

A highly soluble blue light emitting copolymer of anthracene and dialkyloxy benzene prepared by oxidative-coupling reaction

Jinyun Zheng^a, Caimao Zhan^{a,*}, Song Wu^a, Lei Zhou^a, Xi Yang^a, Rui Zhan^{a,b}, Jingui Qin^a

^aDepartment of Chemistry, Wuhan University, Wuhan 430072, People's Republic of China

^bCollege of Life Science, Wuhan University, Wuhan, People's Republic of China

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Abstract

A new kind of soluble copolymers incorporated anthracene and dialkyloxy benzene moieties into main chain have been prepared by oxidative-coupling copolymerization. They were characterized by FT-IR, ¹H NMR, UV-Vis, GPC, X-ray, thermogrametric analysis and fluorescence spectroscopy. The copolymers are amorphous and show excellent solubility in common organic solvents, such as chloroform. Thermogrametric analysis of the copolymers revealed that they have good stability with the onset decomposition temperature above 330 °C. The fluorescence spectra of the copolymers in solid state film display blue light emitting properties with the maximum at 468 nm. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Oxidative-coupling copolymerization; Anthracene; Blue light emitting

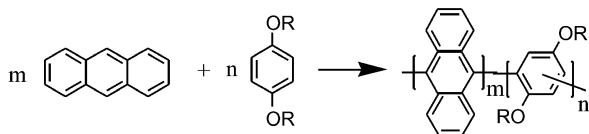
1. Introduction

Polymer with aromatic or heterocyclic units, generally absorb light with wavelengths in the range from 300 to 500 nm due to $\pi-\pi^*$ transitions. The excited states of their chromophores (excitations) release energy radiatively as well as nonradiatively on returning to the ground state. The radiative decay of excitations to the ground state can emit visible light. These excitations are also formed when a bias potential is applied to an emission polymer sandwiched between an anode and a cathode [1] due to the recombination of holes and electrons. Conjugated polymers display suitable properties for photo- and electroluminescent devices that are difficult to obtain using conventional inorganic materials, such as low operating voltages, easy colour tuning, fast response time, high quality of display and an improved processability. A large number of light emitting polymers have been introduced during the last 10 years [2]. The first organic light-emitting diode (OLED) was fabricated with anthracene crystals in 1965 but failed to attract attention because of poor performance [3]. Incorporation of anthracene moieties into polymer main chains contributes to solve the problem of preparation of films with good optical quality, and its electron-rich structure and low electronic

band gap have attracted considerable attention [4]. Anthracene and anthracene-containing fluorophores, such as 9,10-diphenylanthracene and bisstyrylanthracene, were incorporated into polymeric main-chains, or linked as pendent groups [5–15]. The polyesters and polyurethanes containing 9,10-diphenylanthracene moiety in the main chain have the low thermal stability [16]. Whereas the complicated synthetic procedure of anthracene-containing polymers, we propose a facile method of preparing the polymer containing anthracene in the main chain by oxidative-coupling copolymerization of anthracene and dialkyloxy benzene. The route is shown in Scheme 1. In this reaction, the 9,10 positions on the anthracene molecule are very active to link benzene ring to form 9,10-diphenylanthracene structure, which is a well-known high efficient fluorophore. Good thermal ability may be anticipated due to the rigid main chain. The conjugated electronic delocalization results in a smaller electronic band gap than the monomeric repeat units may make the emission wavelength move to longer wavelength compared to poly(1,4-dialkyloxyphenylene), which emits mainly below 400 nm. On the other hand, steric effect may inhibit a planar geometry of the polymer backbone, large torsion angles may then occur, which serve to reduce conjugation along the backbone of the polymer chain, thereby localizing to some extent the frontier electronic states [17]. Because of the delocalization and the steric effects, the emission of the copolymer of anthracene and dialkyloxy benzene may be blue light. In addition, we

* Corresponding author. Tel.: +86-27-8721-9024; fax: +86-27-8764-7617.

E-mail address: cmzhan@whu.edu.cn (C. Zhan).



Scheme 1. Polymer **1**: R = propyl. Polymer **2**: R = hexyl. Note: The feed ratio of anthracene to dialkyloxy benzene are 1/1, 1/2, 1/3, 1/4, 1/5 for **a**, **b**, **c**, **d**, **e**, respectively.

incorporated the alkyloxy pendent groups onto polymers, which can improve the solubility of the copolymer and overcome the inherent insolubility of conjugated molecules.

