Click Polymerization: Facile Synthesis of Functional Poly(aroyltriazole)s by Metal-Free, Regioselective 1,3-Dipolar Polycycloaddition

Anjun Qin,[†] Cathy K. W. Jim,[†] Weixin Lu,[‡] Jacky W. Y. Lam,[†] Matthias Häussler,[†] Yongqiang Dong,[†,§] Herman H. Y. Sung,[†] Ian D. Williams,[†] George K. L. Wong,[‡] and Ben Zhong Tang*,[†,§]

Department of Chemistry, Department of Physics, The Hong Kong University of Science & Technology (HKUST), Clear Water Bay, Kowloon, Hong Kong, China, and Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, China

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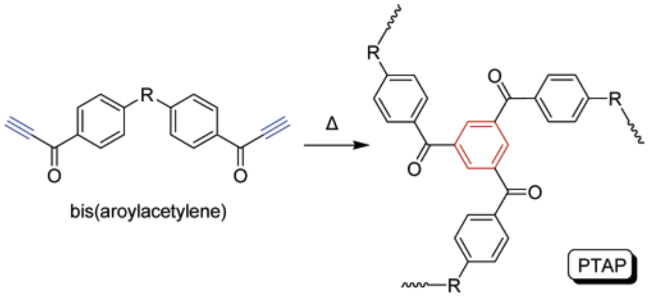
ABSTRACT: Heating mixtures of bis(aroylacetylene)s (**5**/**6**/**9**) and diazides (**7**/**8**) in polar solvents such as DMF/toluene at a moderate temperature of 100 °C readily affects their 1,3-dipolar polycycloadditions, producing poly(aroyltriazole)s (PATAs; P**I**−P**XII**) with high molecular weights (M_w up to 26 700) and regioregularities ($F_{1,4}$ up to ~92%) in high yields (up to ~98%). The metal-free click polymerizations propagate smoothly in an open atmosphere without protection from oxygen and moisture. Through model reaction study and semiempirical calculation, the polymerization mechanism is proposed and discussed. Molecular structures of the PATAs are characterized spectroscopically. All the polymers are soluble in common organic solvents and are thermally stable, losing little of their weights when heated to ~380 °C. The PATAs containing triphenylamine units emit visible light and show unique solvatochromism. The PATAs are nonlinear optically active, exhibiting large two-photon absorption cross sections due to the intramolecular charge transfer between their electron-donating triphenylamine and electron-accepting aroyltriazole units.

Introduction

1,3-Dipolar cycloaddition was systematically studied by Huisgen in the 1980s.[1] Since then, the area of research had remained silent until Sharpless and co-workers found that Cu(I) species could efficiently catalyze the reaction of acetylenes with azides in a 1,4-regioselective fashion. The reaction was coined “click chemistry”,[2] which has aroused much interest among researchers because of its remarkable features such as high yield, mild reaction conditions, and simple product isolation.[3] The click chemistry, for example, has been utilized to synthesize bioconjugates because the reactants (acetylenes and azides) and the products (triazoles) are all biocompatible.[4] Polymer chemists have employed click chemistry to construct dendritic[5] and linear macromolecules.[6] The preparations of dendritic polymers, however, require multistep reactions and tedious product isolations, whereas long reaction times and poor product solubility are the big obstacles in the synthesis of linear polymers via the click reaction route.[7] The Cu(I)-catalyzed 1,3-dipolar polycycloadditions of arylene diazides and arylene diynes, for example, took 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.[7]

Scheme 1



We have been interested in the construction of new macromolecules using acetylenic building blocks and have synthesized a variety of linear and hyperbranched polymers with extended π-conjugations through metathesis,[8] cyclotrimerization,[9] and coupling polymerizations[10] of acetylenic monomers. While acetylene polycyclotrimerizations have been commonly initiated by transition-metal catalysts,[9] we have recently found that bis(aroylacetylene)s can be thermally polycyclotrimerized in DMF or its mixtures in the absence of metallic catalysts, yielding regioregular hyperbranched poly(1,3,5-triaroylphenylene)s or PTAPs with excellent solubility in common organic solvents (Scheme 1).[11] The polymerizations were, however, rather sluggish, taking several days (e.g., 3 days) at high temperatures (e.g., boiling point of DMF) to produce some appreciable amounts of polymeric products, although the reaction temperature can be lowered, the polymerization rate can be accelerated, and the polymer yield can be increased by using secondary amines (e.g., piperidine) as catalysts.[11]

Metallic catalysts have been widely used in polymerization reactions, whose complete removal from the resultant polymers has, however, been very difficult. The catalyst residues can be detrimental to the electronic and optical properties of polymers: for example, light emissions from conjugated polymers can be quenched by the metallic traps. Attracted by the novel metal-free feature of the aroylacetylene cyclotrimerization (cf.

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* To whom all correspondence should be addressed: Ph +852-2358-7375; Fax +852-2358-1594; e-mail tangbenz@ust.hk.
[†] Department of Chemistry, HKUST.
[‡] Department of Physics, HKUST.
[§] Zhejiang University.

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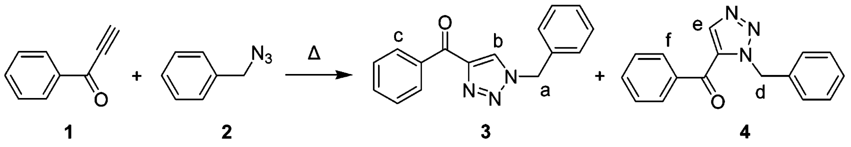
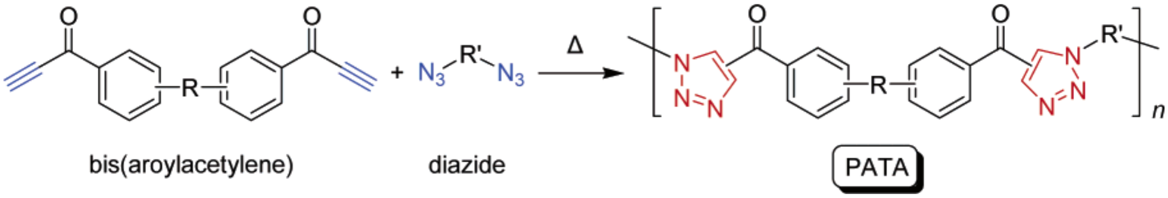
Scheme 2



Scheme 3



Scheme 1), we further worked on the reaction system with an aim of improving its efficiency and expanding its utility. On the basis of the reaction mechanism,[11] we envision that if a more reactive reagent such as an azide (**2**) is used to capture the transit cyclization intermediate of an aroylacetylene (**1**), 1,2,3-triazoles (**3** and **4**) may be readily formed through a 1,3-dipolar cycloaddition mechanism (Scheme 2). In this work, we explored this possibility.

In this paper, we prove that the expected click reaction did occur. Whereas the products of the metal-catalyzed click reactions are regioregular, those of the thermal click reactions are usually regiorandom. The thermal 1,3-dipolar cycloaddition reactions of **1** and **2**, however, proceeded in a regioselective way, yielding 1,2,3-triazole mixtures with high contents of 1,4-regiosomer **3** ($F_{1,4}$ up to 94%). We further show that the metal-free click reaction offers a versatile synthetic tool for preparing new polymers: linear poly(aroyltriazole)s (PATAs) with high regioregularity and excellent solubility are obtained in high yields by simply refluxing mixtures of bis(aroylacetylene)s and diazides in polar solvents such as DNF/toluene at a moderate temperature (100 °C) for a short period of time (6 h) in the absence of externally added catalysts in an open atmosphere (Scheme 3).

