

Synthesis and Characterization of High Thermally-Stable and Good Soluble PVK-Based Polymers with Perylene Moiety

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ABSTRACT: Three new poly(*N*-vinylcarbazole) (PVK)-based copolymers containing *N*-(*n*-butyl)-*N*-ethyl-1,6,7,12-tetra-(4-*tert*-butyl-phenoxy)-3,4,9,10-perylene tetracarboxylic bisimides were successfully synthesized by partially formulated by the standard Vilsmeier reaction, and the formyl groups of high reactivity are condensed with cyanoacetylated perylene to afford PVK-based polymers. The copolymers containing different percentage of perylene were obtained through the percentage of cyanoacetylated perylene unit being controlled by the initial feed ratio. The structures and properties of three copolymers were characterized and evaluated by FT-IR, NMR, UV-vis, FL spectroscopy, gel permeation chromatography, and thermogra-

vimetric analysis measurements. The polymers were highly soluble in conventional solvents such as toluene, CHCl₃, THF, DMF etc., and they were thermally stable up to 442–445°C. Three copolymers have emission spectra with characteristic features of the perylene unit, and fluorescence quantum yields of polymers are higher than that of perylene bisimide, which may be caused by singlet–singlet energy transfer from PVK backbone to perylene in the polymers. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 1778–1783, 2008

Key words: perylene; poly(*N*-vinylcarbazole); synthesis; high solubility

INTRODUCTION

In recent years, conjugated polymers and organic materials have attracted great interest due to their possible applications in light-emitting diodes and photovoltaic cells.^{1–8} Poly(*N*-vinylcarbazole) (PVK) is a well known photoconductive polymer possessing high stability and good processibility. It has been extensively used as hole-transporting species in photoelectronic devices. Perylene derivatives represent a class of *n*-type semiconductor exhibiting relatively high electron affinity among large-band-gap materials. They are well known chromophores combining high quantum yields of photoluminescence with excellent photochemical and thermal stability and are successfully used in effect transistors, solar cells, light-harvesting arrays, and light emitting diodes.^{1,9–29} Perylene bisimides are potential candidates as red light materials in organic light-emitting diodes. Many types of perylene derivatives have been synthesized, but the expected low solubility of these

molecules is a problem for synthesis, purification, and applications in the devices. Therefore, work has shifted to more soluble perylenes and there has been an increasing interest in design and synthesis of PVK derivatives having functional perylene. In this article, we present the synthesis and characterization of three new high thermally-stable and good soluble PVK-based polymers containing different weight percentage of cyanoacetylated perylene bisimide moieties (Fig. 1). The weight percentage of perylene pendants in the side chain was controlled by tuning the initial feed ratio of the perylene chromophore. Three polymers were good soluble in common organic solvents and were characterized by ¹H NMR, IR, UV-vis, FL, TGA, and GPC analyses.

EXPERIMENTAL

Material

Phosphorus oxychloride was purified by two consecutive distillations. PVK was purchased from Acros, its weight-averaged molecular weight was estimated to be 1.1×10^5 g/mol together with a polydispersity of 7.42 by gel permeation chromatography (GPC), using polystyrene as reference. *N*-(*n*-butyl)-1,6,7,12-tetra(4-*tert*butylphenoxy)-3,4,9,10-perylenetetracarboxylic monoanhydride (**1**) and PVK-CHO were

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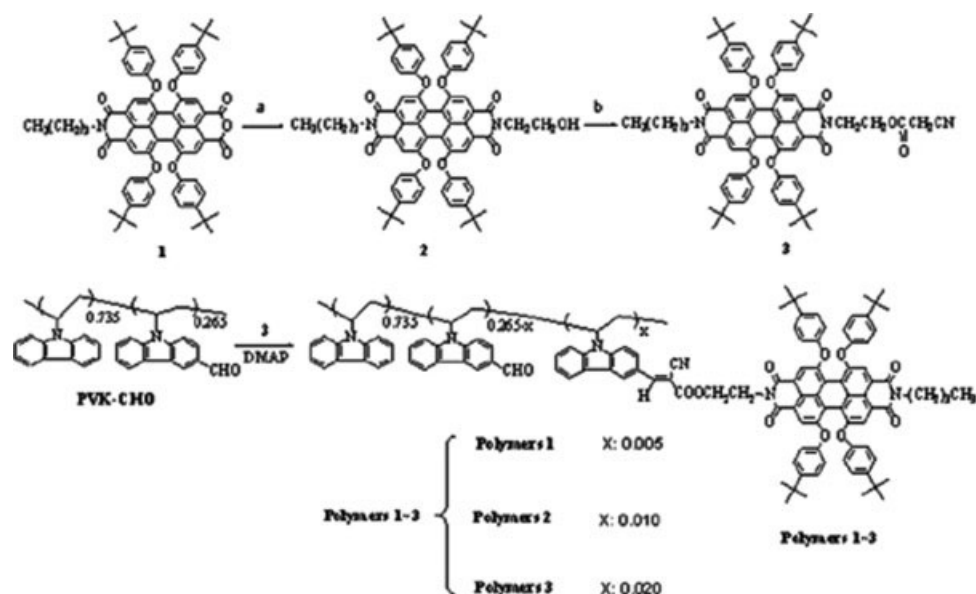


