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Preparation of Functional Poly(aroyltriazole)s by Metal-Free Click Polymerization

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Summary: Functional poly(aroyltriazoles) (PATAs) were synthesized by heating mixtures of bis(aroylacetylene)s and diazides in polar solvents such as DMF/toluene at a moderate temperature of 100 °C with high molecular weights (M_w up to 17 200) and regioregularities (1,4-regioisomeric ratio up to ~95%) in high yields (up to ~95%). The obtained polymers are soluble in common organic solvents and are thermally stable. The PATAs containing triphenylamine units emit visible light and show unique solvatochromism, exhibiting large two-photon absorption cross sections due to the intramolecular charge transfer between their electron-donating triphenylamine and electron-accepting aroyltriazole units. The tetraphenylethene (TPE)-functionalized polymer shows intriguing aggregation-induced emission phenomenon, that is, the polymer is weakly emissive in its solution state but emit strongly in its aggregate/solid state with quantum yield of ~7.1%.

Keywords: aggregation-induced emission; click polymerization; fluorescence; poly(aroyltriazole); two-photon absorption

Introduction

1,3-Dipolar cycloaddition of acetylenes and azides has gained considerable attentions recently since Sharpless' and Meldal's research groups independently discovered that Cu(I) derivatives can efficiently catalyzed this reaction in a 1,4-regioselective fashion.[1,2] This reaction was coined "click chemistry", which has aroused much interest among researchers because of its remarkable advantages such as high yield, mild reaction conditions, and simple product isolation. These appealing features have enabled the reaction to evolve into a powerful synthetic tool, finding applications in diverse areas including drug discovery, bioconjugate chemistry, surface modification, and materials developments.[3] The click reaction has also been utilized in polymer science, mainly in the area of functionalization of preformed polymers through postpolymerization reactions.[4]

Synthetic polymer chemists have attempted to develop the click reaction into a new polymerization technique. The effort, however, has met with limited success. The Cu(I)-catalyzed polymerizations of arylenediazides and arylenediynes were sluggish, taking as long as 7–10 days to finish, whose products often precipitated from the reaction mixtures even at the oligomeric stage or became insoluble in common organic solvents after purifications, unless very long alkyl chains (e.g., dodecyl groups) were attached to the arylene rings of the polymers.[5,6] Furthermore, all the polymers were nonfluorescent in the solid state, although their dilute solutions emitted UV light, suggesting that the polymer luminescence was quenched by aggregate formation.

Our research groups have been interested in the exploration of alkyne-based polymerization reactions, with the aim of

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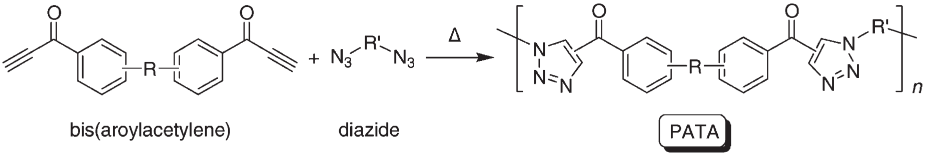


Scheme 1.
Synthetic routes to poly(aroyltriazole)s by metal-free click polymerization.

developing alkyne monomers into versatile building blocks for the construction of new macromolecules with linear and hyperbranched structures and advanced functional properties.[7–9] We recently developed a new, metal-free, effective click polymerization of bis(aroylacetylene)s and diazides to poly(aroyltriazole)s (PATAs) (Scheme 1).[10] This reaction is fast and insensitive to air and moisture and can produce polymers with high molecular weights and high regioregularities in high yields, which helps simplify the reaction procedures and enhance the polymerization efficiency. As no transition-metal catalyst is used in the process, this polymerization enjoys such advantages as being less toxic, environmentally friendlier, and economically sounder. The electronic and optical properties of the polymers suffer free from the detriment by the transition-metals. Attracted by such metal-free feature of the click polymerization, we continued to work on the reaction system with an aim of expanding its applications. In this paper, we will present our efforts on preparation of functional PATAs with two-photon absorption, aggregation-induced emission properties, etc.

Experimental Part

Polymer Synthesis

Click polymerization of the bis(aroylacetylene)s with the diazides were carried out under nitrogen in Schlenk tubes. Typical experimental procedures are given below as an example.

