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Polymer 46 (2005) 5746–5751

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Facile synthesis, high thermal stability, and unique optical properties of hyperbranched polyarylenes

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Received 3 January 2005; received in revised form 1 May 2005; accepted 2 May 2005
Available online 2 June 2005

Abstract

New hyperbranched polyarylenes of high molecular weights are synthesized in high yields by copolycyclotrimerizations of diynes 1,4-diethynylbenzene, 4,4′-diethynylbiphenyl, 2,7-diethynylfluorene and 2,5-diethynylthiophene with monoynes 1-heptyne, 1-octyne and 1-dodecyne catalyzed by $TaCl_5$–Ph_4Sn in toluene. All the polymers show good solubility in common organic solvents, possess excellent thermal stability, and emit strong deep-blue lights of ∼400 nm with quantum efficiencies up to 98%. The polyarylenes effectively limit 532 nm lasers light, some of which show optical limiting performances superior to that of C_{60}, a well-known optical limiter.

Keywords: Hyperbranched polymers; Polyarylenes; Alkyne polycyclotrimerization

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1. Introduction

Hyperbranched polymers have attracted considerable attention over the past years because of the expectation that their unique molecular shape, branching pattern, and surface functionality may impart unusual properties [1,2]. Methodologies for the synthesis of hyperbranched polymers are, however, rather limited. The most common approaches are polycondensation of AB_m monomers developed by Kim and Webster [3–6] and self-condensing vinyl polymerization introduced by Frèchet and co-workers [7–9]. The stoichiometric requirements in such polymerizations are difficult to meet in practice, which often lead to the formation of low molecular weight polymers.

We are interested in synthesizing hyperbranched polymers by transition metal-catalyzed polycyclotrimerizations of diynes [10–15]. Cyclotrimerization of alkynes is an atom-economic reaction to give benzene derivatives [16] and its chemo-and regioselectivity tunable by the catalysts make it perhaps the most general reactions of [2+2+2] cycloadditions [17,18]. The diverse substitution patterns of the resulting benzene rings allow us to obtain conjugated hyperbranched polymers with multiplex linkage styles. Moreover, this polymerization generally involves a single monomer, suffers no stoichiometric constraints, and thus can produce polymers with very high molecular weights. Although chemists have intensively investigated the cyclotrimerizations of various diynes during the last half century, their efforts are mainly focused on low molecular weight compounds such as cyclodimers and cyclotrimers.

In this paper, we used transition metal catalyst to initiate copolycyclotrimerizations of diynes with monoynes and succeeded in synthesizing a group of soluble, high molecular weights hyperbranched polyarylenes (Scheme 1). The electronic communication between the newly formed benzene rings in the polycyclotrimerization and the old aromatic rings in the monomers has endowed the polymers with novel light-emitting and optical limiting properties.

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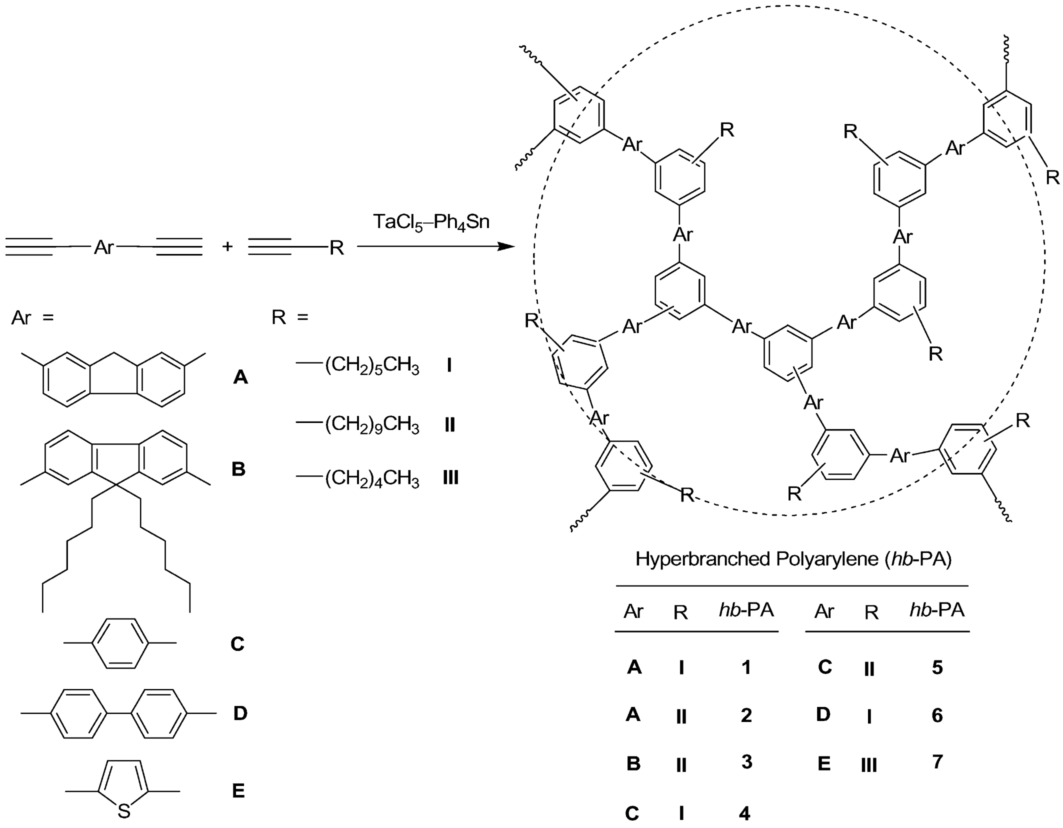
doi:10.1016/j.polymer.2005.05.039



