

SYNTHESIS AND PHOTOPHYSICAL PROPERTIES OF POLY(ARYL IMINO) CONTAINING ACRIDINE UNITS (PAIA)*

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Abstract 1,4-Bis-(4-bromobenzoyl)benzene and proflavine, 3,6-diaminoacridine free base were synthesized first. Using 1,4-bis-(4-bromobenzoyl)benzene and proflavine, 3,6-diaminoacridine free base as the monomers, poly(aryl imino) containing acridine units (PAIA) was synthesized *via* palladium-catalyzed amination. The structure of PAIA was characterized by means of FTIR, ¹H-NMR spectroscopy and elemental analysis, the results show an agreement with the proposed structure. The UV absorption and photoluminescence spectra were tested. The absorption spectrum of the PAIA was dependent on the acidity of the media. The emission and excitation spectra of the two different forms of PAIA were investigated by photoluminescence, the addition of the trifluoroacetic acid (TFA) to the solution of PAIA does not lead to a quenching effect in the photoluminescent spectra. Additionally, DSC and TG measurements show that PAIA possess high glass transition temperature ($T_g > 230^\circ\text{C}$) and good thermal stability with high decomposition temperatures in nitrogen atmosphere ($T_D > 500^\circ\text{C}$).

Keywords: Poly(aryl imino); Acridine unite; Palladium-catalyzed amination; Photoluminescence.

INTRODUCTION

Recently, there has been a great deal of efforts centered on Pd-catalyzed C—N coupling reactions of NH groups with low reactivity halides^[1–4]. The catalytic amination reaction of arylene halides with primary amines using palladium complexes has become an important synthetic procedure for a variety of arylene amines including pharmaceuticals, electronic materials, and ligands for metal catalysts. This reaction has become a widely used practical synthetic method for C—N bond formation^[5–10]. The Pd-catalyzed aryl amination has also been applied to polycondensation reactions to give various polyamines and poly(imino ketone)s with no or scarcely cross-linked structures^[11–15].

During the last twenty years, polymers containing photosensitizers have been investigated for potential use in electron and energy transfers^[16–19]. Meanwhile, 3,6-diaminoacridine has been extensively investigated as photosensitizer for photoinduced hydrogen evolution from water^[20]. However, there have been few reports on the preparation and photoactivities of polymers containing the proflavine structure^[21].

Here the aim is synthesizing poly(aryl imino) containing acridine units in the main chain by palladium-catalyzed polycondensation of 1,4-bis-(4-bromobenzoyl)benzene with 3,6-diaminoacridine and reporting the results of preliminary photophysical processes of the polymer synthesized.

* This work was financially supported by the Foundation of National Key Laboratory of High Temperature and Density Plasma Physics (No. 9140C6806030807) and the Science and Technology Development Foundation of China Academy of Physics Engineering (No. 200708006).

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Received September 25, 2008; Revised December 1, 2008; Accepted December 8, 2008