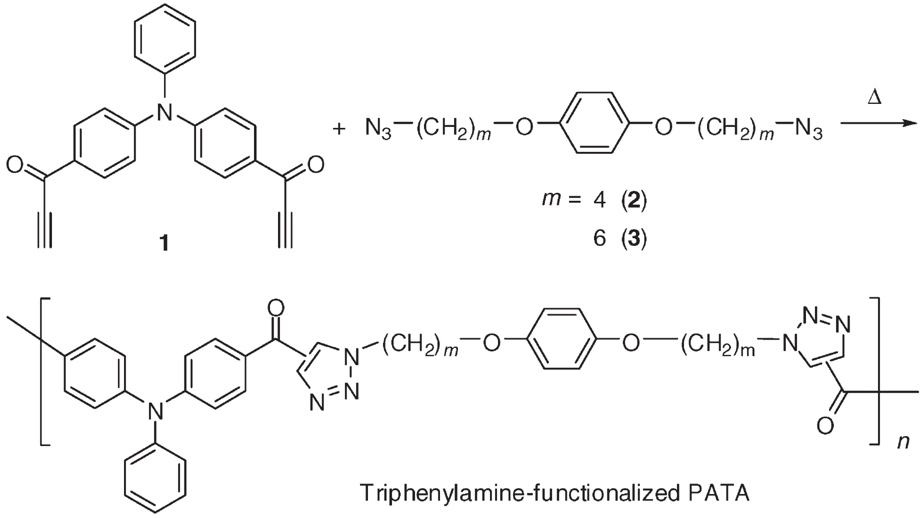
In a 15 mL Schlenk tube were placed 0.2 mmol of bis(aroylacetylene) and 0.2 mmol of diazide. Into the mixture was injected 1.2 mL of a DMF/toluene mixture (1:1 by volume). After stirring at 100 °C for 6 h, the reaction mixture was diluted with chloroform and added dropwise into 300 mL of a 10:1 mixture of hexane and chloroform through a cotton filter under stirring. The precipitates were allowed to stand overnight, collected by filtration, and dried under vacuum at room temperature to a constant weight.

Results and Discussion

Polymer Syntheses

Triphenylamine has been widely used in the development of new organic light-emitting materials and devices due to its excellent solubility and stability as well as high luminescence and hole-transporting efficiencies.[11,12] Synthetically, it can be readily transformed to a dialdehyde, which can be further converted to monomer **1** by established synthetic method. The 1,4-bis(*n*-azidoalkoxy)benzenes (**2** and **3)** were facilely synthesized by etherization of hydroquinone with α,ω-dibromoalkanes in a basic medium, followed by substitution reaction with sodium azide in DMSO.[13] While, 3,3′-(1,6-hexylenedioxy)-bis(benzoylacetylene) (**4**) was prepared according to the experimental procedures described in our previous paper.[14]

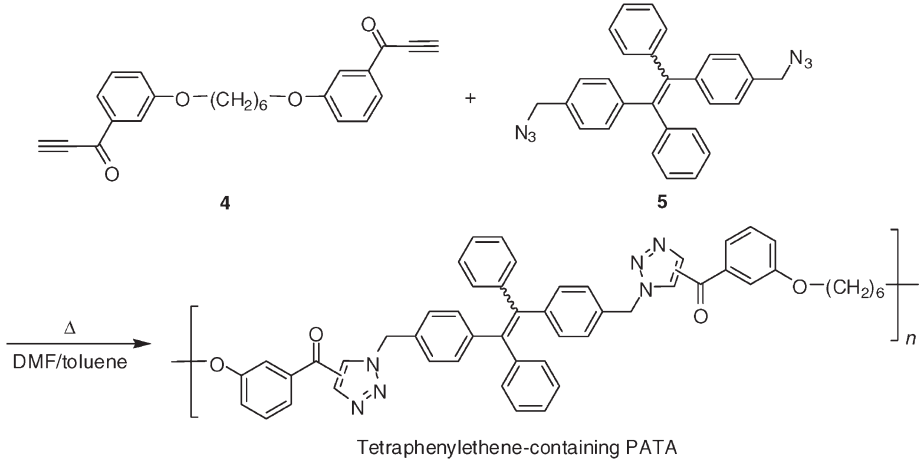
Tetraphenylethene (TPE) and its derivatives are nonemissive in solutions but emit intensely in their aggregation states, showing the unique property of aggregation-induced emission (AIE) phenomenon, which was first observed by our groups in 2001.[15–17] For practical applications, these low molecular weight dyes have to be fabricated into thin solid films by expensive