Experimental Section

General Information. Unless otherwise stated, all the chemicals used in this study were purchased from Aldrich. Tetrahydrofuran (THF; from Labscan), toluene (BDH), and 1,4-dioxane (Aldrich) were distilled from sodium benzophenone ketyl under nitrogen immediately prior to use. Other solvents were purified by standard methods. Benzoylacetylene (**1**) was prepared according to our previously reported procedures,[10] and benzyl azide (**2**) was obtained by substitution of benzyl bromide with sodium azide in DMSO at room temperature for 24 h.[12] *N,N*-Bis(4-ethynylcarbonylphenyl)-aniline (**9**) was prepared by following the experimental procedures described in our previous papers.[11]

^{1}H and ^{13}C NMR spectra were measured on a Bruker ARX 300 spectrometer in chloroform-*d* and DMSO-d_6 using tetramethylsilane (TMS; $\delta = 0$) as internal reference. IR spectra were taken on a Perkin-Elmer 16 PC spectrometer. UV absorption spectra were measured on a Milton Roy Spectronic 3000 Array spectrophotometer. Photoluminescence (PL) spectra were recorded on a Perkin-Elmer LS 55 spectrofluorometer. Fluorescence quantum yields (Φ_F) were estimated using quinine sulfate in 0.1 N sulfuric acid (Φ_F = 54%) as standard by keeping absorbance of the solutions below 0.1.[13] MALDI-TOF spectra were carried out on a GCT Premier CAB 048 mass spectrometer operating in an chemical ionization mode (CI). Elemental analysis was performed on an Eager 300 elemental microanalyzer. Thermal stabilities were evaluated by measuring thermogravimetric analysis (TGA) thermograms on a Perkin-Elmer TGA 7 under dry nitrogen at a heating rate of 20 °C/min. Average molecular weights (M_w and M_n) and polydispersity indices (M_w/M_n) of the polymers were estimated by a Waters 510 gel permeation chromatography (GPC) system, using a set of monodisperse polystyrenes as calibration standards.

Single crystals of 1-benzyl-4-benzoyl-1,2,3-triazole (**3**) were grown at room temperature by slow diffusion of *n*-hexane vapor into a solution of pure **3** in dichloromethane (DCM) in a closed container. Crystal X-ray diffraction data were collected at 295 or 100 K on a Bruker-Nonius Smart Apex CCD diffractometer with graphite-monochromated Mo Kα radiation. The intensity data were processed using the SAINT and SADABS routines, and the structure solution and refinement were carried out by the SHELXTL suite of X-ray programs (version 6.10).

Model Reaction. Model compounds 1-benzyl-4-benzoyl-1,2,3-triazole (**3**) and 1-benzyl-5-benzoyl-1,2,3-triazole (**4**) were prepared by thermal click reaction of **1** with **2** (cf. Scheme 2). Into a 10 mL one-necked, round-bottomed flask were added **1** (0.104 g, 0.8 mmol) and an equivalent amount of **2** in 0.8 mL of a pure or mixture solvent (see Table 1). The solution was stirred and heated at 100 °C for 24 h. After cooling to room temperature, the solvent was evaporated and the crude products were dried in a vacuum oven overnight. The products were analyzed by ^{1}H NMR spectroscopy without purification in order to calculate the isomer ratio between **3** and **4**. Pure **3** was isolated from the crude product (Table 1, entry 2) by a silica gel column chromatography using chloroform as eluent. A white solid of **3** was obtained in 90% yield (0.19 g).

*Characterization Data of Crude Products (**3** + **4**).* ^{1}H NMR (300 MHz, CDCl$_3$), δ (TMS, ppm): 8.43 (d), 8.16 (s), 8.00 (s), 7.80 (d), 7.61 (t), 7.51 (t), 7.44 (m), 7.35 (m), 5.98 (s), 5.61 (s). ^{1}H NMR (300 MHz, DMSO-d_6): 9.12 (s), 8.42 (s), 8.31 (d), 7.95 (d), 7.79 (t), 7.68 (t), 7.50 (m), 6.02 (s), 5.82 (s).

*Pure **3**.* ^{1}H NMR (300 MHz, CDCl$_3$), δ (TMS, ppm): 8.43 (d, J = 7.2 Hz, 2H), 8.16 (s, 1H), 7.61 (t, J = 7.2 Hz, 1H), 7.51 (t, J = 7.8 Hz, 2H), 7.44 (m, 3H), 7.35 (m, 2H), 5.61 (s, 2H). ^{1}H NMR (300 MHz, DMSO-d_6): 9.12 (s, 1H), 8.31 (d, J = 7.2 Hz, 2H), 7.79 (t, J = 7.4 Hz, 1H), 7.68 (t, J = 7.8 Hz, 2H), 7.50 (m, 5H),

Table 1. Effect of Solvent on Regioselectivity of Click Reaction[a]

entry	solvent[b]	$F_{1,4}$[c]
1	DMF	91.8
2	DMF/toluene (1:1)[d]	88.2[e]
3	DMF/dioxane (1:1)[d]	90.9
4	DMSO	93.8
5	DMSO/toluene (1:1)[d]	94.0
6	DMAc/toluene (1:1)[d]	93.4
7	NMP/toluene (1:1)[d]	93.3
8	toluene	79.5
9	benzene	69.0

[a] Carried out at 100 °C for 24 h; [**1**] = 1.0 M. [b] Abbreviations: DMF = *N,N*-dimethylformamide, DMSO = dimethyl sulfoxide, DMAc = *N,N*-dimethylacetamide, and NMP = *N*-methyl-2-pyrrolidinone. [c] Ratio of 1,4-regioisomer **3** in the reaction products {[**3**]/([**3**] + [**4**])} determined by ^{1}H NMR analysis according to eq 2. [d] Volume ratio. [e] Yield of **3**: 90.0%.

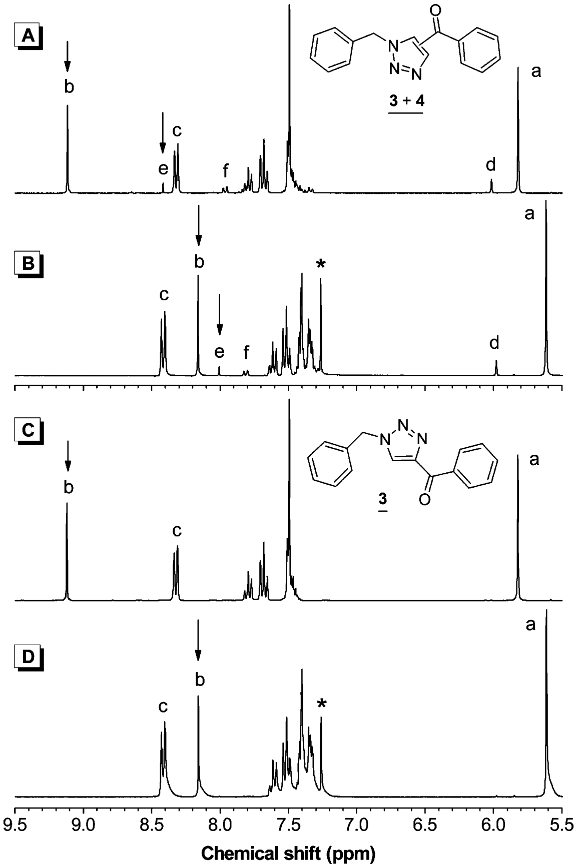


Figure 1. ^{1}H NMR spectra of crude products (a mixture of 1-benzyl-4-benzoyl-1,2,3-triazole (**3**) and 1-benzyl-5-benzoyl-1,2,3-triazole (**4**)) in (A) DMSO-d_6 and (B) $CDCl_3$ (sample taken from Table 1, entry 2) and pure **3** in (C) DMSO-d_6 and (D) $CDCl_3$. Labels for the resonance peaks (a−f) correspond to those given in Scheme 2, while the solvent peaks are marked with asterisks (*).

5.82 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$), δ (TMS, ppm): 185.5, 148.2, 136.4, 133.6, 133.2, 130.5, 129.2, 129.0, 128.3, 128.2, 54.3.