Figure 1 Synthesis of perylene bisimide chromophore **3** and their polymers **1-3**. Footers: Reagents and conditions: (a) ethanolamine, toluene, reflux, 4 h, 77%; (b) DCC, DMAP, TsOH, DCM, rt, 24 h, 62%.

prepared following a procedure described in the literature,^{22,30} respectively. Dichloromethane was dried over anhydrous calcium chloride and distilled before use. All other reagents and solvents were used as received without further purification.

Characterization

¹H NMR spectra were obtained with a Bruker AM-500 spectrometer. FT-IR spectra were recorded on a Nicolet Magna-IR550 in the region of 4000–400 cm⁻¹ using KBr pellets spectrophotometer. UV–visible spectra were determined with a Varian Cary 500 spectrometer in chloroform solution. Photoluminescent spectra were recorded on Varian Cary Eclipse. Thermogravimetric analyses (TGA) was conducted in Mettler Toledo Thermal Analyzer SDTA 851^e at a heating rate of 20°C/min under nitrogen atmosphere. The molecular weights were determined by gel permeation chromatography (Waters HP/GPC), using THF as eluent and polystyrene standards of known molecular weights were used for calibration.

Synthesis of *N*-(*n*-butyl)-*N'*-hydroxyethyl-1,6,7,12-tetra(4-*tert*-butylphenoxy)-3,4,9,10-perylenetetracarboxylic bisimide (**2**)

N-(*n*-butyl)-1,6,7,12-tetra(4-*tert*-butylphenoxy)-3,4,9,10-perylenetetracarboxylic monoanhydride (**1**) (2.0 g, 1.98 mmol) and ethanolamine (0.5 g, 7.69 mmol) were dissolved in 40 mL toluene. The reaction mixture was refluxed for 4 h. After cooling, the solution was concentrated by a rotary evaporator. The product was purified by a silica gel column using chloro-

form/acetone (40 : 1) as eluent. Red solid; yield 77.2%. IR (KBr), ν (cm⁻¹): 2963, 2867, 1698, 1662, 1585, 1503, 1407, 1335, 1286, 1217, 1178, 1005, 975, 837, 552. ¹H NMR (500 MHz, CDCl₃), δ (TMS, ppm): 8.22 (s, 4H), 7.24 (d, *J* = 8.2 Hz, 8H), 6.83 (d, *J* = 8.3 Hz, 8H), 4.38 (t, *J* = 5.1 Hz, 2H), 4.12 (m, 2H), 3.92 (t, *J* = 5.6 Hz, 2H), 1.65 (m, 2H), 1.40 (m, 2H), 1.29 (s, 36H), 0.93 (t, *J* = 6.9 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃), δ (ppm): 164.9, 164.1, 156.8, 156.5, 153.6, 153.5, 148.0, 127.3, 123.3, 122.7, 120.9, 120.4, 120.1, 119.9, 62.4, 43.6, 41.1, 35.1, 32.1, 30.8, 21.0, 14.4.

