

SYNTHESIS AND PROPERTIES OF POLY(AROMATIC DIACETYLENE)S CONTAINING FLUORENE*

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Abstract Novel fluorene-based poly(aromatic diacetylene)s have been synthesized by CuCl-catalyzed oxidative coupling of aromatic diynes. New aromatic diynes 2,7-diethynyl-9,9-bis(triphenylamine)fluorene (M_1) is synthesized by multistep reactions. The structures and properties of the polymers are characterized and evaluated by IR, NMR, TGA, UV, photoluminescence (PL), and cyclic voltammetry analyses. These polymers possess good thermal stability. All the polymers are completely soluble in common solvents such as toluene, THF, chloroform, and dichloromethane. The polymers exhibit strong blue photoluminescence in solution and green photoluminescence in the solid state. The polymer containing triphenylamine-substituted fluorene has lower oxidation potential (–5.45 eV) than the previous polyfluorenes (–5.80 eV).

Keywords: Fluorene; Glaser-Hay reaction; Conjugated polymer; Diacetylene; Poly(aromatic diacetylene)s.

INTRODUCTION

In recent years, a great deal of interest has been focused on the synthesis of novel conjugated diacetylene-containing and fluorene-containing polymers^[1–11], because of their unique properties such as carbonizing precursor^[12], electroluminescence^[13], liquid crystallinity^[14], third-order nonlinear optical properties^[15], magnetic properties^[16] and optical waveguide^[17]. Diacetylene-containing polymers are rigid-rod conjugated materials composed of aromatic rings and diacetylene functions. The high fluorescence quantum yield and excellent stability of the polymers make these materials another class of prospective materials for photoluminescence (PL) applications.

In the previous work, we synthesized a series of carbazole-containing polymers by Glaser-Hay reaction, but found that the performance in LEDs was not satisfying. Polyfluorenes (PF), with their exceptionally high solution and solid-state fluorescence quantum yields, are very promising candidates for LEDs. Although a fluorene homopolymer, poly(9,9-di-*n*-octylfluorene), has been demonstrated as an effective blue emitter. But they tend to form aggregates or excimers on heating during device formation or operation, leading to both a red-shifted emission and lower efficiency. This can be overcome by introducing bulky substituents at the C-9 position of the fluorene^[18, 19].

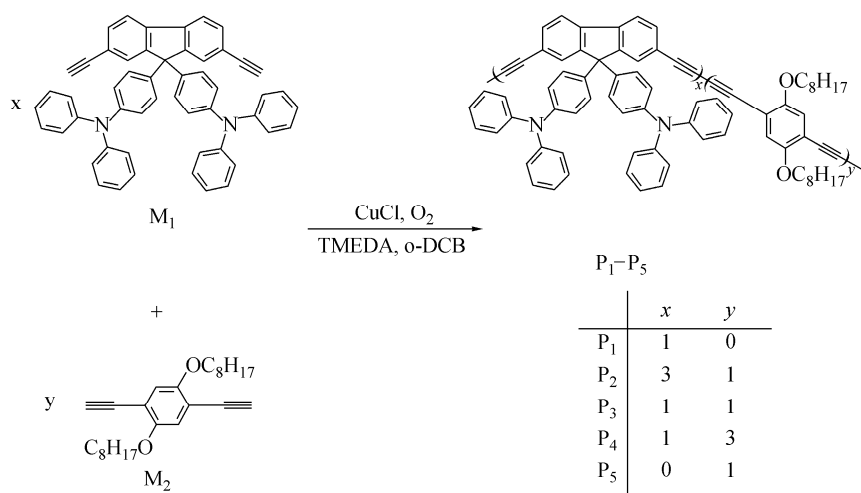
In this work, triphenylamine (TPA) unit is functionalized at the C-9 position of fluorene. A new series of fluorene-based poly(aromatic diacetylene)s are synthesized by CuCl-catalyzed oxidative polycoupling of diynes M_1 and M_2 (Scheme 1). The luminescence behaviors of these polymers are also studied.

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Scheme 1 Synthetic route to polymers

EXPERIMENTAL

Materials

Fluorene, *N,N,N',N'*-tetramethylethylenediamine (TMEDA) and 2-methyl-3-butyn-2-ol were purchased from Acros. Dichlorobis(triphenylphosphine)palladium(II) was purchased from Strem and used as received. Triphenylamine (TPA) was purchased from Hai Tong Co. Triethylamine was distilled under atmosphere and kept over potassium hydroxide under nitrogen. All solvents, unless otherwise specified, were used as received.