Monomer Preparation. Diyne monomers 3,3′-(1,4-phenylenedimethoxy)bis(benzoylacetylene) (**5**) and 3,3′-(1,6-hexylenedioxy)-bis(benzoylacetylene) (**6**) were prepared according to the experimental procedures described in our previous papers.[11] Diazide monomers 1,4-bis(n-azidoalkoxy)benzenes **7** and **8** were prepared by etherification of hydroquinone with α,ω-dibromoalkanes followed by reaction with sodium azide.[12] Detailed procedures for the preparation of 1,4-bis(6-azidohexyloxy)benzene (**8**) are given below as an example.

Into a 250 mL two-necked, round-bottomed flask were added 1,6-dibromohexane (16.8 g, 66 mmol) and K_2CO_3 (20.7 g, 150 mmol) in 100 mL of acetone. Hydroquinone (3.3 g, 30 mmol) in 25 mL of acetone was then added dropwise within 4 h under reflux. Afterward, the mixture was further refluxed for 12 h and then cooled to room temperature. The inorganic salt was filtered and washed with acetone several times. The filtrate was concentrated by a rotary evaporator, and the residue was extracted with 200 mL of chloroform. The organic phase was washed with 50 mL of water three times and 100 mL of brine once and then dried over $MgSO_4$ overnight. After filtration and solvent evaporation, the crude product was purified by a silica gel column using chloroform/hexane (1:1 by volume) as eluent. A white solid of 1,4-bis(6-bromohexyloxy)-benzene was obtained in 70.5% yield (9.16 g). ^{1}H NMR (300 MHz, $CDCl_3$), δ (TMS, ppm): 6.81 (s, 4H), 3.91 (t, J = 6.6 Hz, 4H), 3.42 (t, J = 6.9 Hz, 4H), 1.89 (m, 4H), 1.77 (m, 4H), 1.50 (m, 8H).

Into another 250 mL round-bottomed flask were added 3.05 g of 1,4-bis(6-bromohexyloxy)benzene (7 mmol) and 1.14 g of sodium azide (17.5 mmol) in 100 mL of DMSO. After stirring at room temperature for 24 h, a small amount of water was added to quench the reaction (temperature of the solution was increased slightly). After cooled to room temperature, the solution was extracted with 30 mL of diethyl ether five times. The organic phases were combined, washed with water and brine, and then dried over $MgSO_4$ overnight. After filtration and solvent evaporation, the crude product was purified by a silica gel column using chloroform/hexane (1:1 by volume) as eluent. Monomer **8** was obtained in 89.3% yield (2.25 g) as a white solid. IR (KBr), ν (cm^{-1}): 2097, 1509, 1469, 1231, 827. ^{1}H NMR (300 MHz, $CDCl_3$), δ (TMS, ppm): 6.82 (s, 4H), 3.91 (t, J = 6.3 Hz, 4H), 3.28 (t, J = 8.4 Hz, 4H), 1.77 (m, 4H), 1.63 (m, 4H), 1.47 (m, 8H). ^{13}C NMR (75 MHz, $CDCl_3$), δ (TMS, ppm): 153.8, 116.0, 69.0, 52.0, 29.9, 29.4, 27.1, 26.3. HRMS (MALDI-TOF) m/z Calcd: 360.2274. Found: 360.2270 (M$^+$).

*1,4-Bis(4-azidobutoxy)benzene (**7**).* This monomer was prepared by the similar synthetic procedures. A white solid was obtained in 32.0% yield (based on the amount of hydroquinone used). IR (KBr), ν (cm^{-1}): 2097, 1508, 1472, 1229, 827. ^{1}H NMR (300 MHz, $CDCl_3$), δ (TMS, ppm): 6.82 (s, 4H), 3.94 (t, J = 5.7 Hz, 4H), 3.36 (t, J = 6.3 Hz, 4H), 1.82 (m, 8H). ^{13}C NMR (75 MHz, $CDCl_3$), δ (TMS, ppm): 153.7, 116.0, 68.4, 51.8, 27.2, 26.4. HRMS (MALDI−TOF) m/z Calcd: 304.1648. Found: 304.1650 (M$^+$).

Polymer Synthesis. Polycycloaddition reactions of the bis-(aroylacetylene)s with the diazides were carried out in an open atmosphere or under nitrogen in Schlenk tubes. Typical experimental procedures for the click polymerization of **5** with **7** are given below as an example.

In a 15 mL Schlenk tube were placed 78.8 mg (0.2 mmol) of **5** and 60.8 mg (0.2 mmol) of **7**. 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.

*Characterization Data of **PI**.* White power; 89.6% yield. M_w 15 900; M_w/M_n 1.8 (GPC, polystyrene calibration). Content of 1,4-disubstituted 1,2,3-triazole unit ($F_{1,4}$): 88.5%. IR (KBr), ν (cm^{-1}): 2949, 2872 (CH_2 stretching), 2097 (N_3 and C≡C stretching), 1651 (C═O stretching), 1579 (C═C stretching), 1262, 1229 (C−O−C stretching). ^{1}H NMR (300 MHz, $CDCl_3$), δ (TMS, ppm): 8.27, 8.06, 8.01, 7.94, 7.47, 7.23, 6.78, 5.17, 4.81, 4.52, 3.93, 2.17, 1.80. ^{13}C NMR (75 MHz, $CDCl_3$), δ (TMS, ppm): 185.23, 158.63, 152.90, 147.98, 137.76, 136.48, 129.49, 128.39, 127.84, 123.67, 120.73, 115.56, 115.36, 69.83, 67.36, 50.28, 27.18, 26.13.

PII. The polymer was prepared from 3,3′-(1,4-phenylenedimethoxy)bis(benzoylacetylene), **5** (0.118 g, 0.3 mmol), and 1,4-bis(6-azidohexyloxy)benzene, **8** (0.108 g, 0.3 mmol), in 2.0 mL of a DMF/toluene mixture (1:1 by volume). Yellow powder; 92.0% yield. M_w 26 700; M_w/M_n 2.0 (GPC, polystyrene calibration). $F_{1,4}$: 88.5%. IR (KBr), ν (cm^{-1}): 2939, 2863 (CH_2 stretching), 2095 (N_3 and C≡C stretching), 1650 (C═O stretching), 1578, 1507 (C═C stretching), 1260, 1230 (C−O−C stretching). ^{1}H NMR (300 MHz, $CDCl_3$), δ (TMS, ppm): 8.23, 8.11, 8.03, 7.94, 7.51, 7.24, 6.78, 5.15, 4.74, 4.44, 3.87, 3.27, 1.99, 1.74, 1.47, 1.43. ^{13}C NMR (75 MHz, $CDCl_3$), δ (TMS, ppm): 185.24, 158.62, 153.03, 147.96, 137.75, 136.46, 129.46, 128.23, 127.82, 123.68, 120.71, 115.51, 115.32, 69.81, 68.11, 50.48, 30.03, 29.03, 26.16, 25.49.

PIII. The polymer was prepared by polymerization of 3,3′-(1,6-hexylenedioxy)bis(benzoylacetylene), **6** (74.9 mg, 0.2 mmol), with 1,4-bis(4-azidobutoxy)benzene, **7** (60.8 mg, 0.2 mmol), in 1.2 mL of a DMF/toluene mixture (1:1 by volume). Yellow solid; 91.2% yield. M_w 23 700; M_w/M_n 2.1 (GPC, polystyrene calibration). $F_{1,4}$: 89.3%. IR (KBr), ν (cm^{-1}): 2941, 2869 (CH_2 stretching), 2095 (N_3 and C≡C stretching), 1650 (C═O stretching), 1578, 1508 (C═C stretching), 1263, 1228 (C−O−C stretching). ^{1}H NMR (300 MHz, $CDCl_3$), δ (TMS, ppm): 8.27, 8.03, 7.91, 7.40, 7.16, 6.79, 4.81, 4.52, 4.05, 3.94, 3.35, 2.17, 1.83, 1.50. ^{13}C NMR (75 MHz, $CDCl_3$), δ (TMS, ppm): 185.39, 159.08, 152.93, 148.07, 137.71, 129.36, 128.36, 123.23, 120.45, 115.48, 115.32, 68.04, 67.40, 50.28, 29.12, 27.18, 26.15, 25.84.