Ar	R	*hb*-PA	Ar	R	*hb*-PA
A	**I**	**1**	**C**	**II**	**5**
A	**II**	**2**	**D**	**I**	**6**
B	**II**	**3**	**E**	**III**	**7**
C	**I**	**4**			

Scheme 1. Syntheses of hyperbranched polyarylenes by the copolycyclotrimerizations of diynes (**A**–**E**) with monoynes (**I**–**III**) initiated by transition metal catalyst $TaCl_5$–Ph_4Sn.

2. Experimental section

2.1. Materials

Catalyst $TaCl_5$ and cocatalyst Ph_4Sn were purchased from Aldrich and used as received. Diyne monomers **A**–**E** were prepared according to our previously published synthetic procedures [19–21]. Monoynes **I**–**III** were purchased from Aldrich and distilled over calcium hydride prior to use.

2.2. Instrumentation

IR spectra were measured on a Perkin–Elmer 19 PC IR spectrophotometer. UV spectra were measured on a Milton Ray Spectronic 3000 Array spectrophotometer. Fluorescence spectra of the polymers in dichloromethane (DCM) were recorded on a SLM 8000C spectrofluorometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker ARX 300 spectrometer using chloroform-*d* as solvent and tetramethylsilane (TMS) as internal reference. Molecular weights (M_w and M_n) of the polymers were estimated in THF using a polystyrene calibration by a Waters Associates gel permeation chromatograph (GPC) system. The real or absolute molecular weight of the polymers was determined by a size exclusion chromatograph system (SEC) (Model T60, Viscotek) on line with a refractive index (RI) detector (Model 410, Waters), a right-angle laser-light scattering photometer (RALLS), and a four capillary bridge design differential viscometer (DV) in THF at 25 °C. Thermal stability of the polymers was evaluated on a Perkin–Elmer TGA 7 at a heating rate of 20 °C/min under nitrogen. Optical limiting experiments were performed at 532 nm using 8-ns pulses from a frequency-doubled Q-switched Nd:YAG laser (Quanta Ray GCR-3) operating in a near-Gaussian transverse mode with a repetition rate of 10 Hz. The pulsed laser beam was focused onto 1-cm square quartz cell filled with DCM solutions of the polymers.

2.3. Polymerization

Copolymerization reactions were carried out in a dry nitrogen atmosphere. A typical procedure for the copolymerization of diyne **C** with monoyne **I** is given below. Into a thoroughly baked and moisture-excluded Schlenk tube were placed 18.0 mg of $TaCl_5$ (0.05 mmol) and 21.3 mg of Ph_4Sn (0.05 mmol) in a glovebox. The catalysts were mixed with 1.0 mL toluene and aged at room temperature for 15 min. A solution of 40 mg (0.318 mmol) **C** and 47 μL (0.366 mmol) **I** in 1.45 mL toluene was then added dropwise into the catalyst solution. After stirring at room temperature for 12 h, the reaction was quenched by the addition of a small