Instrumentation

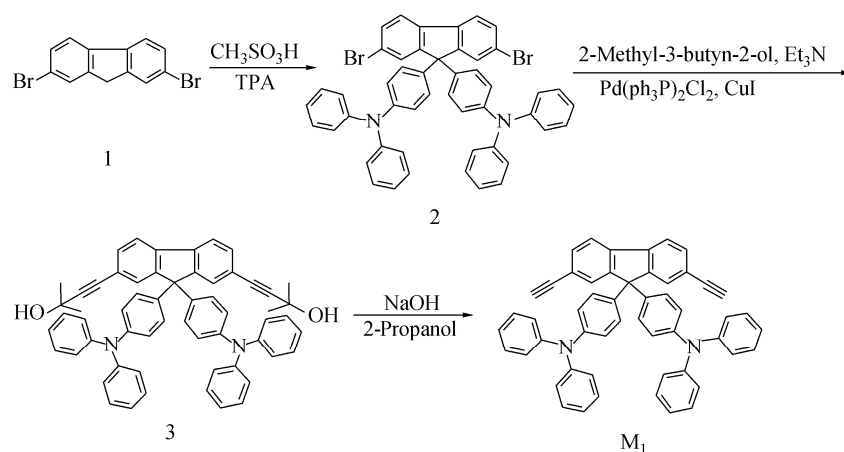
UV spectra were measured on a HP 8453E spectrophotometer in dichloromethane (DCM). Photoluminescence (PL) spectra were recorded on a Fluorolog-3 spectrofluorometer. The PL quantum yields (Φ_{PL}) of polymers in DCM were measured using the literature procedure^[20]. The quantum yield for 9,10-diphenylanthracene in cyclohexane was assumed to be 90% when excited at 316 nm^[21]. IR spectra of the monomers and polymers were obtained on a Bruker Vector 33. ¹H- and ¹³C-NMR spectra were recorded on a Bruker AV 300 spectrometer using chloroform-*d* as solvent and tetramethylsilane (TMS; $\delta = 0$) as internal reference. Molecular weights (M_w) and polydispersities indices (M_w/M_n) were determined by PolyLab (PL210) Gel Permeation Chromatography with a RI detector. The thermal stability of the polymers were evaluated on a TA Instruments Q50 at a heating rate of 20 K/min under nitrogen. Cyclic voltammetry was carried out on a CHI660A electrochemical workstation in an acetonitrile solution of tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) (0.1 mol/L) at a scan rate of 50 mV/s at room temperature under argon.

Monomer Synthesis

Synthesis of monomer M_1 and M_2

The monomer M_1 was synthesized according to Scheme 2. 2,7-Dibromofluorene (1) was reacted with triphenylamine at 140°C in the presence of CH₃SO₃H to give 2,7-dibromo-9,9-bis(triphenylamine) fluorene (2)^[12]. 2,7-Bis(2-methyl-3-butyn-2-ol)-9,9-bis(triphenylamine) fluorene (3) was obtained from the reaction of (2) and 2-methyl-3-butyn-2-ol. 2,7-Diethynyl-9,9-bis(triphenylamine) fluorene (M_1) was derived from (3) and NaOH at 80°C in 2-propanol in the yield of 73%.

The process of preparing monomer M_2 was according to the literature previously^[22].

