Macromolecules
Article
Cite This: Macromolecules XXXX, XXX, XXX−XXX
pubs.acs.org/Macromolecules

Oxygen as a Crucial Comonomer in Alkyne-Based Polymerization toward Functional Poly(tetrasubstituted furan)s

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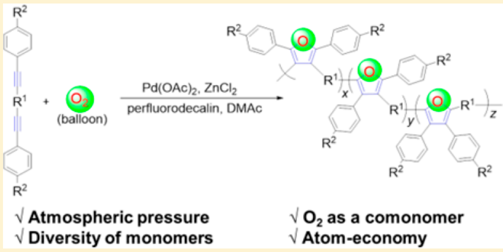
Supporting Information



ABSTRACT: Oxygen (O_2), one of the most essential gases, is abundant, cheap, nontoxic, and environmentally friendly. However, O_2 has not been used as a monomer to synthesize polymers yet, probably because of the difficulty in chain growth. In this paper, we develop a new alkyne-based polymerization in which O_2 serves as a comonomer under mild reaction conditions. Functionalized diynes could react with O_2 in the presence of $Pd(OAc)_2/ZnCl_2$ in *N*,*N*-dimethylacetamide (DMAc) and perfluorodecalin under atmospheric oxygen. Soluble poly(tetrasubstituted furan)s with high weight-average molecular weights (M_w up to 14 900) were obtained in high yields (up to 86%). The ratio of isomeric repeating units of **P1**(*m*) can be identified by analyzing the components of model reaction products. Moreover, **P1**(6) could function as a fluorescent sensor for explosive detection with superamplification quenching effect. **P2**−**P5** with conjugated structures possess large two-photon absorption cross sections up to 1570 GM, showing great potential as two-photon absorption materials. Thus, this work not only establishes a powerful O_2-involved alkyne-based polymerization but also provides poly(tetrasubstituted furan)s with versatile properties, which are potentially applicable in optoelectronic and biological fields.

■ INTRODUCTION

Oxygen (O_2), one of most essential gases, constitutes about 21% (by volume) of the earth's atmosphere, playing an important role in burning, respiration, energy metabolism of living organisms, etc. Nowadays, O_2 is widely used in many fields, including production of steel, plastics, and textiles; oxygen therapy; life support systems in aircraft, submarines, spacecraft, and diving; and so on. In contrast, O_2 can also cause damage, like spoilage of food, corrosion of metals, aging of polymer materials, etc. Thus, utilizing O_2 correctly to bring benefits instead of damage is significant.

Generally, oxygen has to be completely excluded during reactions because of its oxidation properties. Meanwhile, oxygen is also widely used as a green oxidant in organic reactions, because it is abundant, cheap, nontoxic, and environmentally friendly.[1,2] Therefore, O_2 has attracted more attention, and a great diversity of new O_2-involved oxidation reactions have been developed in recent years.[3−9]

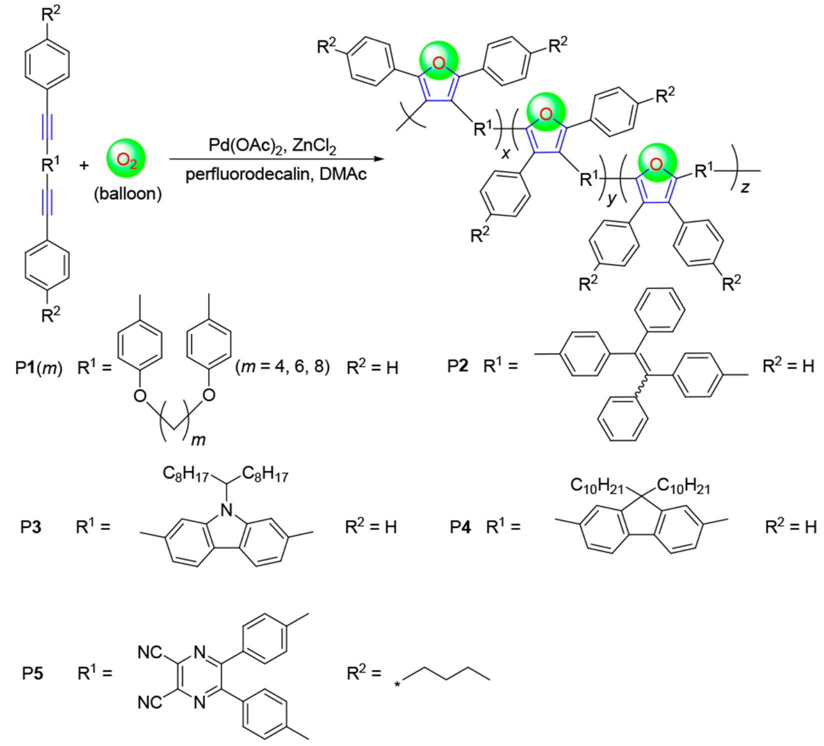
Although there is growing interest in using O_2 as a green oxidant to perform oxidation reactions, O_2 has not been used as a green monomer to synthesize polymers yet. Attracted by the advantages of O_2, we took this challenge to use O_2 as a comonomer in the development of new polymerizations based on triple-bond building blocks.[10−12] Alkyne is one of the most vital triple-bonds and can be oxidized by many oxidants like $KMnO_4$. We wondered whether it can be oxidized by O_2. After searching for a great deal of organic reactions, we found that the answer is "yes". Many alkyne/O_2 reactions have been reported in the past few years.[13−16] However, most of them are difficult to develop into a polymerization because the reactions between O_2 and alkynes will prohibit the chain growth, which is crucial for polymer synthesis. Delightfully, in 2009, Jiang and co-workers reported a $Pd(OAc)_2/Zn(OTf)_2$ catalyzed oxidation and cyclization of aromatic alkynes with O_2 under high oxygen pressure.[17] This reaction can furnish tetrasubstituted furans, which are one of the most prominent classes of five-membered heterocycles and have great significance in medicinal, agricultural, and material chemistry.[18−21] In 2011, the authors simplified this reaction by using fluorous solvents to maximize the solubility of O_2 in the reaction system, and the plausible mechanism is shown Scheme S1.[22] Because of the used fluorous solvents, alkynes can be efficiently oxidized by and cyclized with O_2 simultaneously under atmospheric pressure. Thus, this reaction became suitable for development into a new polymerization.[23,24]