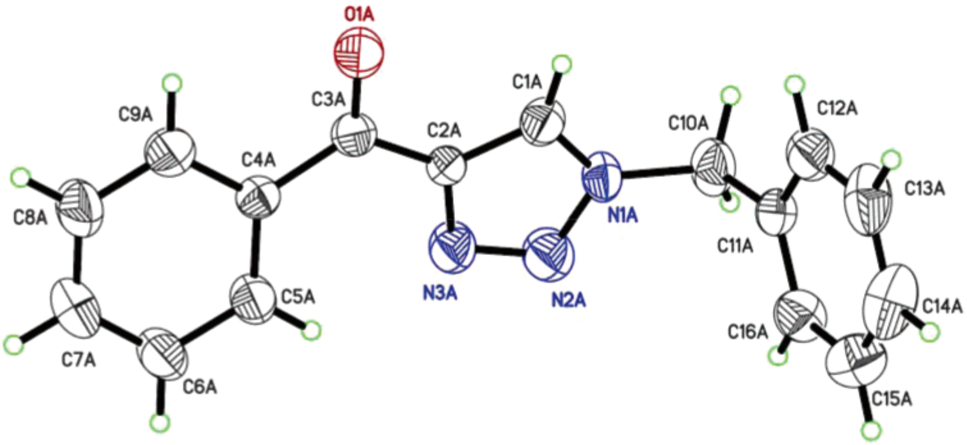


Figure 2. ORTEP drawing of 1-benzyl-4-benzoyl-1,2,3-trazole (**3**).

PIV. The polymer was prepared from 3,3′-(1,6-hexylenedioxy)-bis(benzoylacetylene), **6** (0.112 g, 0.3 mmol), and 1,4-bis(6-azidohexyloxy)benzene, **8** (0.108 g, 0.3 mmol), in 2.0 mL of a DMF/toluene mixture (1:1 by volume). Yellow solid; 83.7% yield. M_w 19 100; M_w/M_n 1.8 (GPC, polystyrene calibration). $F_{1,4}$: 89.3%. IR (KBr), ν (cm^{-1}): 2940, 2863 (CH_2 stretching), 2095 (N_3 and C≡C stretching), 1650 (C═O stretching), 1578, 1508 (C═C stretching), 1262, 1230 (C−O−C stretching). ^1H NMR (300 MHz, $CDCl_3$), δ (TMS, ppm): 8.24, 8.05, 8.01, 7.92, 7.43, 7.16, 6.79, 4.75, 4.44, 4.06, 3.88, 3.27, 1.99, 1.83, 1.75, 1.56, 1.44. ^{13}C NMR (75 MHz, $CDCl_3$), δ (TMS, ppm): 185.41, 159.05, 153.05, 148.03, 137.70, 129.33, 128.19, 123.23, 120.43, 115.34, 115.18, 68.14, 68.01, 50.47, 30.04, 29.11, 29.04, 26.17, 25.83, 25.50.

PIX. The polymer was prepared by polymerization of *N*,*N*-bis-(4-ethynylcarbonylphenyl)aniline, **9** (70.0 mg, 0.2 mmol), with 1,4-bis(4-azidobutoxy)benzene, **7** (60.8 mg 0.2 mmol). Yellow solid; 95.1% yield. M_w 13 700; M_w/M_n 1.8 (GPC, polystyrene calibration). $F_{1,4}$: 90.4%. IR (KBr), ν (cm^{-1}): 2950, 2871 (CH_2 stretching), 2096 (N_3 and C≡C stretching), 1641 (C═O stretching), 1583, 1505 (C═C stretching), 1233, 1178 (C−O−C stretching). ^1H NMR (300 MHz, $CDCl_3$), δ (TMS, ppm): 8.45, 8.31, 8.01, 7.82, 7.37, 7.21, 6.80, 4.80, 4.54, 3.95, 3.35, 2.19, 1.82. ^{13}C NMR (75 MHz, $CDCl_3$), δ (TMS, ppm): 183.82, 152.94, 151.19, 148.39, 145.74, 132.34, 130.85, 129.89, 128.13, 126.93, 122.30, 115.39, 115.31.

PXI. This polymer was prepared from *N*,*N*-bis(4-ethynylcarbonylphenyl)aniline, **9** (70.0 mg, 0.2 mmol), and 1,4-bis(6-azidohexyloxy)benzene, **8** (72.1 mg 0.2 mmol). Yellow solid; 90.2% yield. M_w 14 400; M_w/M_n 1.8 (GPC, polystyrene calibration). $F_{1,4}$: 88.4%. IR (KBr), ν (cm^{-1}): 2939, 2862 (CH_2 stretching), 2095 (N_3 and C≡C stretching), 1638 (C═O stretching), 1583, 1505 (C═C stretching), 1233, 1177 (C−O−C stretching). ^1H NMR (300 MHz, $CDCl_3$), δ (TMS, ppm): 8.46, 8.25, 8.00, 7.83, 7.37, 7.19, 6.79, 4.73, 4.46, 3.89, 3.28, 2.01, 1.76, 1.45. ^{13}C NMR (75 MHz, $CDCl_3$), δ (TMS, ppm): 183.87, 153.07, 151.20, 148.40, 145.76, 132.37, 130.86, 129.89, 127.99, 126.94, 125.75, 122.32, 115.36, 68.15, 50.50, 30.10, 29.08, 26.21, 25.54.

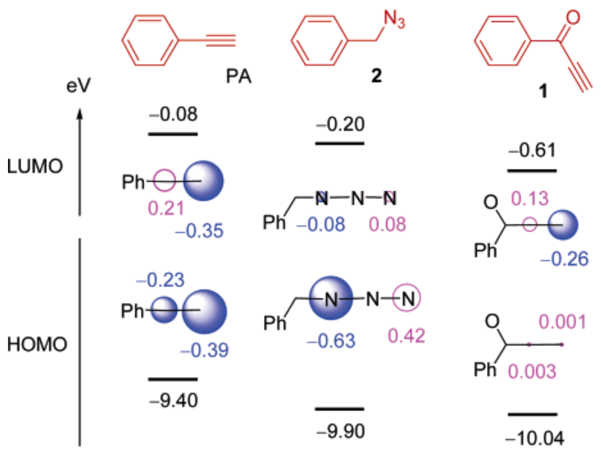


Figure 3. HOMO and LUMO energy levels of benzoylacetylene (**1**) and benzyl azide (**2**) as well as their orbitals and orbital coefficients. Those of phenylacetylene (PA) are shown for comparison.