Scheme 2 Synthetic route to monomer M_1

Polymerization

The polymerization was effected by a mixture of CuCl and TMEDA in *o*-dichlorobenzene (*o*-DCB). A typical procedure for the copolymerization of M_1 and M_2 was given below (Scheme 1). Into a test tube equipped with a magnetic stirrer were placed 2 mg (0.02 mmol) of CuCl and 0.012 mL (0.07 mmol) of TMEDA in 4 mL *o*-DCB. The catalyst mixture was bubbled with air and stirred on an oil bath at 50°C for 15 min. Diynes M_1 (70.0 mg, 0.1 mmol) and M_2 (38.2 mg, 0.1 mmol) were dissolved in 1 mL *o*-DCB and then added into the catalyst mixture. The color of the reaction turned to green. After 40 min, the polymerization was stopped by pouring the reaction mixture into 100 mL of methanol acidified with 0.35 mL of a 37% HCl solution. The polymer precipitate was filtered and washed with methanol, and dried in vacuum overnight at 40°C to afford 86 mg of yellow powder (P_3), yield: 79.6%. IR (KBr), ν (cm^{-1}): 3297 ($\equiv\text{C}-\text{H}$ stretching), 2206, 2140 ($\text{C}\equiv\text{C}-\text{C}\equiv\text{C}$ stretching), 2104 ($\text{C}\equiv\text{C}$ stretching). ^1H -NMR (300MHz, CDCl_3 , δ): 7.70–6.91 (Ar-H), 3.97 (OCH_2), 3.38 ($\equiv\text{C}-\text{H}$), 3.04 ($\equiv\text{C}-\text{H}$), 1.87–1.27 (CH_2), 0.89 (CH_3). ^{13}C -NMR (75MHz, CDCl_3 , δ): 154.79, 152.37, 146.52, 145.73, 138.86, 137.28, 130.76, 129.27, 128.74, 127.77, 124.71, d123.13, 117.61, 112.52, 109.17, 84.31, 83.36, 83.21, 82.40, 81.98, 81.78, 79.78, 69.86, 64.67, 31.75, 29.31, 29.14, 28.93, 27.24, 25.99, 22.69, 14.07.

RESULTS AND DISCUSSION

Polymerization of Diynes

Homo- and co-polymerizations of M_1 and M_2 are carried out in *o*-DCB at 50°C under air using CuCl and TMEDA as catalysts. Copolymerizations of M_1 and M_2 in different feed molar ratios are carried out to afford a series of polymers. Table 1 shows the homo- and co-polymerizations results of M_1 and M_2 . All the polymers are isolated in satisfactory yields. The polymers are well soluble in chloroform, dichloromethane, THF and toluene. The polystyrene-calibrated M_w 's of the polymers are in the range of 1500–186200. The molecular weight of copolymers decreases with decreasing fluorene content, as is expected the relatively reaction activity of heteroatom-containing monomers in the Glaser-Hay reaction. Monomer M_1 and M_2 also showed higher reactivity towards co-polymerization. Due to being regular and rigid structure to easily form crystal state, the low M_w and reactivity are caused by low solubility of the homo-polymers in the reaction medium. Incorporation of another monomer into polymer structure can break the regularization of the homopolymers and increase the reactivity and M_w of polymerization.

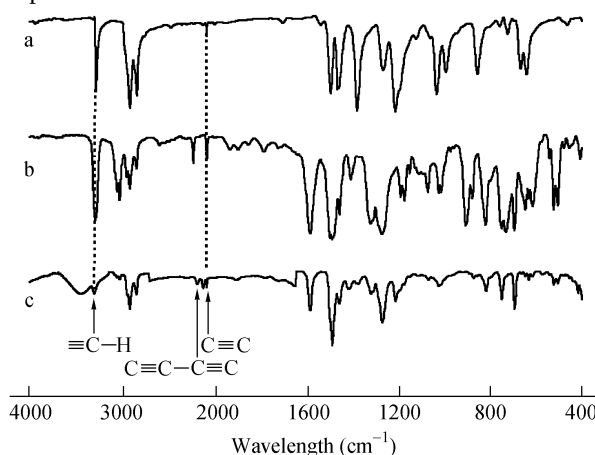
Table 1. Homo- and co-polymerization of diynes^a

Polymer	Molar ratio $x/(x + y)$	Yield (%)	M_w^b	M_w/M_n^b
P ₁	1	63.4	1500	1.5
P ₂	0.75	63.3	31500	4.0
P ₃	0.50	79.6	186200	2.0
P ₄	0.25	64.6	85300	2.2
P ₅	0	60.3	2400	1.1

^a Carried out in *o*-DCB at 50°C under a slow air flow for 40 min using CuCl and TEMDA as the catalysts; ^b Estimated by GPC in THF on the basis of a polystyrene calibration

IR and ¹³C-NMR Results

All the polymers give analytic data satisfactorily corresponding to their expected molecular structures. Figure 1 shows the IR spectra of copolymer P₃ and its monomers. The stretching vibrations of $\equiv\text{C}-\text{H}$ and $\text{C}\equiv\text{C}$ of M₁ and M₂ are observed at 3296 and 2104 cm⁻¹, respectively, which remain in the spectrum of its copolymer P₃, indicating the presence of acetylene moieties in the polymer. Furthermore, two new peaks associated with the formation of diacetylene bonds appear at 2206 and 2140 cm⁻¹. These changes indicate that the oxidative coupling polymerization takes place.