Scheme 2.
Synthetic routes to triphenylamine-functionalized poly(aroyltriazole)s.

techniques such as vacuum sublimation and vapor deposition, which are not well suited to the manufacture of large area flat-panel devices. One way to surmount this processing disadvantage is to make high molecular polymers, which can be readily fabricated into large-area thin solid films by a simple spin-coating process. However, conjugated polymers showing strong light emissions in the aggregative solid state are rare. The incorporation of such TPE moiety of **5** is aimed to construct PATA with AIE properties. **5** was synthesized by McMurry coupling of 4-methylbenzophenone in the presence of titanium tetrachloride and zinc in tetrahydrofuran, followed by bromination with *N*-bromosuccinimide in carbon tetrachloride and substitution reaction with sodium azide in DMSO.

According to the optimal conditions, we carried out the polymerization using bis(aroylacetylene)s and diazides to construct functional PATAs as shown in Scheme 2 and Scheme 3. **PI–PV** with high molecular weights are obtained in high yields (Table 1). The polymers are readily



Scheme 3.
Synthetic routes to tetraphenylethene-functionalized poly(aroyltriazole)s.

Table 1.
Synthesis of Functionalized Poly(aroyltriazole)s[a].

PATA	monomer	solvent[b]	yield (%)	M_w[c]	M_w/M_n[c]	$F_{1,4}$ (%)[d]	T_d (°C)[e]	δ (GM)[f]
PI	**1**+**2**	A	95.1	13 700	1.8	90.4	375	213
PII	**1**+**2**	B	88.1	15 700	1.8	90.0	Nd[g]	223
PIII	**1**+**3**	A	90.2	14 400	1.8	88.4	356	220
PIV	**1**+**3**	B	95.3	17 200	1.8	91.4	Nd	140
PV	**4**+**5**	A	85.0	16 300	2.0	95.0	345	Nd

[a] Carried out at 100 °C for 6 h; $[M_i]_0 = 0.15$ M;
[b] A = DMF/toluene; B = DMAc/toluene; Volume ratio: 1:1;
[c] Determined by GPC on the basis of a polystyrene calibration;
[d] Calculated from ^{1}H NMR spectral data;
[e] Temperature for 5% weight loss;
[f] δ = two-photon absorption cross-section in DCM excited at 800 nm using Rhodamine B in methanol (10^{-4} M) as calibrated standard; GM = 10^{-50} cm^4 · s/(photon · molecule);
[g] Nd = not detected.

soluble in common organic solvents. All the polymers (**PI**–**PV**) are thermally stable. As can be found from Table 1, all the PATAs lose 5% of their weights at a temperature higher than 345 °C.

The polymers were characterized spectroscopically, and all of them gave analysis data correspond to their expected molecular structures. The IR and NMR spectra shows that while most of the ethynyl and azido groups of the monomers have been transformed to the triazole rings of the polymers by the polymerization reaction, some of the functional groups remain unreacted and serve as terminal units in the polymers. From the integrals of the resonance peaks of protons of the methylene groups adjacent to the triazole rings in DMSO-d_6, the 1,4-regioisomeric ratio ($F_{1,4}$) values of the PATAs are found to be higher than 88%. The highest value can reach 95%. This click polymerization is thus indeed a powerful and versatile method for the synthesis of new functional polymers.

Linear Optical Properties

Triphenylamine has been widely used in the construction of organic LEDs because of its good solubility, excellent stability, high PL efficiency and superb hole-transporting capability. It also functions as an electron donor (D) due to its electron-rich nitrogen atom.[18] On the other hand, the new aroyltriazole rings formed by the click polymerization is electron-deficient and serves as an electron acceptor (A). PATAs **PI**–**PIV** are thus expected to exhibit unique optical properties stemming from their conjugated A–π–D–π–A structural units (where π denotes a π-electron bridge).