Optical Nonlinearity Measurements. Two-photon absorption (TPA) cross section was determined by two-photon-induced fluorescence (TPIF) measurement, using picosecond laser pulses as described in the literature.[14] A high-energy picosecond Nd:YAG laser (Continuum Leopard) provides 35 ps pulses of 60 mJ vertically polarized 355 nm radiation at 10 Hz. The beam was pumped into an apparatus of optical parameter amplification (OPA) and generated 2−3 mJ of tunable idler wavelength with a spectral range of 750−2000 nm. The fundamental intensity was altered by a neutral density filter. The beam from the polarizer was focused on the quartz sample cell (1 × 1 cm; ca. 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 photodiode after passing a long-wave filter to remove the incident beam. A 10^{-4} M solution of Rhodamine B in methanol was used as a standard. The measurements were conducted in a regime where the fluorescence signal showed a quadratic dependence on the intensity of the excitation beam, as expected for TPIF.[15] Since the samples do not absorb at longer wavelengths, the sample concentrations were adjusted to $\sim 5 \times 10^{-4}$ M to amplify the signal intensity and to reduce experimental uncertainty. The TPA cross sections were deduced from the following equation:[14]

$$\delta_s = \delta_r \frac{\Phi_r}{\Phi_s} \frac{I_s}{I_r} \frac{c_r}{c_s} \frac{P_r^2}{P_s^2} \frac{n_s^2}{n_r^2} \qquad (1)$$

where subscripts s and r represent the sample and the reference, respectively, δ is the TPA cross section, Φ is the quantum yield, c is the solution concentration, and n is the solution refractive index. The incident beam power and signal intensity measured by a detector were donated as P and I, respectively. The TPA spectra of the polymers were measured by altering the incident wavelength from 750 nm (which could not be lowered further due to the involved technical difficulty) to 880 nm by comparing with that of Rhodamine B at the same time.

Results and Discussion

Model Reaction. We first investigated thermal reaction of benzoylacetylene (**1**) and benzyl azide (**2**) to see whether the two molecules could undergo 1,3-dipolar cycloaddition (cf. Scheme 2) and, if so, what would be the optimal conditions for the click reaction. According to our previous studies,[11] aroylacetylenes could be slowly cyclotrimerized when refluxed in

Table 2. Time Course of Click Polymerization of 6 with 8[a]

time (h)	$M_w{}^b$	$M_w/M_n{}^b$	time (h)	$M_w{}^b$	$M_w/M_n{}^b$
0.5	9900	1.4	2.0	12 300	1.7
1.0	8400	1.6	4.0	13 900	1.8
1.5	9300	1.6	6.0	17 700	1.8

[a] Carried at 100 °C in DMF/toluene (1:1 by volume); [**6**] = [**8**] = 0.14 M. [b] Determined by GPC on the basis of a polystyrene calibration.

Table 3. Synthesis of PATA in DMF/Toluene Mixture[a]

entry	PATA	$M_1 + M_2$	yield (%)	$M_w{}^b$	$M_w/M_n{}^b$	$F_{1,4}$ (%)[c]
1	P**I**	**5** + **7**	89.6	15 900	1.8	88.5
2	P**II**	**5** + **8**	92.0	26 700	2.0	88.5
3	P**II**(*n*)[d]	**5** + **8**	97.6	26 200	1.9	88.5
4	P**III**	**6** + **7**	91.2	23 700	2.1	89.3
5	P**IV**	**6** + **8**	83.7	19 100	1.8	89.3
6	P**IV**(*n*)[d]	**6** + **8**	94.5	22 300	1.9	88.5

[a] Carried out at 100 °C for 6 h; volume ratio of the solvents: 1:1, $[M_i]_0$ = 0.15 M, $[M_1]/[M_2]$ = 1:1. [b] Determined by GPC on the basis of a polystyrene calibration. [c] Calculated from ^{1}H NMR spectral data. [d] Polymerization reaction carried out under nitrogen.

Table 4. Synthesis of PATA in DMAc/Toluene Mixture[a]

PATA	monomer	yield (%)	$M_w{}^b$	$M_w/M_n{}^b$	$F_{1,4}$ (%)[c]
P**V**	**5** + **7**	89.6	20 200	1.8	90.2
P**VI**	**5** + **8**	88.9	24 600	1.8	91.0
P**VII**	**6** + **7**	85.9	25 400	2.0	90.6
P**VIII**	**6** + **8**	95.6	25 300	1.8	91.7

[a] Carried out at 100 °C for 6 h; volume ratio of the solvents: 1:1, $[M_i]_0$ = 0.15 M. [b] Determined by GPC on the basis of a polystyrene calibration. [c] Calculated from ^{1}H NMR spectral data.

DMF or its mixtures for 3 days. We anticipate that aroylacetylenes may undergo faster 1,3-dipolar cycloadditions with azides because the reactive azide species may readily capture the intermediates formed in the initial stages of aroylacetylene cyclization reactions. To verify our expectation, in the first run of tests, we heated a mixture of **1** and **2** in the same solvent, that is, DMF or its mixture, at a lower temperature (100 °C) for a shorter period of time (1 day) in an open atmosphere (Table 1, entries 1−3). After solvent evaporation and proper drying, the crude products were analyzed by ^{1}H NMR spectroscopy.

As can be seen from Figure 1, no resonance peaks for the acetylene proton of **1** and methylene protons adjacent to the azide group of **2** are found at δ 5.23 and 4.54, respectively, in the NMR spectrum of the crude product taken in DMSO-d_6 (panel A). No such peaks are observed either at δ 3.45 and 4.29 in the spectrum measured in $CDCl_3$ (panel B). In the spectrum taken in DMSO-d_6, new peaks corresponding to the resonances of triazole protons appear at δ 9.12 (peak b) and 8.42 (peak e), confirming that the 1,3-dipolar cycloaddition has occurred and that the triple bond of **1** has been completely transformed to the triazole ring by the click reaction with the azide group of **2**. The peaks at δ 6.01 and 5.82 are due to the downfield shift of the benzyl proton resonances of **2** after the cycloaddition reaction. It is known that **1** undergoes cyclotrimerization in DMF at high temperatures to give a 1,3,5-triaroylbenzene.[11] No peaks associated with resonances of such protons are, however, observed at δ 8.45, 7.84, and 7.65 in the spectrum taken in $CDCl_3$,[11,16] thanks to the high reactivity of the azide group of **2**, which has effectively inhibited the reaction from propagating to the step where acetylene cyclotrimerization product of 1,3,5-triaroylbenzene forms.

The appearance of the resonance peaks at δ 9.12 and 8.42 as well as 6.01 and 5.82 in the spectrum taken in DMSO-d_6 indicates that both 1,4- and 1,5-disubstituted isomers of 1,2,3-triazole have formed in the reaction.[17] We tried to separate the mixture by silica gel column chromatography but obtained solely the 1,4-isomer of **3**. The amount of the 1,5-isomer of **4** is so small that it may have been lost during the separation, isolation, and purification processes. The molecular structure of pure regioisomer **3** was further confirmed by ^{13}C NMR spectroscopic and X-ray crystallographic analyses. The ORTEP drawing of **3** is shown in Figure 2. Its crystallographic data, atomic positions, and molecular geometric parameters are given in the Supporting Information.

Comparing the spectra of pure **3** with that of the crude products taken in DMSO-d_6, it is clear that the peaks at δ 8.42 (peak e), 7.95 (peak f), and 6.01 (peak d) are associated with the proton resonances of **4**. Their integrals can thus be used to calculate 1,4-regioisomeric ratio ($F_{1,4}$) or fraction of **3** according to the following equations:

$$F_{1,4} = \frac{A_a}{A_a + A_d} \tag{2}$$

$$F_{1,4}' = \frac{A_b}{A_b + A_e} \tag{3}$$

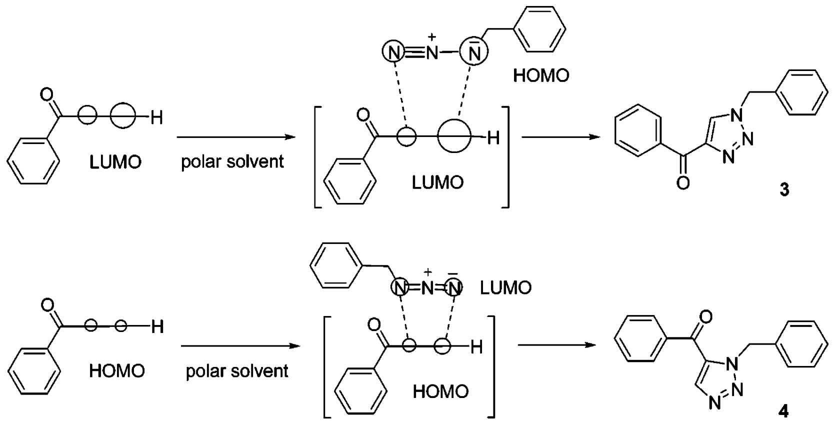
$$F_{1,4}'' = \frac{A_c}{A_c + A_f} \tag{4}$$

where A denotes the integrated area of a resonance peak and its subscript corresponds to the peak label given in Figure 1. Using eqs 2−4, the fractions of **3** ($F_{1,4}$, $F_{1,4}'$, and $F_{1,4}''$) are calculated to be 88.2, 89.8, and 88.4%, respectively, which are identical within experimental error. This manifests a high regioselectivity of the metal-free 1,3-dipolar cycloaddition. It should be noted that that if we use other aromatic acetylenes and azides to conduct the cycloaddition reactions, the chance for the resonances of the protons of the newly formed triazole ring to overlap with those of the "old" aromatic rings will be high. The resonance peaks of the methylene protons adjacent to the new triazole rings at δ 6.0−5.5 (a and d) are completely free of interference, and eq 2 is thus the preferred equation to be used for the calculation of the regioisomeric ratio.

