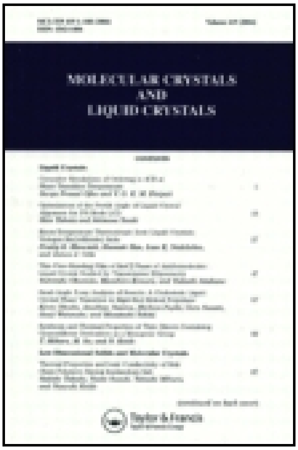

Molecular Crystals and Liquid Crystals

Conjugated Polymers with Linear and Hyperbranched Structures and Advanced Materials Properties

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CONJUGATED POLYMERS WITH LINEAR AND HYPERBRANCHED STRUCTURES AND ADVANCED MATERIALS PROPERTIES

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Alkyne polymerizations are effected by tungsten- and tantalum-based catalysts, giving linear polyacetylenes (LPAs) and hyperbranched polyarylenes (HPAs) of high molecular weights (M_w up to 2.5×10^5) in high yields (up to 93%). All the LPAs and HPAs are thermally stable and completely soluble in common solvents such as THF, toluene, dichloromethane, and chloroform. Incorporation of biphenyl mesogenic pendants into poly(1-phenyl-1-hexyne) structure endows the LCPA with nematicity. Upon photoexcitation, the LPAs and HPAs emit strong UV and blue lights with high quantum yields (up to 94%). Multilayer electroluminescence devices of LPAs emit blue light with maximum luminance and external quantum efficiency of 1065 cd/m^2 and 0.86%, respectively. The HPAs attenuate strong laser pulses, with optical limiting performances comparable to that of C_{60}, a well-known optical limiter.

1. INTRODUCTION

Development of new conjugated polymers with novel structures and unique properties has been the subject of intense research [1,2]. Especially, polymers with liquid-crystalline and light-emitting properties have attracted considerable attention owing to their potential applications in electronics and optics. A typical example is represented by polyphenylene, which was first prepared in 1886 and is still under active investigation [3–5].

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Polyphenylene with a reasonable molecular weight is, however, infusible and insoluble, which severely precludes its commercial utility.

Our group has been working on the synthesis of mesomorphic and luminescent linear polyacetylenes (LPAs) and hyperbranched polyarylenes (HPAs) through transition metal-catalyzed alkyne polymerizations [6–16]. We have developed effective catalyst systems to convert alkyne monomers to high molecular weight LPAs and HPAs. We have evaluated the properties of the polymers and found that most of them display strong photoluminescence (PL) and electroluminescence (EL). In this paper, we report our work on the synthesis of LPAs (**5**–**8**) and HPAs (**14**–**17**) with different mesogenic and chromophoric appendages. The polymers exhibit novel mesomorphic and optical properties originated from their unique molecular structures.

2. EXPERIMENTAL

2.1. Materials

Tungsten(VI) chloride, tantalum(V) chloride, tetraphenyltin, cyclopentadienylcobalt dicarbonyl, poly(9-vinylcarbazole) (PVK), tris(8-hydroxyquinolinato)aluminum (Alq$_3$), lithium fluoride (LiF), *N*,*N*′-diphenyl-*N*,*N*′-bis(3-methylphenyl)-1,1′-diphenyl-4,4′-diamine (TPD), and 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) were purchased from

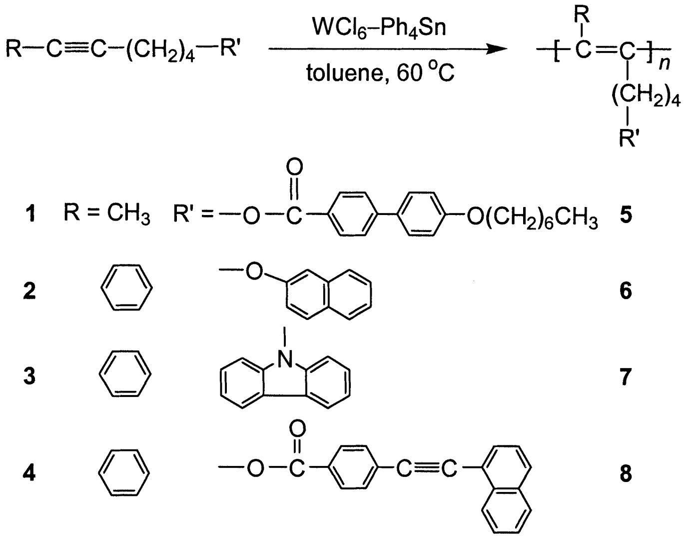

FIGURE 1 Synthesis of linear polyacetylenes.