Synthesis of *N*-(*n*-butyl)-*N*-(2-cyanoacetoxyethyl)-1,6,7,12-tetra(4-*tert*-butylphenoxy)-3,4,9,10-perylenetetracarboxylic bisimide (**3**)

N-(*n*-butyl)-*N*-hydroxyethyl-1,6,7,12-tetra(4-*tert*-butylphenoxy)-3,4,9,10-perylenetetracarboxylic diimide (1.6 g, 1.52 mmol), cyanoacetic acid (0.15 g, 1.67 mmol), dicyclohexylcarbodiimide (DCC) (0.34 g, 1.67 mmol), and 4-(*N,N*-dimethyl)aminopyridine (DMAP) (0.04 g, 0.3 mmol) were dissolved in 80 mL of dry dichloromethane and stirred at room temperature for 24 h. The precipitate was filtered out and washed with dichloromethane for several times. The solution was washed with 1% hydrochloric acid, 2% diluted aqueous solution of sodium bicarbonate and water, and dried by magnesium sulfate. The crude product was purified by column chromatography on silica gel (100–200 m) with chloroform to give the pure product. Yield: 68%. ¹H NMR (500 MHz, CDCl₃): δ 8.24 (s, 4H), 7.24 (d, *J* = 8.25 Hz, 8H), 6.82 (d, *J* = 8.37 Hz, 8H), 4.52 (t, *J* = 5.03 Hz, 2H), 4.46 (m, 2H), 4.11 (t, *J* = 5.73 Hz, 2H), 3.39

(s, 2H), 1.65 (m, 2H), 1.38 (m, 2H), 1.29 (s, 36H), 0.93 (t, $J = 7.35$ Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3), δ (ppm): 167.6, 165.1, 161.1, 157.8, 157.5, 154.7, 154.5, 148.7, 127.9, 124.3, 123.6, 121.7, 120.8, 120.6, 119.5, 116.2, 61.4, 43.7, 42.1, 35.7, 32.5, 30.9, 21.3, 14.2. MS: m/e 1151.3 [$(M + 1)^+$, calcd for 1150.3].

Synthesis of polymers (1–3): Figure 1

General procedure for synthesis of polymers (1–3) is similar, and polymer 3 is as follows: PVK-CHO (0.2 g, 0.09 mmol), cyanoacetylated perylene chromophores (0.018 g, 0.016 mmol), and DMAP (0.004 g, 0.032 mmol) were dissolved in 6 mL of THF under an argon atmosphere. The reaction mixture was stirred at 60°C for 30 h and poured into 50 mL acetone. The resulting red precipitate was collected and purified by reprecipitation from THF solution into acetone. The product was collected and dried in vacuum at 65°C for 48 h.

Polymer 1: FT-IR (cm^{-1} , neat): 2245 (CN); 1739 (COOR); 1687 (CHO); 1623, 1586, 745, 721 (carbazole); ^1H NMR (CDCl_3) δ (ppm): 1.23 ($-\text{CH}_3$), 1.52–1.84 ($-(\text{CH}_2)_4-$), 3.43–3.75 ($N-\text{CH}_2-$), 4.23–4.36 (COOCH_2-), 6.41–8.02 (ArH), 8.18 (CN–C=CH–), 9.37–9.76 (CHO–).

Polymer 2: FT-IR (cm^{-1} , neat): 2246 (CN); 1738 (COOR); 1687 (CHO); 1624, 1585, 745, 721 (carbazole); ^1H NMR (CDCl_3) δ (ppm): 1.23 ($-\text{CH}_3$), 1.51–1.85 ($-(\text{CH}_2)_4-$), 3.45–3.77 ($N-\text{CH}_2-$), 4.25–4.36 (COOCH_2-), 6.41–8.02 (ArH), 8.18 (CN–C=CH–), 9.37–9.76 (CHO–).

Polymer 3: FT-IR (cm^{-1} , neat): 2246 (CN); 1738 (COOR); 1687 (CHO); 1627, 1586, 743, 721 (carbazole); ^1H NMR (CDCl_3) δ (ppm): 1.23 ($-\text{CH}_3$), 1.51–1.85 ($-(\text{CH}_2)_4-$), 3.44–3.76 ($N-\text{CH}_2-$), 4.23–4.37 (COOCH_2-), 6.42–8.03 (ArH), 8.19 (CN–C=CH–), 9.37–9.76 (CHO–).