Encouraged by the exciting results described above, we further investigated the effect of solvent on the 1,3-dipolar cycloaddition reaction. The results are summarized in Table 1. All the reactions have proceeded smoothly, giving the expected products in high yields. The ^{1}H NMR spectral profiles of the products are similar, but the intensities of their resonance peaks vary due to the different amounts of **3** and **4** produced by the reactions. The fractions of **3** in the products obtained from the reactions carried out in polar solvents such as DMAc, NMP, and DMSO or their mixtures with other solvents are all high, with almost all of their $F_{1,4}$ values being higher than 90%. The regioselectivities of the cycloaddition reactions conducted in nonpolar solvents of toluene and benzene are lower, but their $F_{1,4}$ values are still higher than 50%. Thus, different from other thermal click reactions that are commonly regiochemically random, the cycloadditions of aroylacetylenes with azides are regioselective, in which solvent plays an active role in boosting the $F_{1,4}$ values of the reaction products. To understand the experimental results, we conducted mechanistic study of this unique thermal click reaction.

Mechanistic Study. We initially thought that the mechanism of the cycloadditions of aroylacetylenes with azides was similar to that of their cyclotrimerizations and believed that the reaction was catalyzed by a trace amount of secondary amine species generated in situ by the decomposition of DMF or DMAc at

Scheme 4



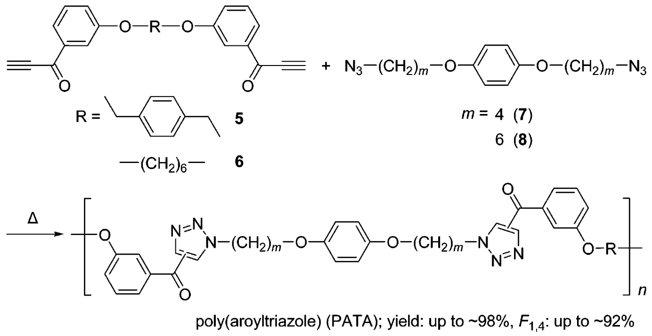
elevated temperatures.[11,18] However, the cycloadditions proceed much faster in non-nitrogenated solvents (DMSO and its mixture with toluene) to give triazole mixtures with higher $F_{1,4}$ values (~94%; Table 1, entries 4 and 5). This suggests that solvent polarity is a critical parameter to be considered in deciphering the reaction mechanism.

In an effort to gain more mechanistic insights, we carried out semiempirical calculation to estimate the orbital characteristics of the reactants. Three typical molecules were chosen for the theoretical study, with phenylacetylene (PA) used as comparison (Figure 3). The geometric structures of the molecules were optimized, and their frontier molecular orbitals were calculated on the basis of PM3 Harmiltonian[19] in the MOPAC package.[20] The keyword "precise" was used as a convergence criterion for the PM3 calculation of the geometry. As can be seen from Figure 3, the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) contribute roughly equally to the orbital properties of PA. In **2**, a large fraction of its orbital is found in the HOMO of the azide, with the nitrogen atom connected with the methylene carbon atom shows a higher orbital coefficient. On the other hand, the orbital of **1** is mainly located in the LUMO of the acetylene triple bond, and the terminal carbon atom shows a higher orbital coefficient. Owing to the electron-withdrawing effect of its carbonyl group, the LUMO energy of **1** drops to a level below that of PA. Clearly, the orbital interaction between the LUMO of **1** and the HOMO of **2** dominates, which favors the formation of 1,4-isomer **3**. The LUMO of **1** is further decreased when the cycloaddition reaction is conducted in a polar solvent due to the involved solvent−solute interaction, thus giving a triazole mixture with a higher $F_{1,4}$ value.[21]

Since the LUMO orbital coefficient of benzoylacetylene **1** is large and its energy is close to that of the HOMO of benzyl azide **2**, the 1,3-dipolar cycloaddition thus becomes a reaction that is controlled by the LUMO of **1**, giving 1,4-disubstituted 1,2,3-triazole **3** as the dominant product (Scheme 4). The reaction driven by the interaction between the HOMO of **1** and the LUMO of **2** to give 1,5-disubstituted 1,2,3-triazole **4** may still proceed, but the probability should be rather low because of the involved very high energy barrier.

Polymer Synthesis. After confirming that an aroylacetylene can undergo facile yet regioselective 1,3-dipolar cycloaddition reaction with an azide, we tried to utilize the novel click reaction to synthesize new polymers (Scheme 5). Bis(aroylacetylene)s **5** and **6** and diazides **7** and **8** were prepared according to our previously published methods,[11,12] and all the monomers were obtained in good yields in high purities (see Experimental Section). The polycycloaddition reactions of the bis(aroylacetylene)s with the diazides were carried out under the conditions similar to those used in the model reactions.

Scheme 5



We first followed time course of the polymerization reaction of **6** with **8** in a DMF/toluene mixture. The molecular weight (M_w) of the polymer product (PATA) generally increases with time, with little change in its polydispersity index observed (Table 2). After 6 h polymerization, the M_w of the resulting PATA becomes high enough (~18 000) for general purpose applications. Most importantly, the obtained PATA is completely soluble in common organic solvents. Structural analysis by ^{1}H NMR spectroscopy reveals that the PATA possesses a high regioregularity with a content of 1,4-disubstituted 1,2,3-triazole unit (or an $F_{1,4}$ value) of ~90%. We thus employed

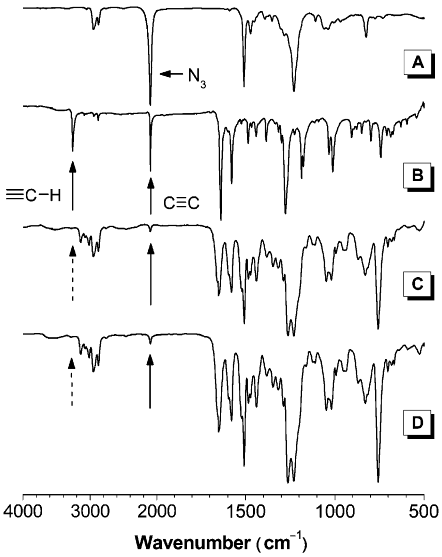


Figure 4. IR spectra of monomers **7** (A) and **5** (B) and their polymers P**I** (C) and P**V** (D).