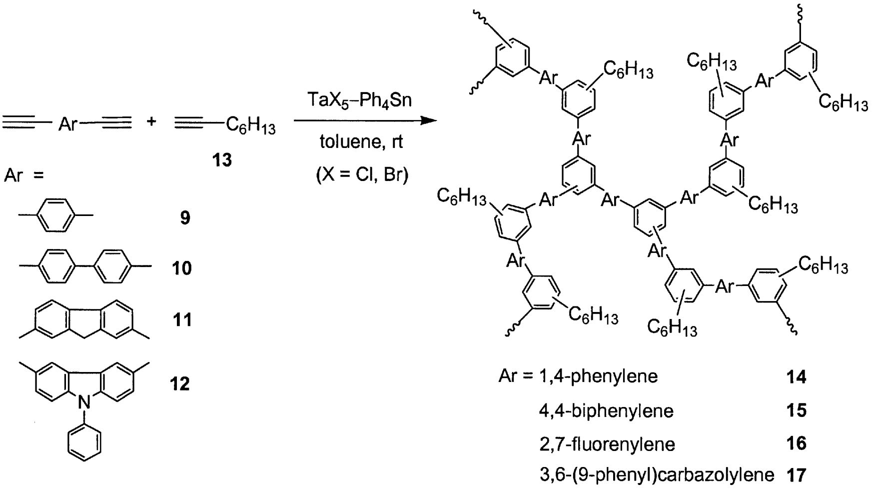

FIGURE 2 Synthesis of hyperbranched polyarylenes.

Aldrich and used as received without further purification. Poly(3,4-ethylenedioxythiophene) doped with poly(styrenesulphonic acid) (PEDOT:PSS) was purchased from Bayer Co. 1-Octyne (**13**) was obtained from Aldrich and distilled over calcium hydride before use. Acetylene monomers of 7-{[(4′-heptyloxy-4-biphenylyl)carbonyl]oxy}-2-heptyne (**1**), 6-(2-naphth oxy)-1-phenyl-1-hexyne (**2**), 6-(9-carbazolyl)-1-phenyl-1-hexyne (**3**), and 6-[({4-[2-(1-naphthyl)ethynyl]phenyl}carbonyl)oxy]-1-phenyl-1-hexyne (**4**) were synthesized according to our published procedures [17–19]. 1,4-Diethynylbenzene (**9**), 4,4′-diethynylbiphenyl (**10**), 2,7-diethynyl fluorene (**11**), and 3,6-diethynyl-9-phenylcarbazole (**12**) were prepared by palladium-catalyzed coupling of silylacetylene with dihaloarenes followed by base-catalyzed desilylation [20].

2.2. Instrumentation

Nuclear magnetic resonance (NMR) spectra of the polymers were recorded on a Bruker ARX 300 spectrometer using deuterated chloroform or dichloromethane as solvent and tetramethylsilane (TMS) as internal reference. Molecular weights of the polymers were estimated by a Waters Associates gel permeation chromatograph (GPC) system. THF was used as eluent at a flow rate of 1.0 mL/min. A set of Waters monodisperse polystyrene standards covering a molecular weight range of $10^3 - 10^7$ was used for the molecular weight calibration. Thermal stability of the polymers was evaluated on a Perkin-Elmer TGA 7 at a heating rate of 20°C/min under nitrogen. A Perkin-Elmer differential scanning calorimeter (DSC) 7 was used to measure phase transition thermograms. An Olympus BX 60 POM equipped with a Linkam TMS 92 Hot stage was used to observe anisotropic optical textures. X-Ray diffraction (XRD) patterns were recorded on a Philips PW1830 powder diffractometer with a graphite monochromator using 1.5406 Å Cu Kα wavelength at room temperature (scanning rate: 0.05°/s, scan range 2–30°). The polymer samples for the XRD measurements were prepared by freezing the molecular arrangements in the liquid crystalline states by liquid nitrogen as previously reported [9]. PL spectra of the polymers in solutions and solid states were recorded on a SLM 8000C spectrofluorometer. EL spectra of the thin films were obtained on a Kollmorgen Instrument PR650 photospectrometer. The luminescence area was 12.6 mm^2. Current-voltage (I-V) characteristics were obtained using a Hewlett-Packard HP4145B Semiconductor Analyzer.

2.3. PL Quantum Yield Measurement

PL efficiency of the polymers was measured using the literature procedure [21]. Both the polymers and the reference (9,10-diphenylanthracene) were excited at the same wavelength to avoid possible errors caused by the difference between excitation light intensities of different wavelengths. The quantum yields for 9,10-diphenylanthracene in cyclohexane and poly (methyl methacrylate) ($\sim$1 wt%) were assumed to be 90% and 83% [21,22].

2.4. Fabrication of EL Devices

Light-emitting diodes of ITO/LPA:PVK/BCP/$\mathrm{Alq_3}$/LiF/Al, ITO/**7**/BCP/$\mathrm{Alq_3}$/LiF/Al, and ITO/PEDOT:PSS/**8**:TPD/BCP/$\mathrm{Alq_3}$/LiF/Al were fabricated by sequentially spin-coating the toluene solutions of the LPAs or their blends. The ratio of the LPA to PVK or TPD was fixed at 1:4 by weight [23]. The thickness of the emitting layers was 22–65 nm. BCP (hole blocking layer; 20 nm), $\mathrm{Alq_3}$ (electron transport layer; 30 nm), LiF (electron injection layer; 0.8 nm], and Al were deposited in turn under vacuum (2×10^{-6} Torr).

2.5. Polymerization

All polymerization reactions were conducted under nitrogen using an inert-atmosphere glovebox (Vacuum Atmosphere).

Polymerizations of **1**–**4** were carried out in toluene at 60°C for 24 h, using a mixture of $\mathrm{WCl_6}$ and $\mathrm{Ph_4Sn}$ as catalyst. The detailed experimental procedures can be found in our previously published paper [24].