EXPERIMENTAL

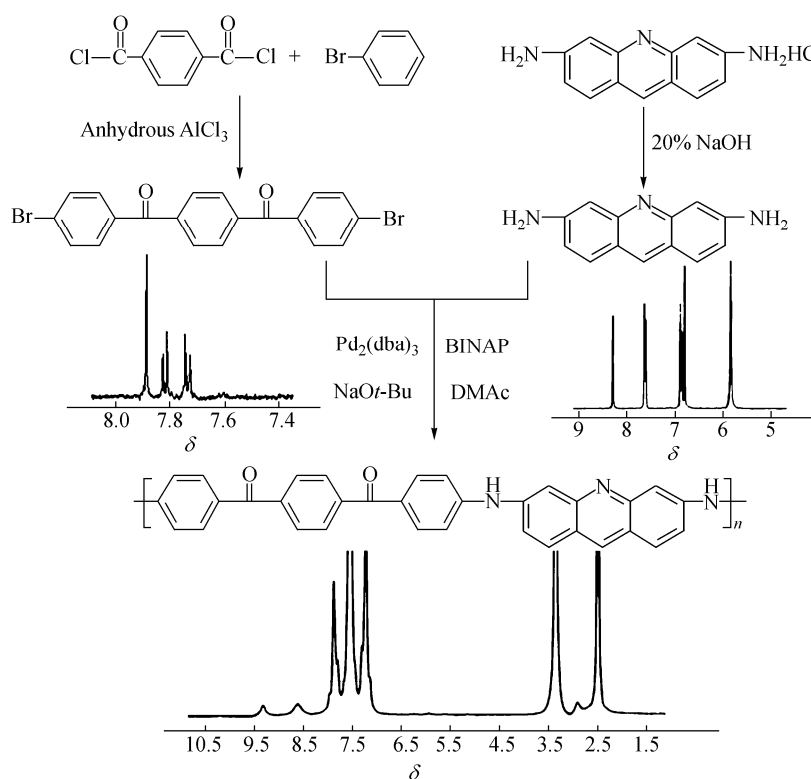
Materials and Measurements

Tris(dibenzylideneacetone)-dipalladium(0) ($\text{Pd}_2(\text{dba})_3$) and 2,2'-bis-(diphenylphosphino)-1,1'-binaphthyl (BINAP) were purchased from Alfa Aesar, a Johnson Matthey Company in USA. 3,6-Diaminoacridine hydrochloride was purchased from Daikin Finechemical Laboratory, Ltd, Japan. *N,N*-DMAc (DMAc) was distilled in our laboratory. The rest materials and reagents were obtained from different commercial sources and used without further purification.

FTIR spectra were recorded on a Nicolet 6700 FTIR spectrometer, elemental analysis was performed on a Perkin-Elmer model 2400 CHN analyzer, ^1H -NMR spectra were recorded using a Bruker AMX500 Hz NMR spectrometer in DMSO-d_6 . GPC measurements were used to determine molecular weights and molecular weight distributions by universal calibration generated with narrow molecular weight distribution polystyrene standards using dimethylformamide as eluent. The DSC curves obtained during the second heating scan were taken into consideration. The samples were heated at a rate of 10 K/min under flowing nitrogen gas. Thermo-gravimetric analysis was performed on a Mettler TG 10A at a heating rate of 10 K/min under air or nitrogen atmosphere.

Synthesis of Monomers

An oven-dried flask (150 mL) equipped with magnetic stirrer, into which were added terephthaloyl chloride (0.05 mol), bromobenzene (0.65 mol) and anhydrous powdered aluminum chloride (0.12 mol). The solution was stirred for 12 h at room temperature and then heated at 92°C for 2 h. After cooling the solution was poured into cold water and washed 4 times. The crude product was filtered and recrystallized from DMAc to give 1,4-bis-(4-bromobenzoyl)benzene as colorless crystals. Yield: 21.1 g, mp $272\text{--}273^\circ\text{C}$, FTIR (KBr pellet): *p*-disubstituted benzene appeared at 840 cm^{-1} and 843 cm^{-1} and carbonyl group appeared at 1640 cm^{-1} , ^1H -NMR (500 Hz, DMSO-d_6 , 100°C): $\delta = 7.89$ (s, 4H,), 7.81 (d, 4H, *m*-Br), 7.74 (d, 4H, *o*-Br), MS (EI): 444.10.



Scheme 1 Synthesis of PAIA via Pd-catalyzed aryl amination

Proflavine, 3,6-diaminoacridine free base was prepared from 3,6-diaminoacridine hydrochloride by neutralization with a sodium hydroxide solution at 0°C under an argon atmosphere. The chemical structure of the 3,6-diaminoacridine was established by $^1\text{H-NMR}$ spectroscopy (Scheme 1).

Synthesis of PAIA

An oven-dried resealable Schlenk flask (50 mL) equipped with magnetic stirrer, a nitrogen outlet, inlet and water-cooled condenser, added to which are 1,4-bis-(4-bromobenzoyl)benzene (5.0 mmol), 3,6-diaminoacridine (5.0 mmol), sodium *tert*-butoxide (1.350 g, 14.0 mmol), tris(dibenzylideneacetone)dipalladium(0) $\text{Pd}_2(\text{dba})_3$ (45.75 mg, 0.05 mmol), 2,2'-bis-(diphenylphosphino)-1,1'-binaphthyl (BINAP) (62.0 mg, 0.10 mmol), and DMAc (10 mL). The reaction mixture was flushed with high purity argon atmosphere. This procedure was repeated 4 times. The flask was immersed in a 100°C oil bath for 24 h, and then in a 160°C oil bath for 10 h with continuous stirring. The resulting polymer solution was allowed to slowly cold to room temperature, filtered and subsequently poured into methanol, filtered, washed with methanol several times, and then dried at 100°C under vacuum. Yield: 2.08 g, 96%. FTIR spectrum (KBr pellet): $\nu(\text{NH})$ at 3330 cm^{-1} , $\nu(\text{C}=\text{O})$ at 1623 cm^{-1} , $\nu(\text{C}-\text{N})$ at 1312 cm^{-1} . Anal. Calcd for $\text{C}_{33}\text{H}_{21}\text{N}_3\text{O}_2$ (491.62): C, 80.65, H, 4.27, N, 8.52. Found: C, 80.42, H, 4.37, N, 8.46. The $^1\text{H-NMR}$ is shown in Scheme 1.