Table 1
Copolymerizations of diynes **A**–**E** with monoynes **I**–**III**

hb-PA	[M_{II}] (M)[a]	[M_I] (M)[a]	Yield (%)	M_w[b]	M_w/M_n[b]
1	0.070 (**A**)	0.11 (**I**)	81.9	41,100	5.6
2	0.070 (**A**)	0.11 (**II**)	70.1	72,300	5.7
3	0.070 (**B**)	0.09 (**II**)	74.1	93,400	8.7
4	0.127 (**C**)	0.153 (**I**)	93.7	38,000	4.0
5	0.127 (**C**)	0.102 (**II**)	76.1	67,200	9.6
6	0.127 (**D**)	0.152 (**I**)	68.9	183,100	5.6
7	0.127 (**F**)	0.114 (**III**)	65.5	33,500	8.1

Carried out in toluene at room temperature under nitrogen for 12 h using $TaCl_5$–Ph_4Sn as catalyst. [cat.] = [cocat.] = 20 mM.

[a] [M_{II}] and [M_I] are molar concentrations of diynes and monoynes, respectively.

[b] Estimated by GPC in THF on the basis of a polystyrene calibration.

amount of methanol. The polymer solution was dropped into 250 mL methanol via a cotton filter under stirring to precipitate the polymer. The crude product was further purified by pouring its chloroform solution into hexane. Light yellow powdery product **4** was collected and dried in vacuum overnight. Yield: 93.7%. M_w 38,000; M_w/M_n 4.0 (GPC, polystyrene). IR (KBr), ν (cm^{-1}): 3024, 2923, 2853, 1595, 1498, 812. ^1H NMR (300 MHz, CD_2Cl_2), δ (TMS, ppm): 7.9–6.8 (Ar–H), 2.63 (Ar–CH_2), 1.64–0.86 [$(CH_2)_4CH_3$]. ^{13}C NMR (75 MHz, CD_2Cl_2), δ (TMS, ppm): 138–145 (aromatic carbons), 124–132 (aromatic carbons), 36.2, 32.0, 31.8, 29.3, 22.9, 22.7, 14.1. Other polymers are prepared in a similar fashion.

2.4. Characterization data

1: light yellow powder; yield 81.9%. M_w 41,100; M_w/M_n 5.6 (GPC, polystyrene). IR (KBr), ν (cm^{-1}): 3022, 2956, 2927, 2856, 1717, 1597, 1465, 1407, 1275, 862, 817, 738. ^1H NMR (300 MHz, CD_2Cl_2), δ (TMS, ppm): 7.92–7.11 (Ar–H), 4.05, 2.62 (Ar–CH_2), 1.91–1.1.10 [$(CH_2)_4$], 0.91 (CH_3). ^{13}C NMR (75 MHz, CD_2Cl_2), δ (TMS, ppm): 144.5–120.3 (aromatic carbons), 36.2, 32.0, 31.8, 29.3, 22.9, 22,7, 14.1.

2: light yellow powder; yield 70.1%. M_w 72,300; M_w/M_n 5.7 (GPC, polystyrene). IR (KBr), ν (cm^{-1}): 3019, 2924, 2853, 1892, 1715, 1596, 1465, 1407, 1275, 862, 816, 758, 718. ^1H NMR (300 MHz, CD_2Cl_2), δ (TMS, ppm): 7.92–7.11 (Ar–H), 4.05, 2.62 (Ar–CH_2), 1.91–1.10 [$(CH_2)_8$], 0.91 (CH_3). ^{13}C NMR (75 MHz, CD_2Cl_2), δ (TMS, ppm): 145.1–120.1 (aromatic carbons), 37.8, 36.8, 32.6, 32.4, 30.4, 29.8, 28.7, 23.3, 14.5.

3: yellow powder; yield 74.1%. M_w 93,400; M_w/M_n 8.7 (GPC, polystyrene). IR (KBr), ν (cm^{-1}): 3025, 2918, 2845, 1594, 1466, 817. ^1H NMR (300 MHz, CD_2Cl_2), δ (TMS, ppm): 7.31–8.01 (Ar–H), 2.67 (Ar–CH_2), 2.10, 1.78, 1.11–1.29, 0.88. ^{13}C NMR (75 MHz, CD_2Cl_2), δ (TMS, ppm): 152.6, 144.5–141.0, 127.1–120.3 (aromatic carbons), 56.1, 41.3, 36.9, 33.7, 32.8, 32.6, 32.3, 30.5, 30.4, 30.2, 24.7, 23.5, 23.4, 14.7, 14.6.