Characterization: **5**: Grey powdery solid; yield 81.4%. M_w 254200; M_w/M_n 2.0 (GPC; polystyrene calibration). ^{1}H NMR (300 MHz, $CDCl_3$), δ (TMS, ppm): 7.94 [broad (br), 2H, Ar-H], 7.41 (br, 4H, Ar-H), 6.97 (br, 2H, Ar-H), 4.34 (br, 2H, $ArCO_2CH_2$), 3.86 (br, 2H, OCH_2), 1.74 (br, 4H, $ArCO_2CH_2CH_2$ and $=CCH_2CH_2$), 1.31 [br, 10H, $(CH_2)_5$], 0.90 (br, 3H, CH_3).

6: Yellow powdery solid; yield 90.0%. M_w 38400; M_w/M_n 2.8 (GPC, polystyrene calibration). ^{1}H NMR (300 MHz, $CDCl_3$), δ (TMS, ppm): 7.56, 7.23, 6.89 (br, 7H, Ar–H), 3.52 (br, 2H, OCH_2), 1.44 (br, 4H, OCH_2CH_2 and $=CCH_2CH_2$).

7: Yellow powdery solid; yield 81.1%. M_w 58100; M_w/M_n 3.3 (GPC; polystyrene calibration). ^{1}H NMR (300 MHz, $CDCl_3$), δ (TMS, ppm): 8.05 (br, 2H, Ar–H), 7.17 (br, 6H, Ar–H), 3.65 (br, 2H, NCH_2), 0.91 (br, 4H, NCH_2CH_2, and $=CCH_2CH_2$).

8: Pale yellow powdery solid; yield 37.9%. M_w 21900; M_w/M_n 2.4 (GPC; polystyrene calibration). ^{1}H NMR (300 MHz, $CDCl_3$), δ (TMS, ppm): 8.07, 7.69, 7.46 (br, 11H, Ar–H), 3.95 (br, 2H, CH_2OCO), 1.26 (br, 4H, CH_2CH_2OCO and $=CCH_2CH_2$).

Copolymerizations of **9**–**12** with **13** were carried out in a dry nitrogen atmosphere. A typical procedure for the copolymerization of **9** with **13** 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) of **9** and 54 µL (0.366 mmol) of **13** in 1.45 mL of toluene was then added dropwise into the catalyst solution. After stirring at room temperature for 12 h, the polymer solution was dropped into 250 mL of methanol *via* a cotton filter under stirring to precipitate the polymer. A light yellow powder (**14**) was collected and dried in vacuum overnight. Yield 88.9%. M_w 38000; M_w/M_n 4.0 (GPC; polystyrene calibration). ^{1}H NMR (300 MHz, $CDCl_3$), δ (TMS, ppm): 7.9–6.8 (br, 14H, Ar–H), 2.63 (br, 2H, Ar–CH_2), 1.64–0.86 [br, 11H, $(CH_2)_4CH_3$]. The procedures for the synthesis of **15** and **16** are similar to that described above, except for that the molar ratios of **13**/**10** and **13**/**11** are 0.90 and 0.86, respectively.

Characterization: **15**: Light gray powder; yield 65.5%. M_w 33500; M_w/M_n 8.1 (GPC; polystyrene calibration). ^{1}H NMR (300 MHz, $CDCl_3$), δ (TMS, ppm): 7.89–7.25 (br, 16H, Ar–H), 2.56 (br, 2H, Ar–CH_2), 1.63–0.85 [br, 11H, $(CH_2)_4CH_3$].

16: Light gray powder; yield 82.6%. M_w 182600; M_w/M_n 2.8 (GPC; polystyrene calibration). ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 7.92–7.11

(br, 10H, Ar–H), 4.05 (br, 2H, CH_2), 2.51 (br, 2H, Ar–CH_2), 1.91–1.10 [br, 11H, $(CH_2)_4CH_3$].

Unlike **14–16**, polymer **17** was prepared by copolymerization of **12** with **13** (feed ratio = 1:1.5) using $TaBr_5 - Ph_4Sn$ as catalyst. Light brown powder; yield 89.2%. M_w 12200; M_w/M_n 3.5 (GPC; polystyrene calibration). ^{1}H NMR (300 MHz, $CDCl_3$), δ (TMS, ppm): 8.5– 7.1 (br, 14H, Ar– H), 2.70 (br, 2H, Ar–CH_2), 1.70–0.79 [br, 11H, $(CH_2)_4CH_3$].

3. RESULTS AND DISCUSSION

To enrich the research field of conjugated polymers, we designed and synthesized a number of new monoacetylenes (**1**–**4**) and diacetylenes (**9**–**12**) with varying mesogenic and chromophoric moieties by multistep reactions. All the reactions proceeded smoothly and the products were obtained in high yields.

Polymerizations of **1**–**3** are effected by WCl_6–Ph_4Sn in toluene at 60°C, producing high molecular weight polymers in high yields. The same catalyst can also selectively polymerize the 1-phenyl-1-hexyne containing a naphthylethynylphenyl pendant (**4**) without generating any crosslinking byproducts.

