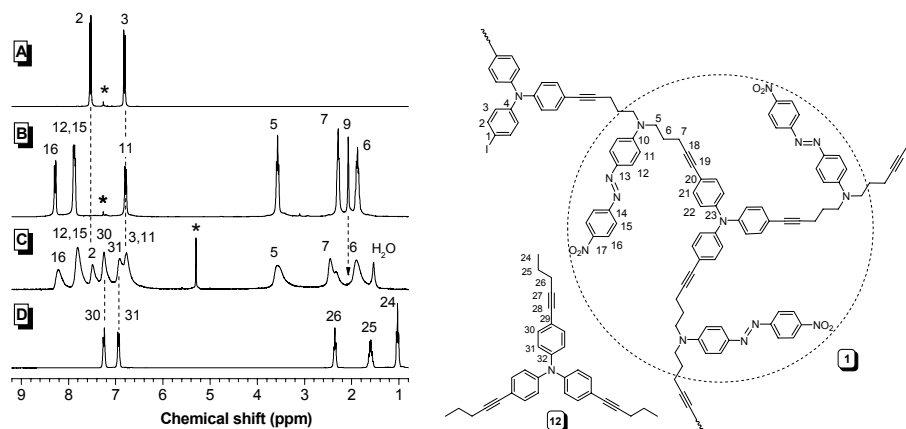


Figure 3. ^1H NMR spectra of monomers **7** (A) and **4** (B), polymer **14** (C) and model compound **12** (D) in chloroform- d (A, B, and D) and dichloromethane- d_2 (C). The labels of the peaks of the protons correspond to those given in Scheme 1 and right of this Figure. The solvent peaks are marked with asterisks.

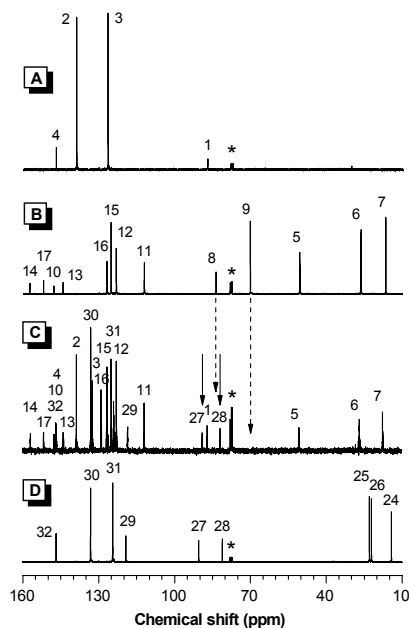


Figure 4. ^{13}C NMR spectra of chloroform- d solutions of monomers **7** (A) and **4** (B), polymer **1** (C), and model compound **12** (D). The labels of the resonance peaks of the carbon atoms correspond to those given in Scheme 1 and right of Figure 3. The solvent peaks are marked with asterisks.

The ^{13}C NMR analyses offer similar structural information. As shown in Figure 4, all the resonance peaks can be readily assigned. Polymer **1** displays no resonance peaks of the carbon atoms of terminal acetylene (8 and 9). Instead, those of

internal acetylenes are observed (18 and 19), again verifying the proceeding of the coupling reaction. Similarly, the spectral data of polymers **2** and **3** well correspond to their expected molecular structures, and no unexpected or strange signals are observed.²⁵

3.3 Linear and nonlinear optical properties

Figure 5 shows the UV spectra of the THF solutions of polymers **1**, **2**, and **3** and its precursor **11**. Polymer **1** absorbs at 238 (K band), 325 (B band) and 485 nm due to the π - π^* transitions of its benzene, triphenylamine, and azobenzene chromophores. Polymer **2** absorbs at 240 and 484 nm owing to the electronic transitions of its benzene and azobenzene chromophores, respectively. Polymer **3** is more transparent and absorbs at 393 nm due to enhancement of the conjugation after reaction of precursor **11** with *p*-ethylsulfonylbenzenediazonium fluoroborate. The amount of NLO chromophore incorporated can be estimated by a literature method.²⁵ The absorbance of **2** at 484 nm is higher than that of **1** 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 **2** has a lower molar mass than that of **1**.

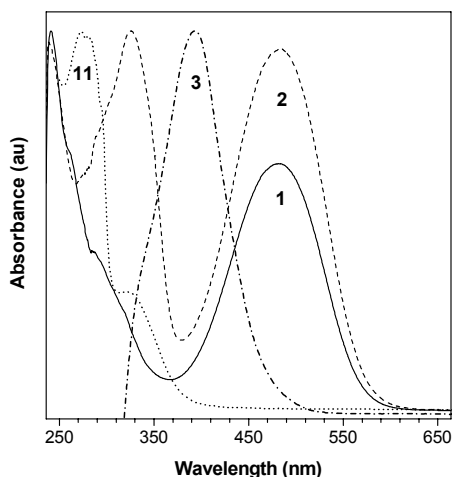


Figure 5. UV spectra of THF solutions of polymers **1**, **2** (concentration: 28 $\mu\text{g}/\text{mL}$), and **3** and precursor **11** (concentration: 36 $\mu\text{g}/\text{mL}$).