2. Experimental section

2.1. Reagents and solvent

1,4-Dialkyloxy benzene was prepared by the reaction of hydroquinone with *n*-alkylbromide in the presence of KOH in ethanol solution. Recrystallization from methanol gave white plates (yield 55%). Anhydrous FeCl₃ was purified by the reaction of FeCl₃·6H₂O with SOCl₂. Chloroform was purified by distillation after dried with CaCl₂. Anthracene was used as supplied.

2.2. Preparation of polymer

The copolymers with different ratio of anthracene to dialkyloxy benzene were prepared. A typical example of the copolymerization is described as follows (polymer **2a**): In a 100-ml three-necked round-bottomed flask fitted with a electro-magnetic stirrer, condenser, argon inlet and argon outlet, were placed anthracene (0.356 g, 2 mmol), 1,4-dihexyloxy benzene (0.278 g, 1 mmol), CHCl₃ (30 ml) and anhydrous FeCl₃ (1.95 g, 12 mmol) in sequence. The solution was stirred at room temperature under a slow stream of Ar and gradually became viscous with progress of the copolymerization. After 30 h, the ferric chloride was separated by centrifuged filtration, the filtrate was poured into ethanol. The precipitated polymer was collected by filtration and extracted in Soxhlet's extractor for 2 days to remove residual monomers and low molecular weight molecules. The recovered polymer was collected and dried in an oven at 60 °C. The yield was 0.26 g (45%). Elemental analysis (%): C 81.8, H 7.7.

2.3. Instruments and characterization methods

FT-IR spectra were recorded on a NICOLET AVATAR 360 FT-IR spectrometer with KBr pellets. The ¹H NMR (300 MHz) was obtained using a MERCURY-VX300 spectrometer with CDCl₃ as solvent. Chemical shifts (δ values) are given in parts per million with tetramethylsilane as an internal standard. UV-Vis spectra were recorded on a SHIMADZU 1601PC spectrometer. The emission spectra were obtained with a SHIMADZU RF-5301PC fluorescence

spectrometer. Thermal analysis was performed on a SHIMADZU DT-40 thermal analyzer at a heating rate of 20 °C/min in nitrogen at a flow rate of 50 cm³/min for thermogravimetric analysis (TGA). The glass transition temperature was measured on a Perkin Elmer differential scanning calorimeter (DSC) at a heating rate of 40.00 °C/min in nitrogen. Molecular weights were determined by a gel permeation chromatography (GPC) with polystyrene calibration using a WATERS 2690D Separation Module and WATERS 2410 Refractive Index Detector equipped with TSK-GEL GMHHR-M and TSK column at 30 °C in CHCl₃. The wide-angle X-ray diffraction patterns were obtained for powder specimens on a SHIMADZU XRD-6000 X-ray diffractometer.

To measure the fluorescence quantum yields, a degassed solution was prepared. The concentration was adjusted so that the absorbance of the solution would be lower than 0.1. The exciting wavelength was 346 nm and a solution in 1N H₂SO₄ of quinine sulphate, which has a quantum yield of 0.546, was used as standard.

3. Results and discussion

3.1. FT-IR spectra

Fig. 1 presents the FT-IR spectra of polymers **1** and **2**. Polymer **2a** shows characteristic absorptions due to aromatic ring at 1499, 1600 cm⁻¹, and the typical C–H out-of-plane bending mode of the four adjacent hydrogen on the anthracene units at 760 cm⁻¹, indicating the 9,10 linkage of the anthracene moieties in the backbone of the copolymer. The saturated C–H stretching vibration at 2927 and 2857 cm⁻¹, bending vibration at 1420 and 1378 cm⁻¹, and the ether vibration at 1206 and 1025 cm⁻¹, also are observed. The other copolymers also show these characteristic absorptions.

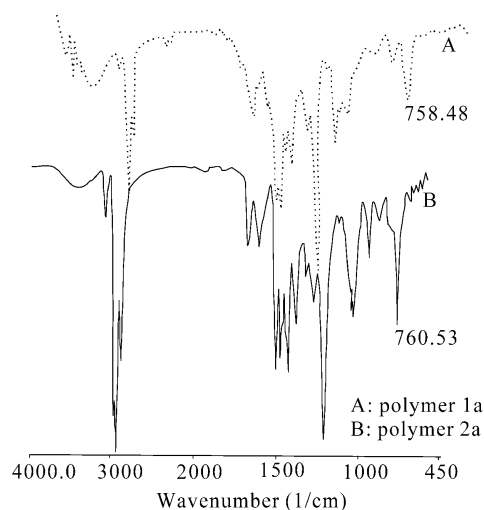


Fig. 1. FT-IR spectra of the copolymers.