Unlike the metathesis polymerizations of **1**–**4**, the homopolycyclotrimerizations of **9**–**12** catalyzed by TaX_5–Ph_4Sn (X = Br, Cl) in toluene at room temperature give only insoluble gels. To suppress the crosslinking reaction and to improve the solubility of the resultant polyarylenes, we carried out copolymerizations of **9**–**12** with 1-octyne (**13**), a monoacetylene. Delightfully, all the diacetylenes copolymerize well with **13** and soluble polymers with high molecular weights (M_w up to 1.8×10^5) are obtained in high yields (up to 94%).

All the LPAs and HPAs give satisfactory spectroscopic analysis data corresponding to their expected molecular structures. Figure 3A shows the TGA thermograms of LPAs **5**–**8**. Polyacetylenes such as poly(1-hexyne) (PH) and poly(phenylacetylene) (PPA) are so unstable that they respectively start to lose their weights at temperatures (T_d) as low as 150 and 220°C [25]. Our LPAs, however, show much superior thermal stability ($T_d \geq 400$°C). The enhanced thermal stability of **5**–**8** is probably due to the "jacket effect" of the aromatic pendants [9,24,26], which well wrap the polyacetylene backbone and thus shield the double bonds from the thermolytic attack. The HPAs, delightfully, show even stronger resistance to thermolysis (Fig. 3B) and carbonize in high yields when pyrolyzed at 800°C. For instance, the 5% weight loss of **17** is 477°C and about 70% of its weight is left after pyrolysis. This is in some sense expected because the HPAs are comprised of thermally stable aromatic rings.

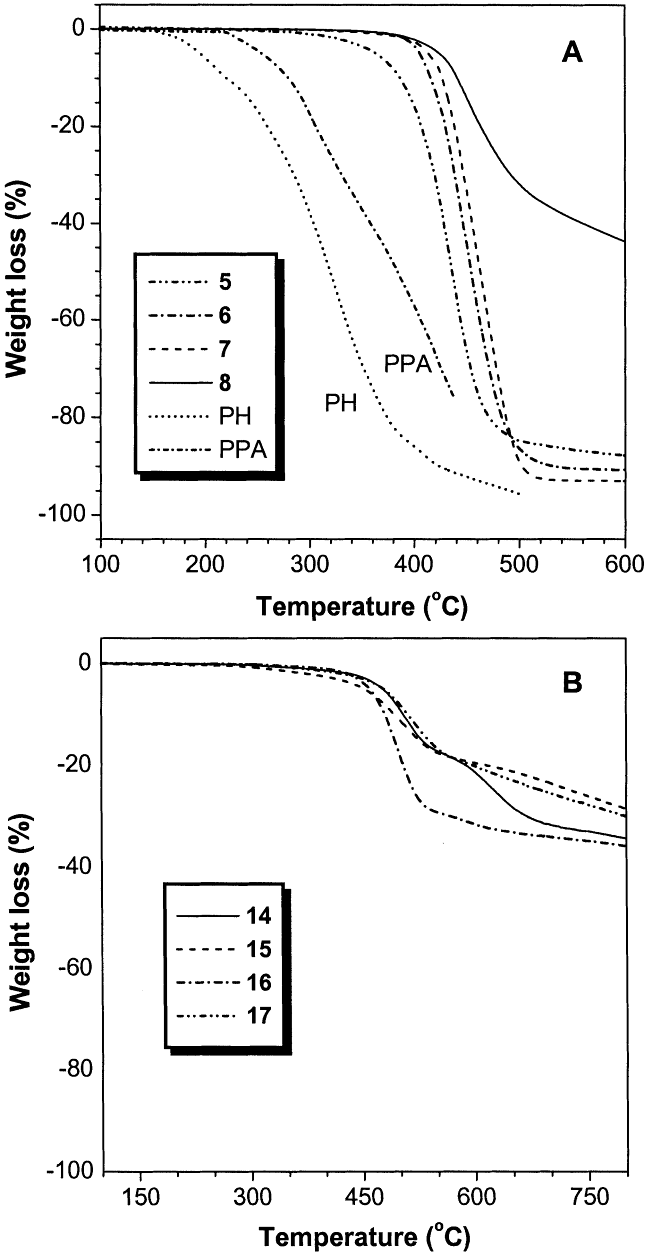

FIGURE 3 TGA thermograms of (A) linear polyacetylenes **5**–**8**, poly(1-hexyne) (PH), and poly(phenylacetylene) (PPA) and (B) hyperbranched polyarylenes **14**–**17** recorded under nitrogen at a heating rate of 20°C.

Our previous study reveals that when biphenyl mesogens are incorporated as pendants into poly(1-hexyne), a monosubstituted polyacetylene, the resultant polymer exhibits unique enantiotropic smecticity [24,27]. We are intrigued to know whether **5**, a biphenyl-containing disubstituted polyacetylene, is also liquid crystalline. DSC analysis shows that **5** enters the nematic phase at 142.0°C in the first cooling cycle. The mesophase temperature range is, however, narrow ($\sim$15°C) and the polymer completely solidifies at $\sim$117.0°C. The second heating cycle shows a broad endothermic peak at 127.6°C associated with g–n transition; that is, the mesomorphism of **5** is enantiotropic. We also studied the mesomorphic properties of other LPAs but found that none of them displayed liquid crystallinity.

Figure 4 shows the POM micrograph of the mesomorphic texture of **5**. When the isotropic liquid of the polymer is cooled from 150 to 128°C, a birefrigent texture is observed, from which, the exact nature is, however, difficult to identify. We tried to grow the crystals with care but still could not obtain any identifiable characteristic mesomorphic texture.