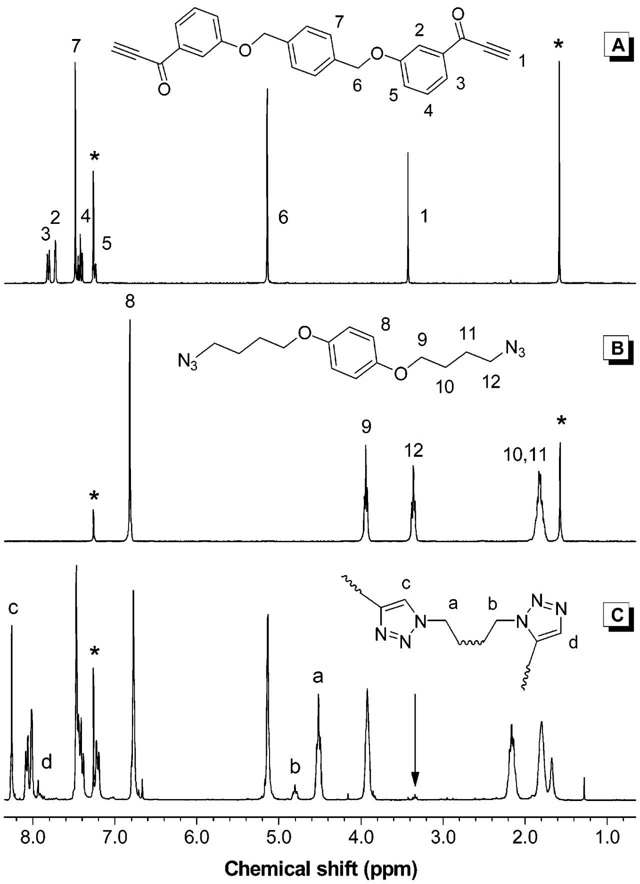


Figure 5. ^{1}H NMR spectra of monomers **5** (A) and **7** (B) and their polymer P**I** (C) in $CDCl_3$. The solvent and water peaks are marked with asterisks.

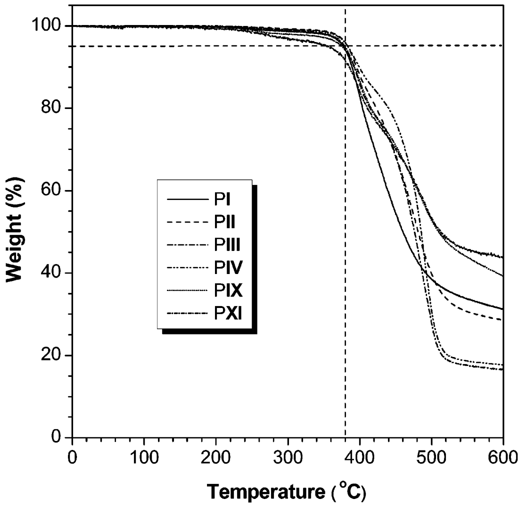


Figure 6. TGA thermograms of PATAs recorded under nitrogen at a heating rate of 20 °C/min.

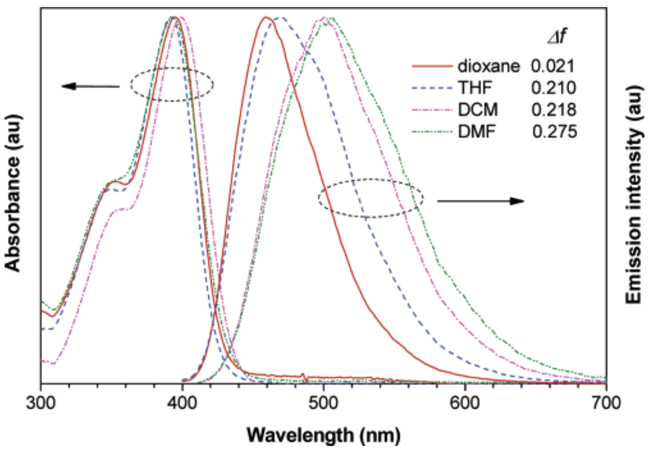


Figure 7. Absorption and emission spectra of P**XII** in solvents with different polarity parameters (Δf). Concentration: 3.5 μg/mL; excitation wavelength: 395 nm.

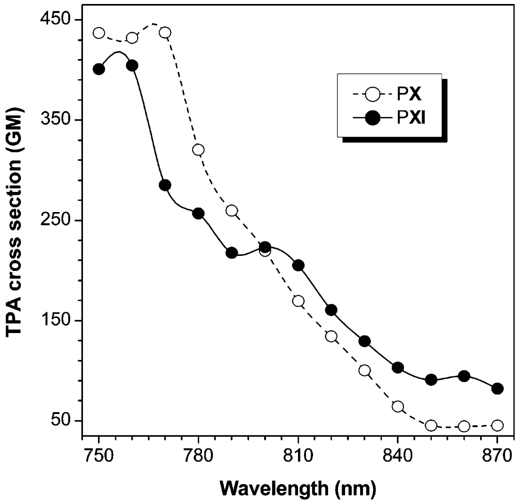


Figure 8. TPA spectra of P**X** and P**XI** in DCM.

these reaction conditions for the polycycloadditions of other monomer combinations. Tables 3 and 4 list the polymerization results of these monomer pairs.

The click reactions catalyzed by the Cu(I) species are sensitive to oxygen,[2,3] which is, however, not a problem in our reaction system. Comparing the results of the polycycloaddition reactions of **5** with **8** in open atmosphere and under nitrogen (Table 3, entries 2 and 3), it is clear that oxygen and moisture exert little effect on the click polymerization: the polymer yields, molecular weights, polydispersities, and regioregularities of the polymer products, i.e., P**II** and P**II**(*n*), are almost identical. Similar results are obtained for the polymerizations of **6** with **8** (Table 3, entries 5 and 6). This 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. All the PATAs are obtained in high yields, in high molecular weights, and in high regioregularities, which remain completely soluble in common solvents even after being stored under ambient conditions for several months.

We characterized the molecular structures of the PATAs by spectroscopic methods. Examples of IR spectra of P**I** and P**V** as well as their monomers **5** and **7** are given in Figure 4. The

Scheme 6

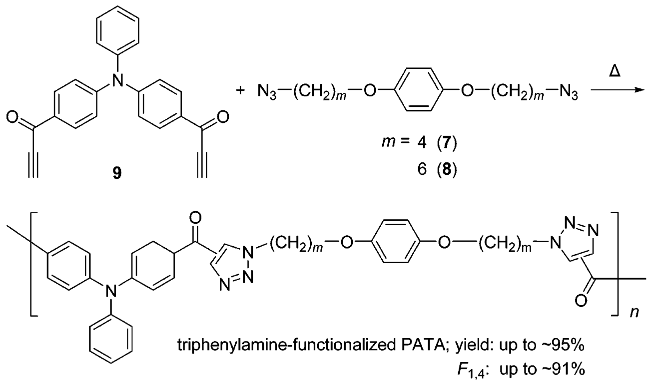


Table 5. Synthesis of Triphenylamine-Functionalized PATA[a]

PATA	monomer	solvent[b]	yield (%)	M_w[c]	M_w/M_n[c]	$F_{1,4}$ (%)[d]
P**IX**	**9** + **7**	DMF/toluene	95.1	13 700	1.82	90.4
P**X**	**9** + **7**	DMAc/toluene	88.1	15 700	1.84	90.0
P**XI**	**9** + **8**	DMF/toluene	90.2	14 400	1.78	88.4
P**XII**	**9** + **8**	DMAc/toluene	95.3	17 200	1.76	91.4

[a] Carried out at 100 °C for 6 h; $[M_i]_0 = 0.15$ M. [b] Volume ratio: 1:1. [c] Determined by GPC on the basis of a polystyrene calibration. [d] Calculated from ^{1}H NMR spectral data.