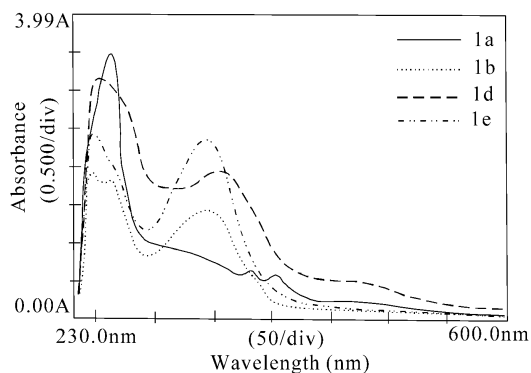


Fig. 2. UV–Vis spectra of polymer **1** in chloroform solution.

With decreased anthracene feed ratio proportion, the characteristic vibration corresponding to the anthracene structure weakened and shifted from 760 to 750 cm^{-1} gradually from copolymer **a** to **e**, indicating the decreased anthracene content in the copolymers.

3.2. $^1\text{H NMR}$

The $^1\text{H NMR}$ spectrum of polymer **2a** displays rather broad signals owing to the polymeric structure. There are two signals at 8.65 ppm (1H) and 7.99 ppm (2H) attributed to the anthracene moieties. The signals positioned at $6\text{--}7.7\text{ ppm}$ (7H) are assigned to the hydrogen of the benzene rings. The high field signals result from the hydrogen of the alkyl groups.

3.3. UV–Vis spectra

The UV–Vis spectra of the copolymers in chloroform solutions were recorded and depicted in Figs. 2 and 3. All of them exhibit the first absorption band around 250 nm assigned to the benzene (245 nm) and anthracene (257 nm) moieties and the second absorption at $320\text{--}400\text{ nm}$, which is similar to the absorptions of 9,10-diphenylanthracene. The copolymers with higher anthracene content such as polymers **1a** and **2a** show absorption at $370\text{--}400\text{ nm}$, resulted from adjacent anthracene moieties, which disappears when anthracene content decreased. With the

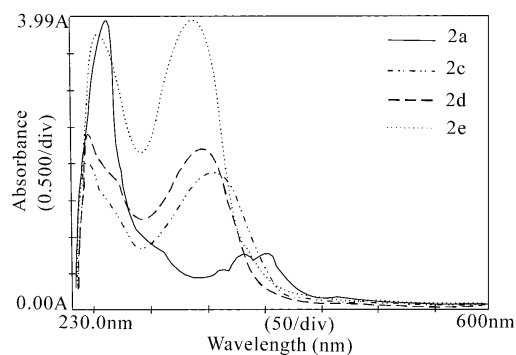


Fig. 3. UV–Vis spectra of polymer **2** in chloroform solution.

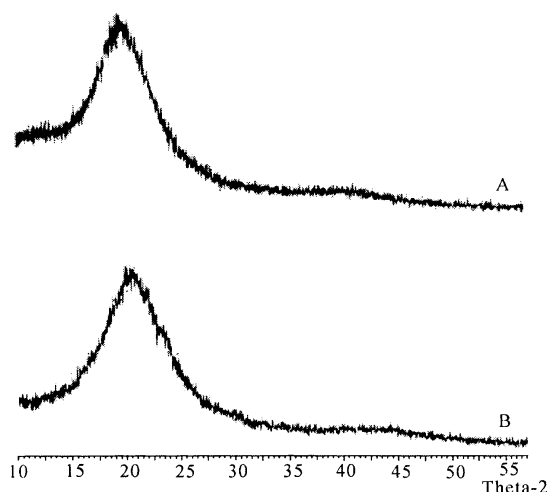


Fig. 4. Wide-angle X-ray diffraction curves of polymer **2**: curve A: polymer **2a**; curve B: polymer **2e**.

anthracene content decreased, the first absorption band becomes weak, while the second becomes strong, indicating the 9,10-diphenylanthracene moieties increase with decreasing anthracene moieties.