To determine the texture displayed by **5** and to gain more information on the molecular packing arrangement in the mesophase, we carried out an

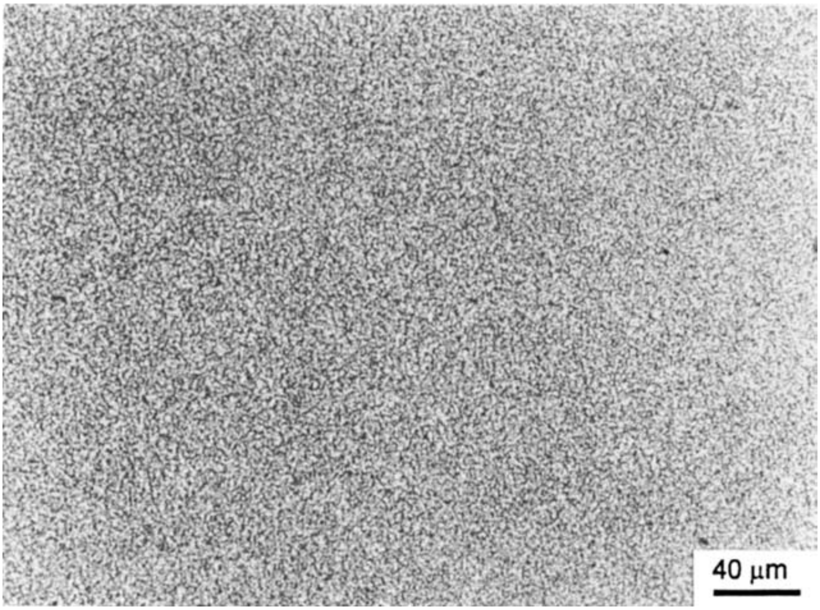

FIGURE 4 Mesomorphic texture observed on cooling **5** to 128°C from its isotropic melt.

XRD analysis of the polymer. According to literature [28], a typical XRD pattern of a nematic liquid crystal is characterized by (i) a diffuse peak in the high-angle region and (ii) a broad peak in the low-angle region. The XRD diffractogram of **5** quenched from 128°C (Fig. 5) actually has the two features: it shows a diffuse halo at $2\theta = 20.35^\circ$ and a barely recognizable hump at $2\theta = 3.46^\circ$, thus verifying the nematicity of the mesophase of **5** at the high temperature. The packing of the mesogenic pendants is poorer than that of its monosubstituted counterpart because of comparably rigid backbone of the disubstituted polyacetylene, which hampers the mesogenic pendants from packing in an ordered fashion.

We checked the fluorescence behaviors of our LPAs and HPAs. When **5** is photoexcited at 333 nm, it emits a strong UV light of 369 nm (Fig. 6A). Our previous studies on the luminescence behaviors of mesogen-containing monosubstituted polyacetylenes reveal that the heptyloxybiphenylylcarbonyloxy pendant emits in the UV region with a $\lambda_{\max}$ of ~369 nm [29,30]. It thus becomes clear that the emission from **5** is from the pendant chromophore. Using 9,10-diphenylanthracene as reference, its quantum efficiency (Φ_F) is calculated to be 69%, much higher than that of poly

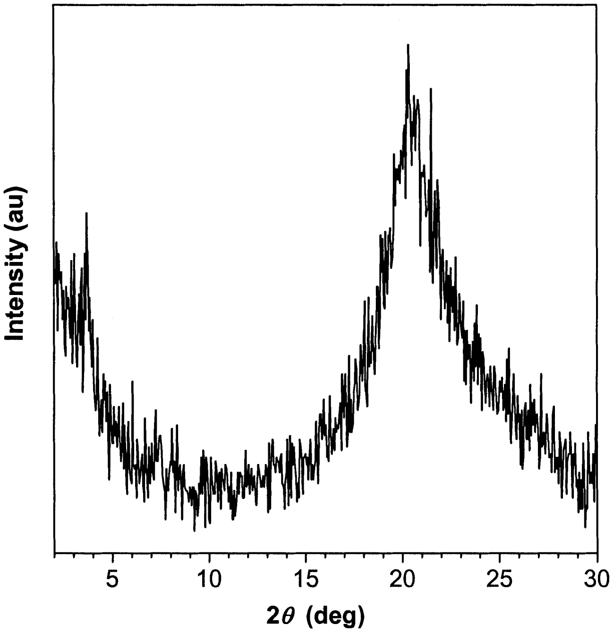

FIGURE 5 X-ray diffraction pattern of **5** quenched with liquid nitrogen from its liquid crystalline states at 128°C.