RESULTS AND DISCUSSION

The synthetic route shown in Figure 1 describes the preparation of perylene diimide 3 and polymers 1–3 with varying wt % cyanoacetylated perylene chromophore in side chain. The important intermediate *N*-(*n*-butyl)-*N'*-hydrogen-1,6,7,12-tetra (4-*tert*-butylphenoxy)-3,4,9,10-perylenetetracarboxylic bisimides 2 was synthesized by condensation of *N*-(*n*-butyl)-1,6,7,12-tetra(4-*tert*-butylphenoxy)-3,4,9,10-perylenetetracarboxylic monoanhydride with ethanolamine, which can readily convert into perylene diimide 3 by reaction with cyanoacetic acid, in the presence of DCC and 4-(*N,N*-dimethyl)aminopyridine (DMAP). All the reactions went smoothly and the monomers were isolated in good yields. All the intermediates and perylene bisimide 3 were characterized by standard spectroscopic methods, from which satis-

TABLE I
Chromophore Contents and Physical Properties of Polymers 1–3

Polymers	x^a (g %)	x^b (g %)	M_n ($\times 10^{-5}$)	M_w ($\times 10^{-5}$)	T_d (°C)	T_g (°C)
PVK-CHO			0.14	1.1	302	212
1	0.50	0.49	1.5	5.8	444	240
2	1.00	1.05	1.6	6.7	445	241
3	2.00	2.01	1.8	9.6	443	243

^a The initial weight feed ratio of perylene chromophore in polymer.

^b The content of incorporated perylene units as calculated from ^1H NMR spectra.

factory analysis data were obtained. The formylation degree of PVK-CHO, which is defined as the molar percentage of the formylated carbazole ring in the PVK long chain, is estimated to be 26.5% from the comparison of the integration of the aldehyde and carbazolyl aromatic protons, and according to the procedure, PVK can be formylated to different degrees by modulating the ratio of reagents and the length of the reaction period.³⁰ The formyl groups of high reactivity are condensed with cyanoacetylated perylene bisimide 3 to afford polymers. The weight percentage of perylene pendants of three polymers containing PVK was controlled by controlling the initial feed ratio of the cyanoacetylated perylene chromophore. The actual content of the perylene bisimide moiety was calculated from the integration of the peaks at $\delta = 4.52$ and 9.37–9.76 ppm in ^1H NMR spectra of the polymer, which are attributed to the methylene proton close to the oxygen atom in the carboxylic ester unit and aldehyde group, respectively. The weight fraction of incorporated cyanoacetylated perylene chromophore in the polymers can be determined to be 0.49, 1.05, and 2.01 wt %, respectively. The perylene contents in polymers 1–3 and their physical properties data are also given in Table I. As seen in Table I, the actual composition of polymers is almost consistent with the feed ration.

An example of the IR spectrum of polymer 3 is given in Figure 2. The spectrum of perylene bisimide 3 and PVK-CHO are also shown in the same figure for comparison. In the IR spectrum of PVK-CHO, a strong absorption band is observed near 1690 cm^{-1} , which is in the frequency range expected for the carbonyl stretching vibration of an aromatic aldehyde. After being further functionalized with cyanoacetylated chromophores, new absorption bands at 1742 and 2231 cm^{-1} emerge, respectively, contributed by the carbonyl stretching vibration of a conjugated carboxylic ester and the nitrile stretching vibration.³⁰ In addition, the aromatic aldehyde absorption band of polymer 3 remains visible, which is due to lower initial feed ratios of cyanoacetylated perylene bisimide

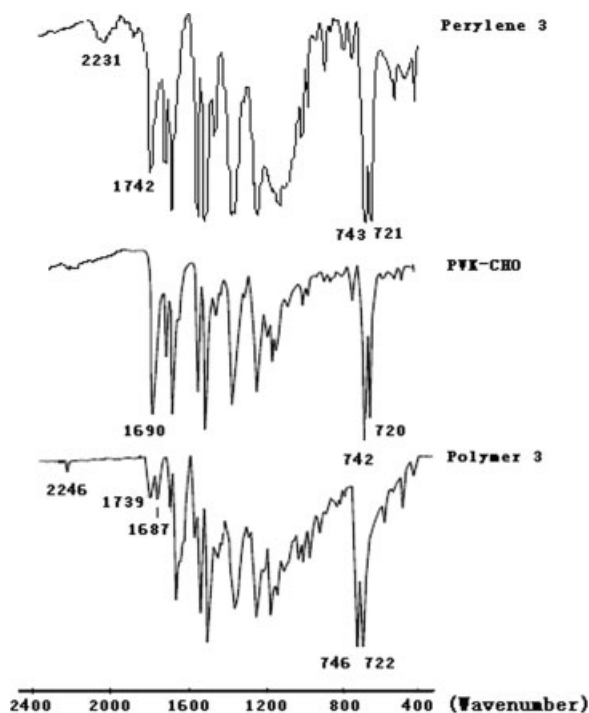


Figure 2 IR spectra of perylene bisimide 3, PVK-CHO and polymer 3.