**Fig. 1** IR spectra of diyne M₂ (a), M₁ (b) and its copolymer P₃ (c)

The ¹³C-NMR spectra data further proves the molecular structures of the polymers derived from their IR spectral analyses. Figure 2 shows the ¹³C-NMR spectra of diyne M₁, diyne M₂, and polymer P₃. The terminal acetylene carbons of M₁ and M₂ resonate at $\delta = 79.78, 64.67$, and $\delta = 83.36, 81.78$, respectively, which remain in the spectrum of its copolymer P₃. The ¹³C-NMR spectra show that the terminal ethynyl carbons are transformed into diacetylene carbons after polymerization. For polymer P₃ the significant features in the ¹³C-NMR spectra are the appearance of four new peaks at $\delta = 84.31, 83.21, 82.40$ and 81.98 attributed to the diacetylene carbons of the polymer fragments.

Optical and Thermal Properties

The photophysical characteristics of the polymers are investigated in solution and in the solid state. The absorption and emission data for the five polymers in solutions and in the films cast from solution in DCM are summarized in Table 2. The absorption spectra of the three polymers obtained for diluted DCM solutions are shown in Fig. 3(a). These polymers all show two absorption bands. The polymer P₁ in DCM solution exhibits an absorption with a λ_{max} at 393 nm due to a $\pi-\pi^*$ transition derived from the conjugated polyfluorenes backbone. An additional absorption band around 306 nm is originated from the combined absorption from the triphenylamine pendant groups. The polymer P₅ has a band centered at about 407 nm, which corresponds to $\pi-\pi^*$ transition derived from the conjugated 2,5-dialkoxy-*p*-phenylene backbone. Films of the five polymers show the UV peak at a slightly longer wavelength than in solution (Table 2), indicating the presence of intermolecular

interactions arising from stacking of the polymers in the solid state. However, the intermolecular interaction is not very strong.

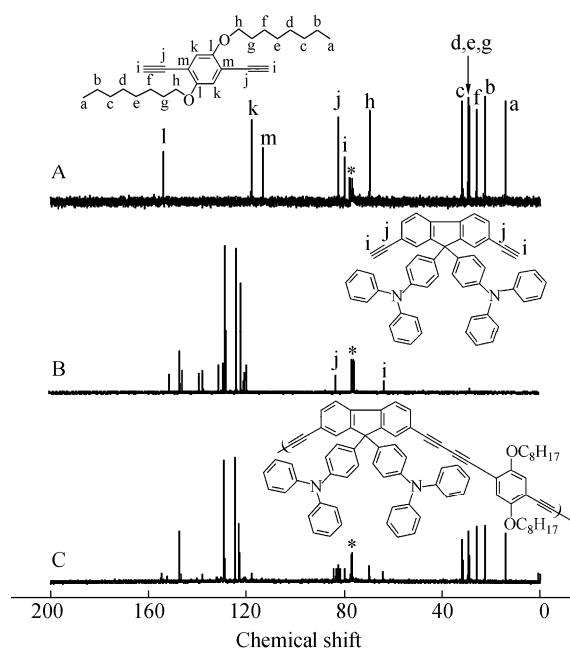


Fig. 2 ^{13}C -NMR spectra of diyne M_2 (A), diyne M_1 (B) and their polymer P_3 (C) in chloroform- d . The solvent peaks are marked with asterisks (*).