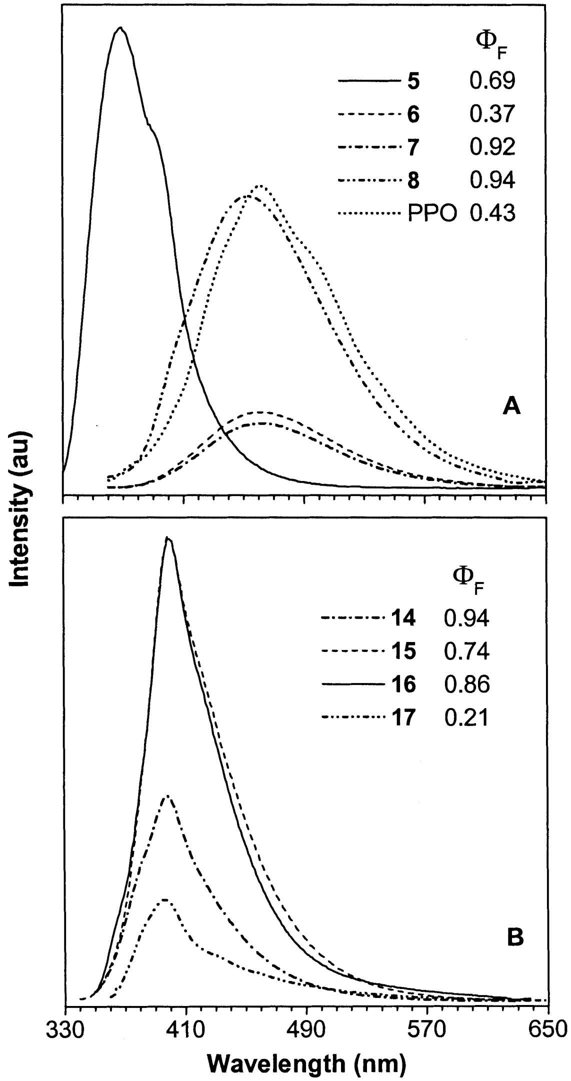

FIGURE 6 Photoluminescence spectra of (A) linear polyacetylenes **5**–**8** and poly(1-phenyl-1-octyne) (PPO) in THF and (B) hyperbranched polyarylenes **14**–**17** in dichloromethane. Concentration: 0.05 mM (**5**–**8** and PPO) and 0.0025 mg/mL (**14**–**17**). Excitation wavelength (nm): 333 (**5** and **14**), 342 (**15**), 352 (**16**), 355 (**6**, **7**, and PPO), 358 (**17**), and 370 (**8**).

(1-phenyl-1-octyne) (PPO), a well-known highly emissive disubstituted polyacetylene [31–34]. The liquid crystallinity of **5** seems to have little effect on its optical properties. Polymer **6**, however, shows very different luminescence behaviors. Upon photoexcitation at 355 nm, the emission from the naphthalene pendant ($\sim$350 nm) is not observed. Instead, its PL spectrum is dominated by an emission at 460 nm. Since poly(1-phenyl-1-alkyne)s such as poly(1-phenyl-1-butyne) and PPO emit blue light of 460 nm when excited, the emission of **6** thus should be stemmed from the poly(phenylhexyne) backbone. As the emission spectrum of the naphthalene pendant partially overlaps with the absorption spectrum of the polyene main chain, the light emitted by the appendage is likely absorbed by the polyacetylene backbone. This energy transfer has probably quenched the emission from the side group. The chromophoric pendants in **7** and **8** are more emissive than that of **6**. The emissions from the polymers are also found in the similar wavelength region but with higher efficiencies ($\Phi_F > 90\%$), revealing that the optical properties of polyacetylenes are readily tunable by incorporating different chromophoric units into the polymer structures.

The HPAs are also strong emitters. As shown in Figure 6B, the HPA carrying phenyl chromophore (**14**) emits a UV light of 400 nm with an Φ_F as high as 94%. The PL peak maximum is not sensitive to the change of molecular structures but the quantum yield varies dramatically. While Φ_F of **15** and **16** all exceeds 70%, the emission from **17** is, however, four fold lower.

Many conjugated polymers emit intensely in solutions but become weakly luminescent when fabricated into films [35,36]. This is mainly caused by strong interchain interactions in the solid state. We are interested to know whether the same phenomenon is also observed in our polymers. Figure 7 shows the PL spectra of a few LPAs and HPAs in their thin solid film states. Compared to those in solution, no significant shift in the emission maximum is observed in our polymers, suggestive of little aggregate formation in the solid state.

Several research groups have studied electroluminescence of disubstituted polyacetylenes in the late 1990s [32–34,37–39]. They fabricated light-emitting diodes (LEDs) of single-layer structures, using the polyacetylenes as emitting materials. Light of low luminance and efficiency was, however, observed. For the blue emission, the best results are obtained in the PPO-based LED, with luminance and efficiency being 0.5 cd/m^2 and 0.01%, respectively. These poor results are in some sense expected because the injection and transport of electrons and holes are normally imbalanced in single-layer devices. One remedy to improve the device performance is to built devices with multilayer configurations. We constructed a multilayer device with a configuration of ITO/**6**:PVK/BCP/Alq$_3$/LiF/Al,