3 in polymer. This is shown more clearly in the ^1H NMR spectrum (Fig. 3) where the peaks assigned to the formyl groups of polymer 3 still remains. At the same time several new peaks of polymer 3 emerge distinctively at almost the same sites as those of cyanoacetylated perylene bisimide 3.

The UV-vis absorption spectra of polymers 1–3 and perylene bisimide 3 in dichloromethane at dilute concentration are shown in Figure 4, and their absorption data are listed in Table II. In the UV-vis spectra, perylene bisimide 3 show three typical perylene absorption peaks at ~ 450 , 541, and 571 nm with high coefficients, while three polymers absorption are stronger at 329–343 nm due to the π - π^* transition of carbazolic groups in PVK backbone. As can be seen in Figure 4, the spectra of the polymer 3 is almost identical and similar to those of perylene bisimide 3 at visible region, suggesting that there is no significant electronic interaction between the PVK backbone and perylene bisimide chromophore in the ground state. However, the UV-vis absorption spectra of polymers 1–2 mainly show absorption bands from PVK conjugated backbone at 329–343 nm due to lower perylene contents in polymer. In addition, the absorption spectra of PVK (Fig. 4) further reveals that the singlet excited state of the perylene unit lies below that of the PVK backbone. As a result, excitation of the PVK backbone may result in singlet energy transfer to the perylene unit.

Figure 5 shows the fluorescence spectra of polymer 2 and perylene bisimide 3 in dichloromethane

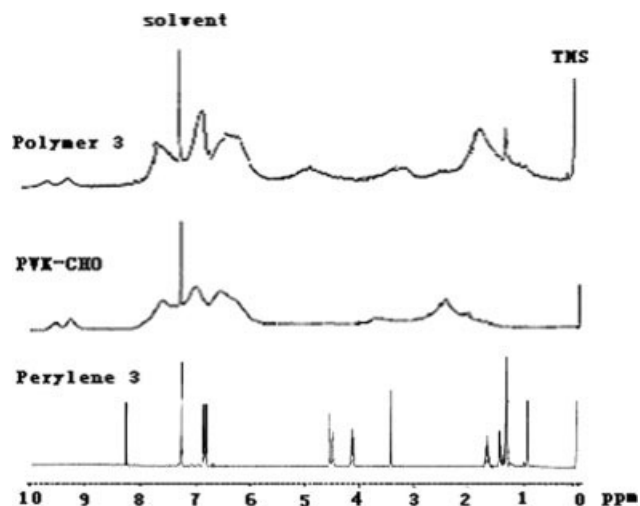


Figure 3 ^1H NMR spectra of perylene bisimide 3, PVK-CHO and polymer 3 in CDCl_3 .

at excitation wavelength 575 nm. Perylene bisimide 3 shows intense fluorescent maxima at 610 nm, and polymers 1–3 have also emission spectra with characteristic features of the perylene unit. To estimate PL efficiencies of the polymers, their emission spectra are measured in dilute dichloromethane solutions. Using perylene bisimide 3 as a standard,²² fluorescence quantum yields Φ_{PL} of polymers 1–3 are estimated to be 1.06, 1.28, 1.01%, respectively, (Table II). When the initial feed ratio of the cyanoacetylated perylene bisimide is 1.0%, fluorescence quantum yield of polymer 2 is the most high. Fluorescence enhancing is probably caused by photoinduced electron/energy transfer from the PVK backbone to perylene unit.

The TGA thermograms of polymers 1–3 are shown in Figure 6. It was found that these polymers 1–3 are

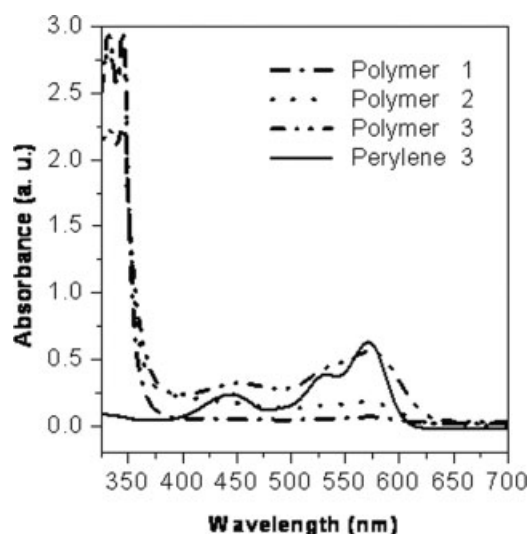


Figure 4 UV-vis absorption spectra of perylene bisimide 3 and polymers 1–3 in CH_2Cl_2 . Concentration: 2.5×10^{-5} M.