In addition, the UV–Vis spectra of the copolymers in thin film were recorded. The film was prepared by spin coating on quartz plate from the solution polymers. Upon comparing the absorption spectra in solid state with that of the polymers in solution, it is seen that they have similar absorption band and the second absorptions of solid film become stronger than in solution.

3.4. Morphology

The wide-angle X-ray scattering curves (Fig. 4) of the copolymers reveal that they are amorphous owing to the statistical copolymerization and irregular chain structure. The amorphous structure may afford a high optical quality solid film.

3.5. Solubility

The solubility of the typical copolymers was measured and the results are shown in Table 1. The results reveal that the copolymers have excellent solubility in chloroform and toluene, and polymer **2** have better solubility than polymer **1** due to the long pendent alkyl chains.

3.6. The molecular weight

The molecular weights obtained by GPC reveal that the copolymers have the M_n of several thousand and the M_w of $5600\text{--}22\,000$, and the polydispersity of $1.5\text{--}5.0$. Polymers **1d** and **2d** have M_n of 9100 , M_w of $22\,000$, polydispersity of 2.45 ; and M_n of 4800 , M_w of $21\,000$, polydispersity of 4.48 , respectively. The GPC curve of polymer **2a** shows a Gaussian peak with 97.6% of the total area. It means that

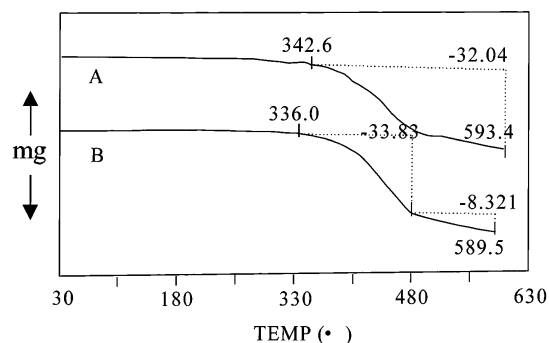


Fig. 5. TGA curves of copolymers A: polymer **1a**; B: polymer **2a**.

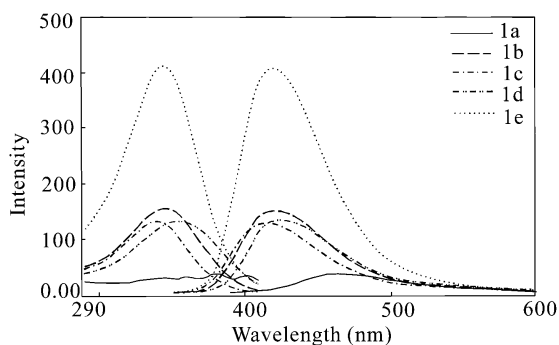


Fig. 6. The fluorescence spectra of polymer **1** in chloroform solution (Slit width: Ex, 3 nm; Em, 3 nm).

the copolymerization was the major reaction and the homopolymerization of the monomers was negligible.

3.7. Thermostability

The good thermal stability of the copolymers was ascertained by TGA. The TG curves are shown in Fig. 5. The weight loss of polymer **1a** started at 342.6 °C, and reached at 33.0% till 593.4 °C, while polymer **2a** started at 336.0 °C and reached at 33.8% till at 481.5 °C when heated in Ar atmosphere. Polymer **1a** has better thermal stability than polymer **2a** owing to the shorter aliphatic side-chains. The glass transition temperature (T_g) of polymers **1a** and **2c** determined by DSC were 173.6 and 160.3 °C, respectively.

3.8. Fluorescence

The fluorescence spectra of the copolymers in solution show they are violet to blue light emitting materials (Figs. 6

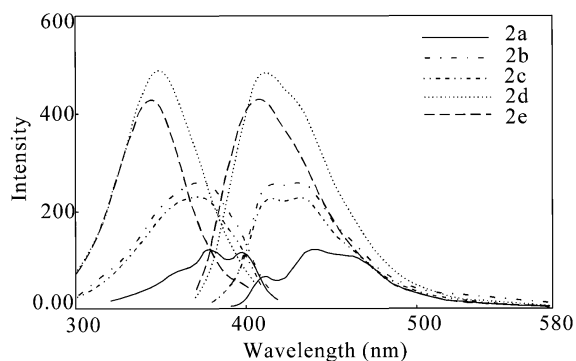


Fig. 7. The fluorescence spectra of polymer **2** in toluene solution (Slit width: Ex, 3 nm; Em, 3 nm).