RESULTS AND DISCUSSION

Polymer Synthesis

Using 1,4-bis-(4-bromobenzoyl)benzene and 3,6-diaminoacridine as the monomers, poly(aryl imino) containing acridine units in the main chain was synthesized *via* palladium-catalyzed polycondensation reaction. The catalytic system was generated from the combination of tris(dibenzylideneacetone)dipalladium(0) $\text{Pd}_2(\text{dba})_3$ and 2,2'-bis-(diphenylphosphino)-1,1'-binaphthyl (BINAP) (Scheme 1).

The polymer synthesized was characterized by FTIR, $^1\text{H-NMR}$ and elemental analysis. The results showed good agreement with the proposed structure. As an example, the $^1\text{H-NMR}$ spectrum of PAIA is shown in Scheme 1. The molecular weight of the polymer was measured by GPC (calibrated by polystyrene standards). The $M_n = 57400$, $M_w = 117600$.

UV Spectra of PAIA

The absorption spectrum of the neutral form of PAIA in DMAc shows two major absorption bands of different intensity at 366 and 445 nm (Fig. 1, curve a). This latter band is typical of the $\pi-\pi^*$ transition of the acridine chromophore. The absorption properties of the PAIA are dependent on the acidity of the media. Figure 1 shows the changes in the absorption spectra of DMAc solutions of PAIA with increasing the concentration of

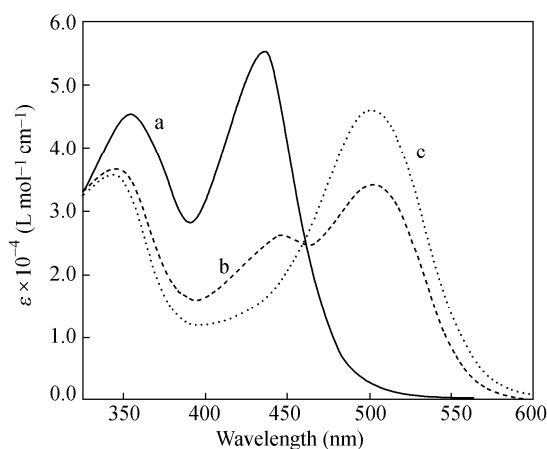
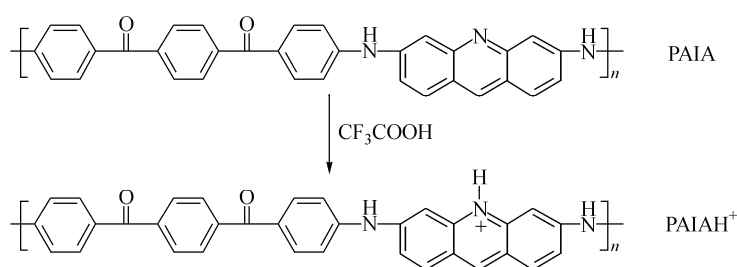


Fig. 1 Changes in the absorption spectra of PAIA (2×10^{-5} mol/L of the acridine unit in DMAc)
a) TFA = 0 mol/L; b) TFA = 1×10^{-5} mol/L; c) TFA = 3×10^{-5} mol/L

trifluoroacetic acid (TFA). On addition of TFA to this solution, a new band appears at 500 nm, whereas the two absorption bands at 366 nm and 445 nm decrease (Fig. 1, curve b). The result is assigned to the singly protonated form of the polymer (PAIAH⁺) (Scheme 2). The long wavelength transition observed for PAIAH⁺ can be assigned to the intramolecular charge-transfer transition, where charge transfer occurs from the two imino groups toward the electron-poor acridinium moiety. Continued addition of TFA leads to the complete disappearance of the absorption band at 445 nm accompanied by the formation of a new band around 500 nm (Fig. 1, curve c). From above, the absorption properties of PAIA were found to be dependent on the acidity of the medium as it can exist in neutral and singly protonated forms in solution (λ_{max} typically red shifts from 445 nm to 500 nm).