All the polymers are soluble in common organic solvents such as chloroform, THF, DMF, and DMSO. They can form tough, thin solid films by solution spin-coatings. All the polymers are thermally resistant: **1**, **2**, and **3** lose 5% of their original weights at temperatures as high as 265, 258 and 326 $^{\circ}\text{C}$, respectively. No glass transitions are detectable when they are heated to 180 $^{\circ}\text{C}$ (the highest temperature allowable for the DSC measurements at our instrumentation center), that is, the polymers possess high T_g values. The polymers are thus macroscopically processable, thermally resistant, and morphologically stable, which will be benefit to the orientation thermal stability of the chromophores when the polymers are fabricated into EO devices.

To evaluate the optical nonlinearity of these polymers, 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 given below:³⁵

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

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, 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 polymers **1**, **2**, and **3** are calculated to be 55, 177, and 17.9 pm/V, respectively, at the fundamental wavelength of 1064 nm (Table 1). Various d_{33} values have been reported for different

polymers containing azo dye moieties similar to polymers **1** and **2**, with the highest value of 169 pm/V being reported by Yu et al.³⁶ The d_{33} value of an NLO polymer can be totally different when measured by different testing systems, which makes direct data comparison difficult. However, compared with the d_{33} values of the polymers bearing similar azobenzene chromophores and measuring with the same apparatus, the d_{33} values of the synthesized polymers, especially the value for **2**, are outstandingly high.^{37,38} The impressively high d_{33} values of polymers **1** and **2** 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 **1** and **2** may mainly stem from their structural difference. According to the one-dimensional rigid orientation gas model,³⁹

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

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, **2** possesses a relatively small comonomer unit and hence a relatively high azo-dye density, in comparison to **1**. Assuming a same poling efficiency and according to eq 2, **2** should exhibit a higher d_{33} value.

The dynamic thermal stability of the poling-induced orientation of the poled films was evaluated by a depoling experiment in which the poled film was heated with an increasing temperature rate of 5 °C/min without the applied electric field. The decay of the SHG intensity was monitored as a function of temperature. The depoling curve can provide information about the decay of the SHG intensity and quick, effective access to evaluate the temporal stability of the poled polymers. The onset depoling temperatures (T_d) of **1**, **2**, and **3** are found to be as high as 152, 133, and 160 °C, respectively (Figure 6). The reason is that these high T_d values of chromophore-containing polymers are partially due to the high T_g values of polymers, thanks to their rigid molecular structures. Especially, the thermal curing of *hb*-PAEs 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 cross-linking reaction by moderate heating.⁴⁰ The resultant thermosetting networks impede the depoling relaxation processes, hence shifting the T_d values to the high temperature region.

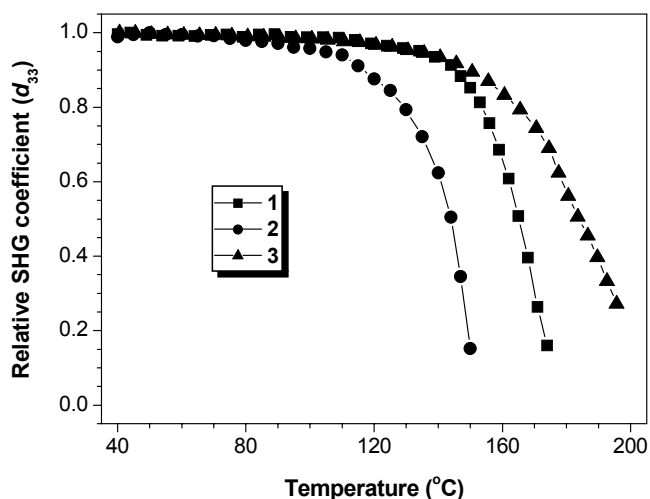


Figure 6. Depoling curves of poled polymer films of **1**, **2**, and **3**.

4. CONCLUSION

In summary, trying to solve the encountered challenges in the field of organic/polymeric NLO materials, we prepared two types of azobenzene-containing polymers. The *hb*-PAEs **1** and **2** are synthesized through a simple Sonogashira

coupling. We demonstrated the beneficial effects of the spherical shape of, and site isolation in, these *hb*-PAEs on their optical nonlinearities, which result in large d_{33} values and high orientation thermal stabilities. The linear polymer **3** was obtained by post-functionalization reaction, and it shows the trade-off the nonlinearity-transparency-orientation thermal stability. These advanced properties make them potential materials in electro-optical applications in the future.^{41,42}

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