TABLE II
Absorption and Fluorescence Data for
Polymers 1–3 and 3 in THF

	λ_{\max}^a (nm)			λ_{\max}^{fl} (nm)	ϕ^b
	1	2	3		
Perylene 3	571	541	450	602	1
PVK-CHO	343	329		414	
Polymer 1	570	345	331	601	1.06
Polymer 2	571	345	332	601	1.28
Polymer 3	571	345	331	601	1.01

^a For polymers 1–3 and perylene bisimide 3 fluorescence spectra.

^b Quantum yields were obtained upon excitation on their absorption maxima (λ_{ex} : 575 nm); Fluorescence quantum yields Φ_{PL} were measured with the method by using perylene bisimide 3 as a standard.²²

thermally-stable up to around 442°C. The weight of polymer 3 at high temperature area (>500°C), however, lost seriously when compared with that in polymers 1–2, suggesting that higher contents of the perylene bisimide side chain attached to the carbazole ring can weaken the thermal resistance of the polymer. Molecular weights of the polymers determined by GPC are as high as hundreds of thousands, and it indicates PVK main-chain is stable during the reactive process. Polymers 1–3 are readily soluble in common organic solvents, such as THF, CHCl_3 , $\text{ClCH}_2\text{CH}_2\text{Cl}$, DMF, and NMP. The polymer systems are built up with long alkylene spacers which can explain the observed good solubility.

CONCLUSION

In this work, a new class of highly soluble and good thermally-stable copolymers based on PVK and perylene are designed and synthesized in moderate

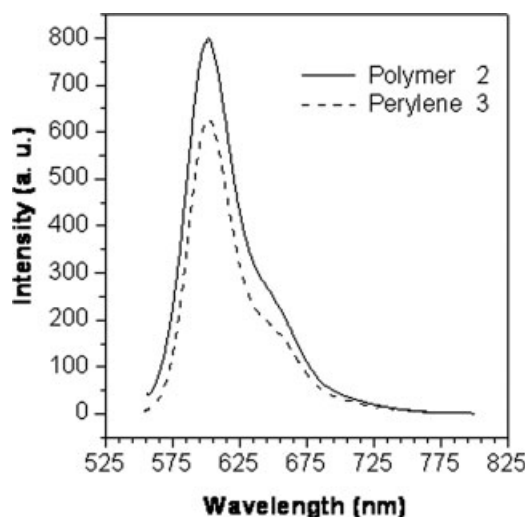


Figure 5 Photoluminescence spectra of CH_2Cl_2 solutions of perylene bisimide 3 and polymer 2. Concentration: 1×10^{-6} M. Excitation wavelength: 575 nm.

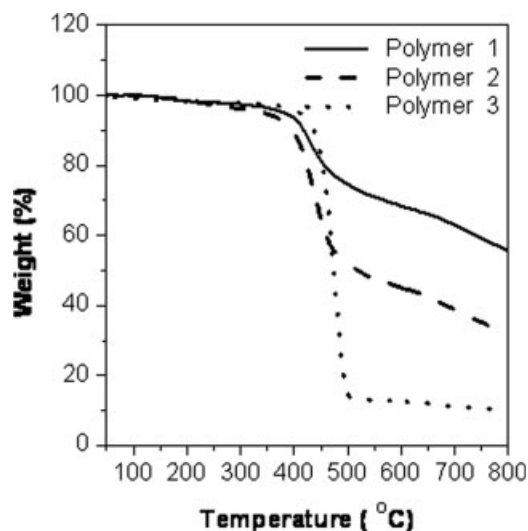


Figure 6 TGA thermograms of polymers 1–3 recorded under nitrogen at a heating rate of 20°C/min.

yields by two successive postfunctionalizations, whose number-average molecular weights are from 1.5×10^5 to 1.8×10^5 . The structures and properties of three copolymers are characterized by FTIR, NMR, UV-vis, and FL spectra as well as GPC and TGA measurements. These copolymers have emission spectra with characteristic features of the perylene unit, and their fluorescence quantum yields are higher than that of perylene bisimide, suggesting that they will be a good candidate for exhibiting multifunctional properties for light-emitting diodes applications.

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