Table 2
Molecular weight and intrinsic viscosity of hyperbranched polyarylenes

hb-PA	M_w	PDI[a]	IV (dL/g)[a]
1	1,139,000	7.3	0.164
4	2,961,000	4.1	0.157
5	2,323,000	3.7	0.264
6	1,049,000	14.3	0.205

Determined by SEC/RI/RALLS/DV in THF at 25 °C.

[a] Abbreviations: PDI, polydispersity index and IV, intrinsic viscosity.

5: light yellow powder; yield: 76.1%. M_w 67,200; M_w/M_n: 9.6 (GPC, polystyrene). IR (KBr), ν (cm^{-1}): 3028, 2924, 2853, 1907, 1786, 1596, 1512, 1465, 1379, 1216, 1112, 10006, 887, 819, 758, 705. ^1H NMR (300 MHz, CD_2Cl_2), δ (TMS, ppm): 6.8–7.8 (Ar–H), 2.63, 0.86–1.64. ^{13}C NMR (75 MHz, CD_2Cl_2), δ (TMS, ppm): 136–144, 121–133 (aromatic carbons), 36.8, 32.6, 32.3, 30.3, 30.0, 23.4, 14.8.

6: yellow powder; yield 68.9%. M_w 183,100; M_w/M_n: 5.6 (GPC, polystyrene). IR (KBr), ν (cm^{-1}): 3024, 2923, 2853, 1595, 1498, 812. ^1H NMR (300 MHz, CD_2Cl_2), δ (TMS, ppm): 6.8–7.9 (Ar–H), 2.6, 0.6–1.8. ^{13}C NMR (75 MHz, $CDCl_3$), δ (TMS, ppm): 137–143, 124–132 (aromatic carbons), 31.5, 31.0, 22.4, 22.2, 14.0.

7: yellow powder; yield 65.5%. M_w 33,500; M_w/M_n: 8.1 (GPC, polystyrene). IR (KBr), ν (cm^{-1}): 2952, 2925, 2854, 1592, 1456, 799. ^1H NMR (300 MHz, $CDCl_3$), δ (TMS, ppm): 6.5–8.0 (Ar–H), 2.6, 0.6–1.8.

3. Results and discussion

3.1. Polymerization reaction

We synthesized a group of diyne monomers containing aromatic rings by Pd-catalyzed coupling of silylacetylene with dihaloarenes followed by base-catalyzed desilylation. The homopolymerizations of diynes **A**–**E** catalyzed by $TaCl_5$–Ph_4Sn all give insoluble gels. To suppress cross-linking reactions and improve the solubility of the resulting polymers, we carried out copolymerizations of the diynes with monoynes or 1-alkynes. Delightfully, all the reactions proceed smoothly and soluble polymers with high molecular weights are obtained in high yields (Table 1). It should be noted that the M_w data in Table 1 are relative to

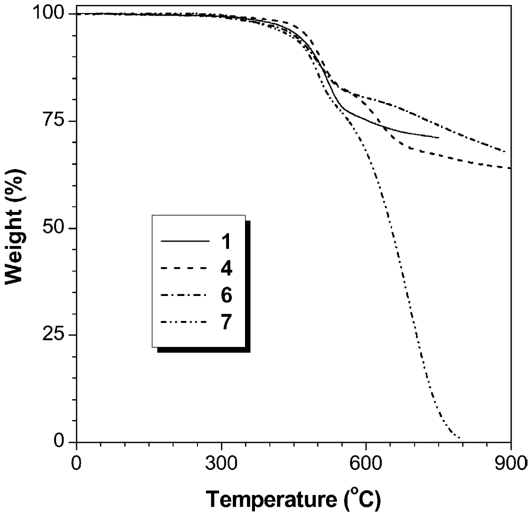


Fig. 1. TGA thermograms of hb-PAs **1**, **4**, **6** and **7** recorded under nitrogen at a heating rate of 20 °C/min.