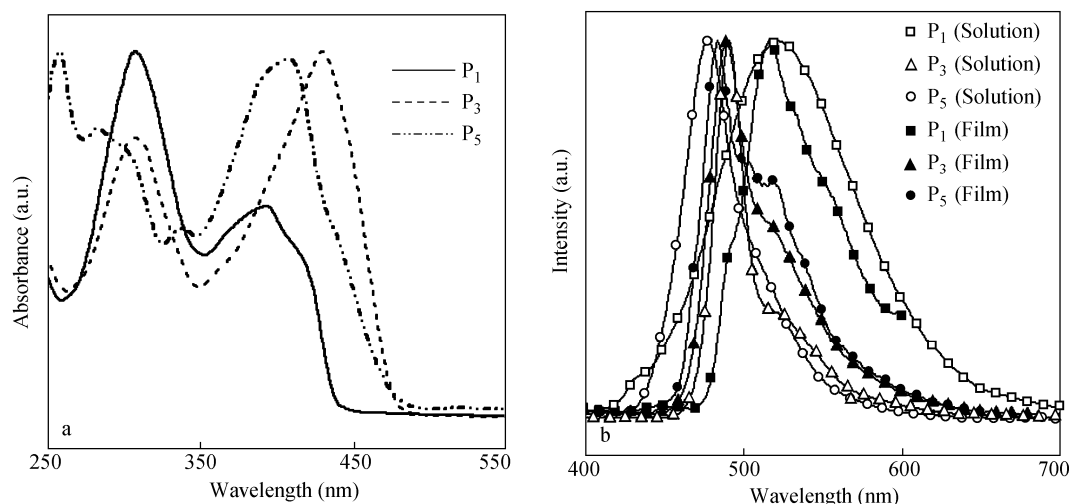


Fig. 3 UV absorption (a) in the DCM solution, fluorescence spectra (b) in DCM solution and in the solid state. Concentration: 0.015 mg/mL; Excitation wavelength (nm): 306

All the copolymers in DCM solutions emit blue fluorescence under ultraviolet irradiation. The PL spectra in the solutions, which are attributed to fluorescence because of the short lifetime of the excited state, show emissions around 521–478 nm as shown in Table 2. Because P_3 and P_5 have the similar structure with poly(fluorene-*alt*-phenylene) (0.4984 ns)^[23] and poly(diacetylene-*alt*-dialkoxyphenylene) (0.49 ns)^[24], which their lifetimes are shorter than that of Cz-PPV (1.1 ns)^[25], the fluorescence of P_3 and P_5 in the excited state have the same short lifetime. The PL spectrum of the polymer (P_1) in solution is red-shifted relative to that for the

copolymers (Fig. 3b). The PL spectrum of P₃ in solid state is red-shifted *ca.* 20 nm relative to that in solution (Fig. 3b). Such red-shift could be attributed to the presence of rotational conformers in the solution reducing the conjugation of the chromophore, or to the effect of packing and local geometry of the polymers.

Table 2. Absorption, PL emission spectral and thermal data of polymers

Polymer	UV-Vis $\lambda_{\max}$ (nm) ^a		PL $\lambda_{\max}$ (nm)		Φ_F ^b	T_d (°C) ^c	W_r (%) ^d
	Solution	Film	Solution	Film			
P ₁	306, 393	319, 418	521	518	0.59	423	66.7
P ₂	306, 398	315, 420	497	515	0.53		
P ₃	306, 429	313, 438	491	512	0.52	402	52.5
P ₄	302, 399	312, 407	484	510	0.48		
P ₅	407	345, 479	478	506	0.54	355	33.7

^a DCM as solvent with a concentration of 0.015 mg/mL; ^b Solution fluorescence quantum efficiency measured in DCM, relative to 9,10-diphenylanthracene in cyclohexane (Φ_{PL} = 0.9); ^c Temperature for 5% weight loss; ^d Weight residue at 800°C

Figure 4 shows an interesting phenomenon that the PL $\lambda_{\max}$ of polymers in the solid state increase linearly with the content of M₁. It indicates that the component molar ratios in the final polymers are in the direct proportion to the feed molar ratios and the emitting wavelength of the polymer films can be easily tuned by changing the feed molar ratios of monomers.