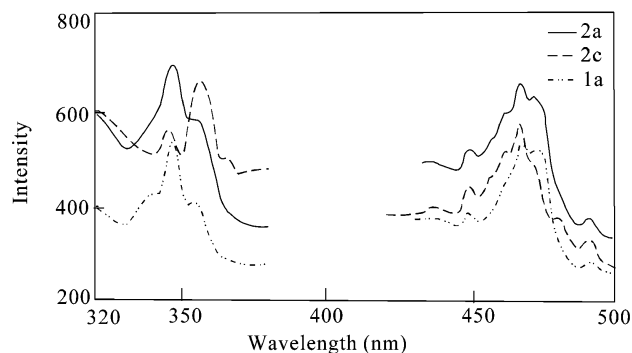


Fig. 8. The fluorescence spectra of the copolymers in solid film (Slit width: Ex, 3 nm; Em, 3 nm).

and 7). Polymers **1a** and **2a** with the high anthracene content display longer emission wavelength with the maximum at 466 and 468 nm in solutions, while others with low anthracene content with the maximum at 410–430 nm, which demonstrated the accuracy of incorporating anthracene into polymer backbone can decrease the electric gap.

Fig. 8 depicts the fluorescence spectra of the copolymers in solid film, the emitting curves become narrower than those in solution and the maxima are all at ca. 468 nm in spite of their different anthracene content. The photoluminescent (PL) properties of the copolymers in solid film are quite different from those in solution, which are positively related to their anthracene content as discussed earlier. The PL behaviour of the copolymers in solid state can be attributed to the ‘antennae effect’, or ‘photo-harvest effect’. The dialkylloxy benzene moieties absorb photons and are excited to the high energy level, then the energy is transferred to the anthracene moieties, which is promoted

Table 1
Solubility of the copolymers (g/100 ml)

	Polymer 1a	Polymer 1c	Polymer 1e	Polymer 2a	Polymer 2c	Polymer 2e
Chloroform	1.04	2.00	4.68	6.10	1.92	7.59
Toluene	1.42	1.39	0.88	3.50	2.14	2.55

Table 2

Quantum yield of the copolymers (notes: PDPP: poly(1,4-dipropoxyphenylene); PDHP: poly(1,4-dihexyloxyphenylene))

Solvent	Polymer 1a	Polymer 1b	Polymer 1c	Polymer 1d	Polymer 1e	PDPP
Toluene	0.10	0.16	0.19		0.28	0.14
	Polymer 2a	Polymer 2b	Polymer 2c	Polymer 2d	Polymer 2e	PDHP
Toluene	0.13	0.15	0.16	0.34	0.37	0.28

to the excited state then returns to the ground state emitting light with maximum ca. 468 nm.

The fluorescence quantum yield of the copolymers in toluene solution were measured relative to quinine sulphate ($\phi = 0.546$) and the results were summarized in Table 2. The quantum yield for emission decreases with increased anthracene concentration. In the copolymers with low anthracene contents, the probability of forming 9,10-diphenylanthracene increased, which results in a higher quantum yield. The quantum yields of polymers 1c and 1e and polymers 2d and 2e are higher than the homopolymers of dipropoxy benzene and dihexyloxy benzene accordingly, meaning the copolymerization can promote the PL emitting yield.

4. Conclusion

The copolymers containing anthracene and dialkyloxy benzene moieties have been synthesized by oxidative-coupling copolymerization. The GPC measurement shows that the molecular weights of the copolymers are several to 20 000 and the copolymerization was the main reaction. The copolymers are amorphous and have excellent solubility in common organic solvents and polymer 2 have better solubility than polymer 1 due to the longer alkyl pendent groups. TGA determination shows the copolymers 1a and 2a have onset decomposing temperature at 342.6 and 336 °C, respectively, since polymer 1a has shorter aliphatic side-chains. The UV–Vis spectra of the copolymers in solution reveal that the absorptions of the copolymers shift to a longer wavelength with the higher anthracene content, so do the fluorescence spectra in solution. The quantum yields of the copolymers increase with the decreased anthracene

content and are higher than the dialkyloxy benzene homopolymer when the anthracene content was very low. The fluorescence spectra in solid state film show the similar emitting wavelength with the maximum at ca. 468 nm in spite of their different anthracene content, which exhibits the antennae effect of the anthracene moieties on the polymer backbone.

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