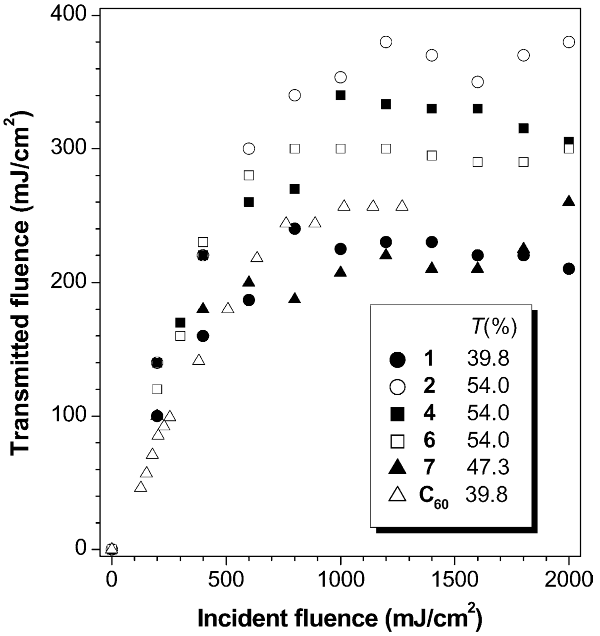


Fig. 3. Optical limiting responses to 8-ns, 10-Hz pulses of 532 nm laser light, of hb-PAs **1**, **2**, **4**, **6** and **7** in dichloromethane. Polymer concentration: 0.86 mg/mL. Optical pathlength: 10 mm. A toluene solution of C_{60} with a concentration of 0.11 mg/mL is shown for comparison.

polystyrene standards. In our previous study [12], we have found that the polystyrene calibration often underestimates the molecular weights of hyperbranched polymers, with up to seven fold differences. This is also the case here. As can be seen from Table 2, the molecular weights of hb-PAs **1**, **4**, **5** and **6** measured by SEC/RI/RALLS/DV are much higher than those by GPC, suggesting that they are hyperbranched, instead of linear in structures. Their intrinsic viscosities are very low, further substantiating their hyperbranched structures shown in Scheme 1.

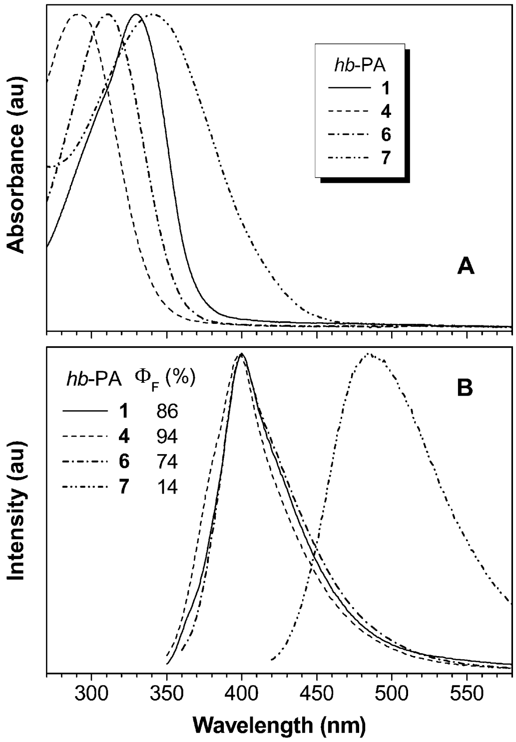


Fig. 2. (A) Absorption and (B) emission spectra of hb-PAs **1**, **4**, **6** and **7**. Excitation wavelength (nm): 352 (**1**), 333 (**4**), 341 (**6**) and 367 (**7**). Polymer concentration: 2.5 μg/mL.

3.2. Thermal stability

All the hb-PAs give satisfactory spectroscopic data corresponding to their expected molecular structures. The polymers show excellent thermal stability. The TGA thermograms of a few polymers are given in Fig. 1. Polymer **1** shows a 5% weight loss at ~451 °C (T_d), while T_d's of **4** and **6** are ~459 and ~438 °C, respectively. The stability of the hb-PAs is similar to that of poly(p-phenylene) [$-(C_6H_4)_n-$], which degrades at ~550 °C [22]. This is understandable because the hb-PAs are constructed from thermally stable aromatic rings, which should possess high resistance to thermolytic decomposition.