The absorption maximums (λ_{ab}) of **PI**–**PIV** are all found in the neighborhood of ~395 nm. Upon photoexcitation, their solutions emit blue to green lights ($\lambda_{em} \sim 460$–506 nm) with quantum yields (Φ_F) up to 58%. Figure 1 shows the UV and PL spectra of the solutions of **PIV** in different solvents as examples. Its absorption spectrum does not change much with solvent, but its PL spectrum progressively red-shifts from 459.5 nm (in dioxane) to 505.5 nm (in DMF) with increasing solvent polarity parameter (Δf).[19] Its Φ_F decreases with an increase in Δf. Since the polymer possesses D–A structural units, its solvatochromism is believed to be caused by photoinduced intramolecular charge transfer (ICT) in the excited state, suggesting that the ICT excited state has a larger dipolar moment than the ground state due to substantial charge redistribution.

Aggregation-Induced Emission of PV

The AIE-active TPE and its derivatives have received much attention because of their facile synthesis, ready functionalization, good photostability, and high FL quantum yields (ΦF). As mentioned previously, the emissive polymers have advantages in terms of film-forming and practical

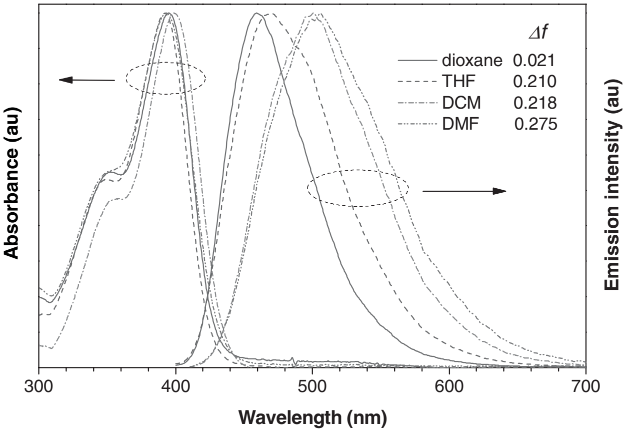


Figure 1.
Absorption and emission spectra of P**IV** in solvents with different polarity parameters (Δ*f*). Concentration: 3.5 μg/mL; excitation wavelength: 395 nm.

applications over the small organic molecules. But whether its AIE feature still remains when the TPE is incorporated into poly(aroyltriazole)s?

P**V** was then investigated by adding water into its THF solution. A dilute THF solution of P**V**, for example, emits a faint greenish-blue light (Figure 2A). When a large amount of water (90%) is added, the resultant mixture shows an intense fluorescence spectrum with a peak at 472 nm. As water is a poor solvent of P**V**, its molecules aggregated in the aqueous mixture. P**V** is therefore induced to emit light by aggregate formation; in other words, it is AIE active. The mixture is transparent and homogeneous, suggesting that the dye aggregates suspended in the mixture are nanosized. In the dilute THF solution, the phenyl rings of TPE can rotate against its central olefinic double bond, which nonradiatively deactivates the excited state and renders the dye nonemissive. The intramolecular rotations are largely restricted in the nanoaggregates

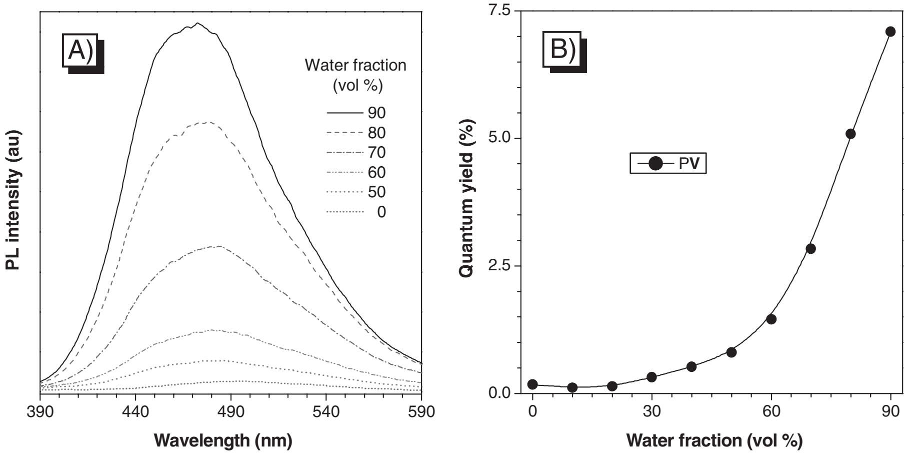


Figure 2.
(A) PL spectra of P**V** in pure THF and THF/water mixtures. Concentration: 10 μM, excitation wavelength for PL: 316 nm. (B) Variations in the quantum yield (Φ_F) of P**III** with water fractions in the THF/water mixtures. Φ_F was estimated using quinine sulfate in 0.1 N H_2SO_4 ($\Phi_F = 54.6\%$) as standard.

in the THF/water mixture. This blocks the nonradiative decay channel of the dye and makes it highly luminescent. The results indicated that the AIE feature of TPE has been successfully transferred to polymers.