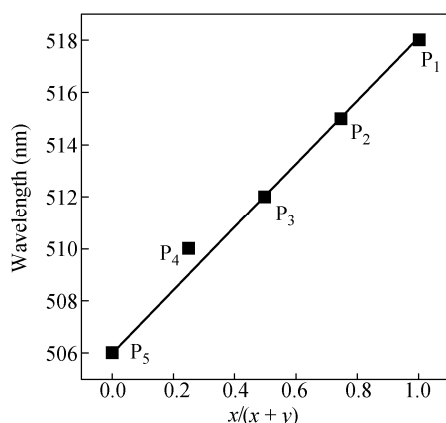


Fig. 4 The curve of PL $\lambda_{\max}$ in the solid state and content of M₁

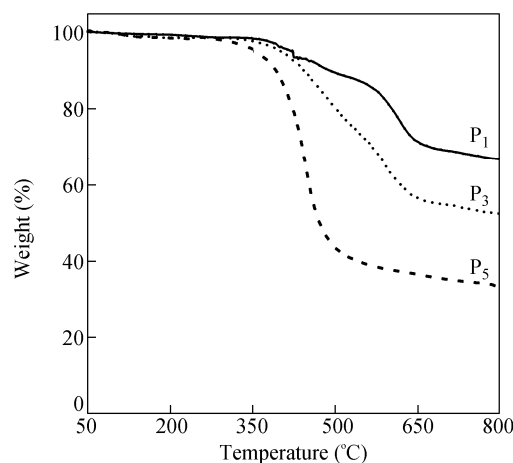


Fig. 5 TGA thermograms of polymers recorded under nitrogen at a heating rate of 20 K/min

The thermal properties of the polymers are evaluated by thermogravimetric analysis (TGA). The polymers bearing C $\equiv$ C–C $\equiv$ C show good thermal stability with their degradation temperatures as high as 400°C. Homopolymer P₁ shows a 5% weight loss at *ca.* 423°C (Table 2), whereas a 5% weight loss of the copolymer P₃ occurs at *ca.* 402°C. Compared among the polymers, the thermal stability are in the order of P₁ > P₃ > P₅ (Fig. 5). This is understandable because the octyloxy groups on the phenyl pendant in P₃ and P₅ are easily degraded upon thermolysis. The residues of P₁ are still more than 66.7% after pyrolyzed at 800°C (Table 2). These polymers are promising candidates as precursors of ceramic materials.

Electrochemical Properties

The redox behaviors of the polymers are studied by cyclic voltammetry. Conversion of these to potentials versus silver, which has a known work function of 4.4 eV, show that P₁ and P₃ have an onset oxidation potentials of 1.03 and 1.05 V, while those for the reductions are –2.10 and –2.07 V, respectively. According to the empirical formula^[26] $E_{HOMO} = -(E_{ox} + 4.4)$ eV and $E_{LUMO} = -(E_{red} + 4.4)$ eV, the HOMO and LUMO energy levels for P₁ and P₃ are –5.43 and –5.45 eV, –2.30 and –2.33 eV, respectively. Table 3 summarizes electrochemical properties of the three polymers. The oxidation potentials of copolymers are similar to that of

triphenylamine itself (−5.30 eV), indicating that it is a much better hole acceptor than previous polyfluorenes. Interestingly the electrochemical bandgap (3.12 eV) closely matches the optical bandgap (3.25 eV) for P₃.

Table 3. Electrochemical properties of P₃^a

Polymer	E_{ox} (V)	E_{red} (V)	HOMO (eV)	LUMO (eV)	E_g (eV) ^b	E_g (eV) ^c
P ₁	1.03	−2.10	−5.43	−2.30	3.13	3.31
P ₃	1.05	−2.07	−5.45	−2.33	3.12	3.25
P ₅	1.24	−0.64	−5.64	−3.76	1.88	1.83

^a Performed in acetonitrile solution of tetrabutylammonium hexafluorophosphate (0.1 mol/L) at a scan rate of 50 mV/s under argon at room temperature; ^b Band gaps determined using $E_g = \text{LUMO} - \text{HOMO}$; ^c Estimated from the onset wavelength of the optical absorption of the solid thin films

CONCLUSIONS

Novel fluorene-based poly(aromatic diacetylene)s have been synthesized by Glaser-Hay reaction of diynes using CuCl and TMEDA as catalysts. The structures of the polymers are confirmed by standard spectroscopic analyses. All the polymerizations proceed smoothly. The polymers are completely soluble in common organic solvents and show good thermal stability. The temperature of loss 5% weight (T_d) of P₁ is up to 423°C and the remains weight (W_r) was up to 66.7% at 800°C. These copolymers exhibit blue emission in DCM and green emission in the solid state. Photoluminescence quantum yields in DCM solution are up to 0.36–0.54. Such materials may find an array of high-tech applications.

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