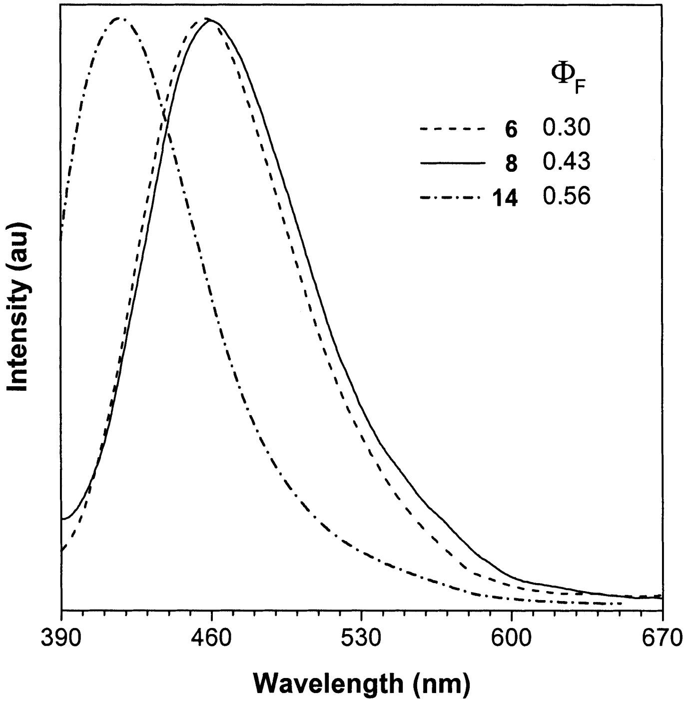

FIGURE 7 Photoluminescence spectra of linear polyacetylenes **6** and **8** and hyperbranched polyarylene **14** in solid states. Excitation wavelength (nm): 355 (**6**), 370 (**8**), and 333 (**14**).

using a blend of **6** and PVK as emitting layer. The device is turned on at ~8 V, emitting a blue light of 460 nm (Fig. 8). The EL spectrum is single peaked and symmetrically shaped, with no sidebands associated with such emitting species such as excimers. The luminance reaches 1065 cd/m^2 at an applied voltage of 19 V and the maximum quantum efficiency reaches 0.85% at 13 V, which is 85-fold superior to the previously reported results [32–34]. We also constructed an LED of PPO with the same device configuration. No light from the PPO layer is, however, observed, demonstrating that **6** is a better EL material than PPO.

Encouraged by the result of **6**, we further studied the EL performances of other polymers. Table 1 summarizes the results. All the devices of the LPAs emit blue light, although the emission from the devices of **7** is somewhat greenish, as revealed by the CIE coordinates. The emission efficiency of the LPA varies with both of its molecular structure and device configuration. In comparison to **6**, **7** is a less efficient emitter.

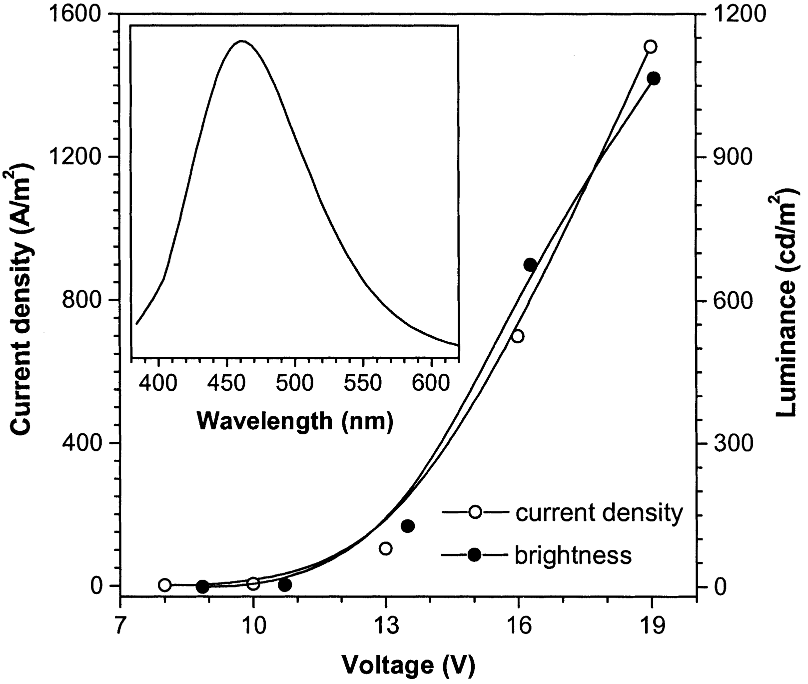

FIGURE 8 Changes of current density and luminance with applied voltage in a multilayer EL device of **6** with a configuration of ITO/**6**:PVK (1:4 by weight)/ BCP/Alq$_3$/LiF/Al. Inset: electroluminescence spectrum. Abbreviations: ITO = indium tin oxide, PVK = poly(9-vinylcarbazole), BCP = 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline, Alq$_3$ = tris(8-hydroxyquinolinato)aluminum.

Interestingly, however, it performs well in the absence of PVK, possibly due to its "build-in" hole-transport carbazole moiety. The external quantum efficiency of the LED of **8** with a hole-injection layer of PEDOT:PSS is as high as 0.86%, which is comparable to some of the best results reported by other groups for blue LEDs [40,41]. As can be seen from the comparison data given in Table 1, all the LPAs are more efficient emitters than PPO.