Photoluminescence of PAIA

The emission and excitation spectra of the various forms recorded in DMAc are shown in Figs. 2 and 3. The emission spectra of PAIA show a broad band with the maxima around 510–600 nm, although the absorption maximum of PAIA is considerably blue shifted compared to that of PAIAH⁺. The excitation spectra are similar to the absorption spectra of the corresponding species. This indicates that the emission does not arise from any trace amounts of the neutral PAIA which might be present in these solutions. The addition of the trifluoroacetic acid (TFA) to the solution of PAIA does not lead to a quenching effect in the photoluminescent spectra as was reported for other polymers containing acridine^[22]. This is due to the protonation of the proflavine unit. The photoluminescence spectra of PAIA are a prerequisite for an application in the electronic devices. Further parameters such as the photoluminescent efficiency need to be measured whether these materials are suitable for application in electronic devices.

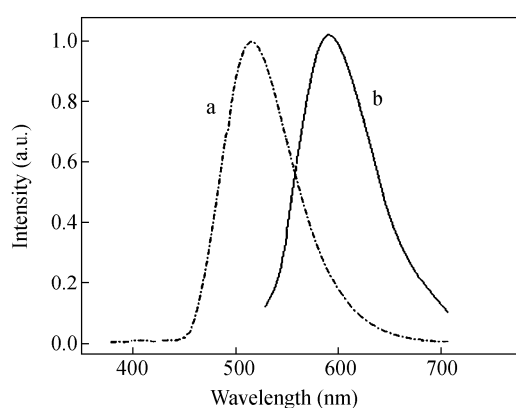


Fig. 2 Emission spectra of photoluminescent PAIA in DMAc at 25°C
a) PAIA neutral form; b) PAIA singly protonated form

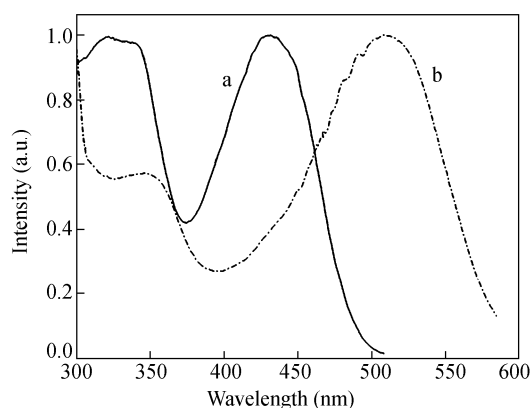


Fig. 3 Excitation spectra of photoluminescent PAIA in DMAc at 25°C
a) PAIA neutral form; b) PAIA singly protonated form

Thermal Behavior of PAIA

One of the essential requirements of a new polymer material for high temperature applications is the thermal stability which makes polymers attractive for potential applications. Hence, typical TG trace and DSC in nitrogen are demonstrated in Fig. 4 for PAIA. The TG curve revealed that PAIA was thermally stable at up to 500°C. The 5% weight loss took place at 500°C, and 50% weight loss took place at over 800°C in nitrogen. Differential scanning calorimetry (DSC) of PAIA up to 230°C showed a single T_g (the inset in Fig. 4).

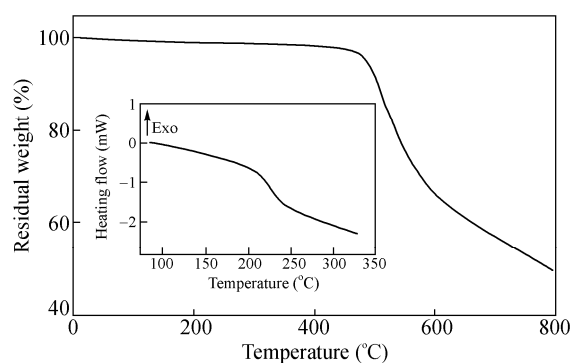


Fig. 4 TG and DSC curves of PAIA

CONCLUSIONS

Poly(aryl imino) containing acridine units was synthesized *via* palladium-catalyzed amination of aryl 1,4-bis-(4-bromobenzoyl)benzene with proflavine, 3,6-diaminoacridine free base. The absorption spectra of the PAIA were dependent on the acidity of the media because it can exist in neutral and singly protonated forms in solution. The emission and excitation spectra of the two forms of PAIA were investigated by photoluminescence, the addition of the trifluoroacetic acid (TFA) to the solution of PAIA does not lead to a quenching effect in the photoluminescent spectra. Additionally, PAIA was thermally stable up to 500°C in nitrogen atmosphere.

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