Table 6. Photophysical Properties of Triphenylamine-Functional PATAs[a]

	P**IX**				P**X**				P**XI**				P**XII**			
	λ_{ab} (nm)	λ_{em} (nm)	Φ_F (%)	δ (GM)	λ_{ab} (nm)	λ_{em} (nm)	Φ_F (%)	δ (GM)	λ_{ab} (nm)	λ_{em} (nm)	Φ_F (%)	δ (GM)	λ_{ab} (nm)	λ_{em} (nm)	Φ_F (%)	δ (GM)
dioxane	395.0	460.5	54	108.6	394.7	462.5	50	65.4	395.0	460.5	58	114.4	394.7	459.5	53	120.9
THF	392.5	472.5	49	121.8	392.0	475.5	43	68.1	392.2	466.0	53	109.4	392.2	469.5	47	116.3
DCM	398.3	504.0	36	212.6	398.6	503.5	29	223.3	398.6	498.5	38	219.5	398.6	501.0	44	139.5
DMF	392.5	504.5	19	178.8	392.5	500.5	21	164.4	392.5	504.5	26	130.2	392.9	505.5	24	143.7

[a] Abbreviations: λ_{ab} = absorption maximum; λ_{em} = emission maximum; Φ_F = fluorescence quantum yield estimated using quinine sulfate in 0.1 N H_2SO_4 ($\Phi_F = 54\%$) as standard; δ = two-photon absorption cross section excited at 800 nm using Rhodamine B in methanol (10^{-4} M) as calibrated standard; and GM = 10^{-50} cm^4·s/(photon·molecule).

similarity between the spectra of P**I** and P**V** implies that polymerization solvent does not affect molecular structures of the resultant polymers. In the spectra of P**I** and P**V**, the very weak absorption bands associated with the vibrational stretching of ≡C−H at 3257 cm^{-1} and C≡C and N_3 at 2096 cm^{-1} indicate that most of the acetylene and azide groups of the monomers have undergone the polycycloaddition reactions to give the triazole rings in the polymers.

Since the ^{1}H NMR spectrum of P**V** is virtually identical to that of P**I**, thus only are the spectra of P**I** and its monomers **5** and **7** shown in Figure 5. The acetylene protons of **5** resonate at δ 3.42; this peak almost completely disappears after the click polymerization. The resonance of the methylene protons adjacent to the azide group of **7** becomes very weak, further substantiating the conclusion drawn from the IR analysis (vide supra).

New resonance peaks are, however, observed at δ 8.26, 7.94, 4.81, and 4.52. The strong peaks at δ 8.26 and 4.52 are associated with the resonances of the protons of triazole ring (c) and methylene group (a) of 1,4-isomeric unit, while the weak signals at δ 7.94 (d) and 4.81 (b) are related to those of 1,5-unit. As discussed above, the integrals of resonance peaks a and b in Figure 5C can be used for calculation of regioisomer ratios. The results are summarized in Tables 3 and 4. P**I** and other PATAs prepared under different conditions are all regioregular, with $F_{1,4} \geq 88.5\%$. The higher regioselectivity of the click polymerization in the DMAc/toluene mixture than that in the DMF/toluene mixture is presumably due to the higher polarity of DMAc ($\epsilon = 37.8$; cf. for DMF, $\epsilon = 36.7$).

Preparation of Functional PATAs. Transition-metallic catalysts used in polymerization reactions are often difficult to be completely removed from the polymeric products, which can be very harmful in terms of adversely affecting materials properties of the polymers. Even with trace amounts, the metallic residues can, for example, worsen the performances of the polymers in the light-emitting diodes (LEDs). Since no metallic catalyst is used in our 1,3-dipolar polycycloaddition, the new click reaction thus offers an excellent synthetic route to functional materials with high purities. Triphenylamine is optically and photonically active. As a demonstration, we prepared triphenylamine-functionalized PATAs from the click polymerizations of a triphenylamine-containing diyne monomer (**9**) and diazides **7** and **8** (Scheme 6) under the conditions similar to those used for the preparation of P**I**.

PATAs P**IX**−P**XII** with high molecular weights are obtained in high yields (Table 5). The polymers are readily soluble in common organic solvents, enabling the use of "wet" spectroscopic techniques for their structure characterization. From the integrals of the resonance peaks of protons of the methylene groups adjacent to the triazole rings, the $F_{1,4}$ values of the PATAs are found to be higher than 88%. This polycycloaddition reaction is thus indeed a powerful and versatile method for the synthesis of new functional polymers. Thermal stabilities of the PATAs were evaluated by TGA. All the polymers (P**I**−P**XII**) are thermally stable. As can be seen from Figure 6, most of the PATAs lose about 5% of their weights at a temperature as high as ∼380 °C.

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.[22] It also functions as an electron donor (D) due to its electron-rich nitrogen atom. On the other hand, the new aroyltriazole ring formed by the click polymerization is electron-deficient and serves as an electron acceptor (A).[23] PATAs P**IX**−P**XII** 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 maxima (λ_{ab}) of P**IX**−P**XII** are all found in the neighborhood of ∼395 nm (Table 6). Upon photoexcitation, their solutions emit blue to green lights ($\lambda_{em} \sim 460-506$ nm) with Φ_F up to 58%. Figure 7 shows the UV and PL spectra of the solutions of P**XII** in different solvents as examples. Its UV 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).[24] 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.[25] The observed solvatochromic effect suggests that the ICT excited state has a larger dipolar moment than the ground state due to substantial charge redistribution and is probably derived from the relaxation of the initially formed Franck−Condon excited state (vertical transition from the ground state to the vibrational levels of the excited state and then relaxation to the ICT state) instead of the direct transition from the ground state.[14c]

Nonlinear Optical Properties. Molecular TPA processes are of current interest because they are involved in many technological applications such as three-dimensional fluorescence imaging, optical limiting, photodynamic therapy, and multidimensional microfabrication.[26] 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 δ values.[27] PATAs P**IX**−P**XII** possess A−D−A units and may thus show large optical nonlinearity. As can be seen from Table 6, all the polymers are absorptive in the UV spectral region but transparent at longer wavelengths. We thus carried out the TPIF experiments at 800 nm. Large δ values up to 223.3 GM are obtained from the DCM solutions. These values are similar to that of the reference (210 GM) and are comparable to those of their branched small molecule analogues ($\sim$240 GM).[23b]

The dependence of the δ value on the wavelength is shown in Figure 8. It is found that the maximum δ values are not obtained at 800 nm but at 760 nm, with the values at the shorter wavelength being $\sim$2-fold higher than those at the longer wavelength. The high δ values (up to 437 GM) of the polymers, combined with their facile synthesis and excellent biocompatibility, may enable them to find biomedical applications for two-photon fluorescence imaging of biological samples with significantly reduced photoinduced damage.

Conclusion

In this work, we succeeded in establishing a new, metal-free, effective synthetic route to PATAs. The 1,3-dipolar polycycloaddition of the bis(aroylacetylene)s with the diazides is fast and insensitive to air and moisture and can produce polymers with high molecular weights and high regioregularities in high yields. The polymers are all soluble in common organic solvents and hence macroscopically processable. The polymers are thermally stable, losing little of their weights when heated to temperatures of $\sim$380 °C.

The utility of this new polymerization technique is demonstrated by the synthesis of triphenylamine-functionalized PATAs. Because of the formation of triazole rings in the click polymerization, the polymers are comprised of numerous A−D−A units. This structural motif endows the polymers with novel linear and nonlinear optical properties including efficient PL, unique solvatochromism, and large TPA cross sections. It is anticipated that further optimization of polymerization reaction conditions and new efforts in molecular structure design will make the click polymerization an even more versatile synthetic tool for the generation of new advanced materials with mulitifaceted functionalities.

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Supporting Information Available: Time course of click polymerization of **6** with **8**, GPC curves of P**IX**−P**XII**, ^{1}H NMR spectra of triphenylamine-functionalized PATAs P**IX**−P**XII** in CDCl$_3$, crystal data, structure solution and refinement, atomic coordinates, bond lengths and angles, and anisotropic displacement parameters of 1-benzyl-4-benzoyl-1,2,3-trazole (**3**). This material is available free of charge via the Internet at http://pubs.acs.org.

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