Molecules of fused aromatic rings may limit optical power. The HPAs are aromatic polymers and are hence good candidates for optical limiters. As we can be seen from Figure 9, the HPAs effectively attenuate the power of intense 532 nm laser pulses. The transmitted fluene of **14** initially increases with the incident fluence in a linear fashion. It starts to deviate from linearity at an incident fluence of ~1000 mJ/cm^2 and reaches a saturation plateau at ~340 mJ/cm^2. The optical limiting threshold (1016 mJ/cm^2) and signal suppression (0.15) are similar to those of C$_{60}$,

TABLE 1 Electroluminescence Performances of Linear Polyacetylene-based Light-emitting Diodes[a]

No.	LPA	λ_{max} (nm)	CIE (x, y)[b]	V$_{on}$ (V)	L$_{max}$ (cd/m^2)	C_{max} (cd/A)	P_{max} (lm/W)	η_{max} (%)
1	**6**	460	0.18, 0.21	8	1065	1.23	0.30	0.85
2	**7**	488	0.25, 0.37	15	6.9	0.21	0.04	0.10
3	**7**[c]	468	0.20, 0.26	11	314	0.49	0.14	0.40
4	**8**	456	0.17, 0.20	10	498	0.69	0.18	0.47
5	**8**[d]	464	0.19, 0.22	9	455	1.25	0.36	0.86
6	PPO[e]	455		14	0.5			0.01

[a] Device configuration: ITO/PA:PVK(1:4 by weight)/BCP(20 nm)/Alq$_3$(30 nm)/LiF(0.8 nm)/Al. Abbreviations: PVK = poly(9-vinylcarbazole), BCP = 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline, Alq$_3$ = tris(8-hydroxyquinolinato)aluminum, λ_{max} = emission maximum, V_{on} = turn-on voltage, L_{max} = maximum luminance, C_{max} = maximum current efficiency, P_{max} = maximum power efficiency, η_{max} = maximum external quantum efficiency.

[b] Color coordinates of CIE 1931 chromaticity diagram.

[c] With a device configuration of ITO/**7**/BCP(20 nm)/Alq$_3$(30 nm)/LiF(0.8 nm)/Al.

[d] Device configuration: ITO/PEDOT:PSS(60 nm)/**8**:TPD (1:4 by weight)(40 nm)/BCP(20 nm)/Alq$_3$(20 nm)/LiF(1 nm)/Al. Abbreviations: PEDOT = polyethylenedioxythiophene, PSS = poly(styrenesulfonate), TPD = *N*,*N*′-diphenyl-*N*,*N*′-bis(3-methylphenyl)-1,1′-biphenyl-4,4′-diamine.

[e] Device configuration: ITO/PPO(100 nm)/Mg(20 nm)/Al(200 nm). Data taken from reference 28.

a well-known optical limiter [42,43]. Polymers **15–17,** compared to **14**, are better optical limiters, with **16** showing the best performance. This suggests that the optical limiting properties of HPAs are sensitive to their molecular structures, offering the opportunity to tune their properties by molecular engineering endeavors.

4. CONCLUSIONS

Linear polyacetylenes and hyperbranched polyarylenes of high molecular weights are prepared in high yields by one-pot alkyne polymerizations initiated by tungsten- and tantalum-based catalysts. All the polymers are soluble in common solvents and are thermally stable. The biphenyl mesogen endows poly(1-phenyl-1-hexyne) with mesomorphism. Upon photoexcitation, all the LPAs and HPAs emit strong blue and UV lights in solution with efficiency up to 94%. No significant red-shift in the peak maximum is observed in the PL spectra of the polymers in solid state. Multilayer EL devices utilizing LPAs as emitters are constructed, which emit strong blue light of ~460 nm with maximum luminance and external quantum

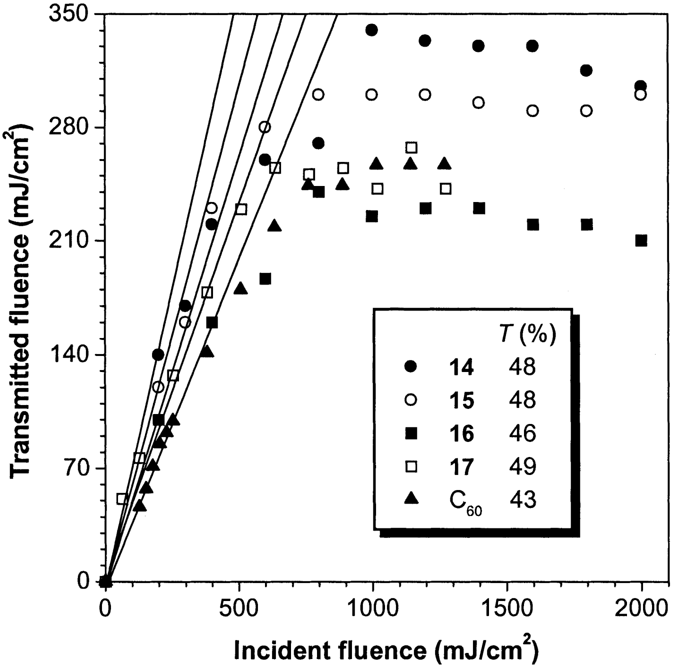

FIGURE 9 Optical limiting responses to 8 ns, 532 nm optical pulses, of dichloromethane solutions of hyperbranched polyarylenes **14–17;** concentration: 0.86 mg/mL. Data for a toluene solution C_{60} (0.16 mg/mL) is shown for comparison.

efficiency of 1065 cd/m^2 and 0.86%, respectively [44]. The HPAs strongly attenuate intense laser pulses. The high thermal and optical stabilities of the HPAs make them promising candidate materials for high-tech applications [45].

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