Changes in the Φ_F values of P**V** in the THF/water mixtures with different water contents further confirm its AIE nature. In the THF solution, P**V** exhibits a negligibly small Φ_F value ($\sim$0.18%), which remains almost unchanged until up to approximately 30% of water is added (Figure 2B). Afterwards, the Φ_F value starts to increase swiftly. In the THF/water mixtures with lower water fractions, P**V** is genuinely dissolved, whereas in the aqueous mixtures with higher water fractions (>30%), the polymer chains entangled together owing to the deterioration of the salvation power of the mixture. When the water fraction is further increased to 90%, the Φ_F value is increased to $\sim$7.1%, which is approximately 40-fold higher than that in the pure THF solvent. The absolute Φ_F values of the aggregates should be much higher than the relative ones.

Nonlinear Optical Properties

It has been reported that for a given π bridge, molecules with structural motif of D–A–D or A–D–A can exhibit large two-photon absorption (TPA) cross-section (δ) values.[20] P**I**–P**IV** possess A–D–A units and may show large optical nonlinearity. We thus carried out the two-photon-induced fluorescence (TPIF) experiments using pico-second laser pulses (35 ps, 10 Hz) with tunable idler wavelengths in the range of 750–2000 nm.[21] The laser beam was focused on the quartz sample cell (1 × 1 cm; $\sim$3 mL) employing a lens with a focus length of 20 cm. The incident beam was adjusted to locate near the cell wall on the collection signal side to avoid self-absorption. The fluorescence was collected perpendicularly using a silica photodiodes after passing a long-wave filter to remove the incident beam. We first measured their δ values at 800 nm, which is the most used wavelength for bio-testing. We measured the values in different solvents, such as dioxane, THF, DCM, and DMF and found that the largest values were obtained in DCM. Furthermore, P**II** has the largest value (223 GM) among the polymers. These values are similar to that of the reference (210 GM).

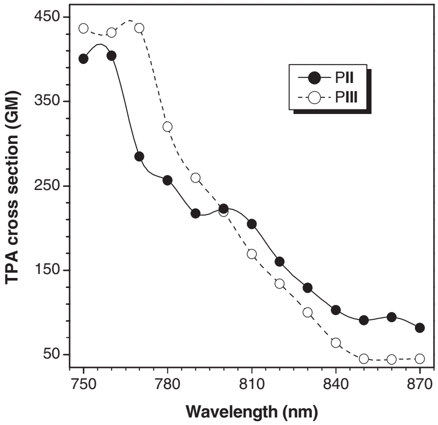


Figure 3.
TPA spectra of P**II** and P**III** in DCM.

The dependence of their δ values on the wavelength is shown in Figure 3. Large δ values up to 437 GM are obtained from the DCM solutions. Combing their facile synthesis and excellent biocompatible, the polymers may find biomedical applications for two-photon fluorescence imaging of biological samples with significantly reduced photoinduced damage.

Conclusions

In this paper, we succeeded in preparation of triphenylamine and TPE-functionalized PATAs by metal-free click polymerization of bis(aroylacetylene)s and diazides with high molecular weight and high regioregularities in high yields. The polymers are all thermally stable and soluble in common organic solvent and hence macroscopically processable.

The triphenylamine-functionalized PATAs exhibit novel linear and nonlinear optical properties including efficient PL, unique solvatochromism, and large TPA cross sections because the formed aroyltriazole rings in the click polymerization is electron-deficient. The TPE-containing PATA show the AIE activity like its small molecular analog. The highest quantum yield of it in THF/water mixtures with 90% water fraction can reach 7.1%. It is anticipated that further elaborate design of monomer structures will make the click polymerization an even more versatile synthetic tool for the generation of new advanced materials with multiple functionalities.

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