3.3. Absorption and emission

Fig. 2(A) shows the UV spectra of hb-PAs **1**, **4**, **6** and **7** in DCM. Polymer **1** shows a peak maximum (λ_{max}) at 331 nm, while λ_{max}'s of **4** and **6** are 292 and 311 nm, respectively. The fluorene rings in **1** are more conjugated than the phenyl and biphenyl moieties in **4** and **6**, which makes **1** more absorptive in the longer wavelength region. The absorption spectrum of thiophene-containing polymer (**7**) red-shifts from that of **1**. Clearly, the electronic transitions of the hb-PAs not only depend on the polarizability of the aromatic rings but are also affected by their molecular structures.

The fluorescence spectra of some hb-PAs are shown in Fig. 2(B). Strong fluorescence is emitted when the DCM

Table 3
Thermal and optical properties of hyperbranched polyarylenes

hb-PA	T_d[a] (°C)	W_r[b] (wt%)	λ_{max}[c] (nm)	λ_{em}[d] (nm)	Φ_F (%)[e]	F_L[f] (mJ/cm^2)	F_t/F_i[g]
1	451	68(892)	331	400	86	1000	0.15
2	459	63(900)	333	400	98	1107	0.19
3	438	47(909)	337	400	91	–	–
4	452	71(750)	292	400	94	1016	0.15
6	463	64(900)	311	400	74	1265	0.15
7	440	0(800)	340	486	14	881	0.13

[a] Temperature for 5% weight loss.
[b] Weight of residue at the temperature given in the parentheses.
[c] Absorption maximum in dichloromethane.
[d] Maximum emission wavelength in dichloromethane.
[e] Quantum efficiency using 9,10-diphenylanthracene as standard.
[f] Optical limiting threshold (incident fluence at which nonlinear transmittance is 50% of initial linear one).
[g] Signal suppression (ratio of saturated transmitted fluence to maximum incident fluence).

solutions of **1**, **4**, **6** and **7** are photoexcited. The fluorescence intensities are much higher than that of poly(1-phenyl-1-octyne), a well-known highly luminescent polyacetylene [23,24]. The interconnection of the new benzene rings formed by polycyclotrimerization and the 'old' aromatic rings from the monomers enhances electronic communications and thus endows the polymers with high emission intensity. We determined their fluorescence quantum yield (Φ_F) and found that all but **6** exhibit $\Phi_F > 70\%$, which are much higher than those of the hyperbranched polymers previously prepared by $CpCo(CO)_2$ [19]. Analysis by ^1H NMR spectroscopy reveals that those polymers contain small amounts of cobalt complexes, which causes partial emission quenching and decreases their Φ_F values.

3.4. Optical limiting

Fig. 3 shows the optical limiting behaviors of hb-PAs **1**, **2**, **4**, **6** and **7** in DCM. The transmitted fluence of **1** increases initially with the incident fluence at low fluence region but starts to deviate from linearity at a value of ~391 mJ/cm^2. It then reaches a plateau and saturates at ~230 mJ/cm^2. The transmittance from a toluene solution of C_{60} with the same linear transmittance ($T = 39.8\%$) begins to depart from linearity at an incident fluence of ~507 mJ/cm^2 and saturates at ~257 mJ/cm^2, both being higher than those of **1**. Thus **1** is a better optical limiter than C_{60}. The optical limiting performance of **7** is also better than C_{60}, which shows a higher linear transmittance but a lower saturation transmittance. All other polymers perform well and effectively limit the 532 nm laser pulses. Clearly the hb-PAs are a group of strong optical limiters. The hb-PAs consist of various clusters of aromatic ring structures, which is the intrinsic factor for them to exhibit optical limiting properties.

Table 3 summaries the thermal and optical properties of the hb-PAs. It is noteworthy that the amount of residue left after pyrolysis is high for all polymers expect for **7**. Together with their good light-emitting and optical-limiting properties, these thermally stable polymers may find an array of high-tech applications.

4. Conclusions

Soluble hyperbranched polyarylenes with high molecular weights have been prepared by one-pot copolycyclotrimerizations of diynes with monoynes. All the hb-PAs show excellent thermal stability. Upon photoexcitation, the DCM solutions of the polymers emit strong deep-blue light of ~400 nm in high efficiencies. The hb-PAs effectively attenuate 532 nm laser pulses, with some of them performing better than C_{60} as optical limiters.

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