After systematic investigation of the reaction conditions, a new polymerization of diynes and oxygen was successfully established for the first time. The polymerization can be

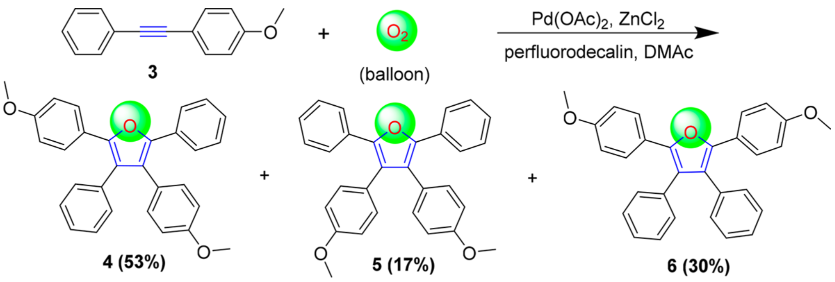
Received: June 20, 2018
Revised: August 14, 2018

DOI: 10.1021/acs.macromol.8b01293
Macromolecules XXXX, XXX, XXX−XXX

Scheme 1. Polymerization of Diynes and O_2



Scheme 2. Model Reaction of Monoyne 3 and O_2



carried out in the presence of $Pd(OAc)_2/ZnCl_2$ in *N*,*N*-dimethylacetamide (DMAc) and perfluorodecalin under atmospheric oxygen at 70 °C, and soluble poly(tetrasubstituted furan)s with high molecular weights were obtained in high yields after 8 h (Scheme 1). The ratio of isomeric repeating units in P**1**(*m*) can be identified via analyzing the products of the model reaction. Moreover, P**1**(6) could be used as a fluorescent sensor for explosive detection with superamplification quenching effect. Because of the conjugation structures of P**2**−P**5**, they possess large two-photon absorption cross sections up to 1570 GM.

■ RESULTS AND DISCUSSION

Model Reaction. Before exploring this O_2-involved alkyne-based polymerization, we examine whether the internal monoyne **3** could react with O_2 (Scheme 2). The reaction was catalyzed by $Pd(OAc)_2$ in the presence of $ZnCl_2$ in DMAc and perfluorodecalin under atmospheric oxygen, which generated three tetrasubstituted furan isomers **4**−**6** in a total yield of 85% after purification. Because **4**−**6** possess similar physical properties, it is hard to purify them by column chromatography and characterize them by ^1H and ^{13}C NMR spectroscopy as they also resonate at very similar chemical shifts. Fortunately, they could be separated by recycling preparative high-performance liquid chromatography (HPLC) using dichloromethane (DCM) as eluent after 6 cycles (Figure S1). Eventually, the isomeric structures were confirmed by ^1H NMR (Figure S2) and high-resolution mass spectroscopy (Figure S3). Moreover, from HPLC spectra of **4**−**6**, we could calculate their molar ratios, which are shown in Scheme 2.

Polymerization. With the successful experience of the highly efficient model reaction of monoyne **3** and O_2, we optimized the reaction conditions of polymerization of diynes and O_2 (Scheme 1). First, we used **1**(6) and O_2 as monomers to investigate the time course of the polymerization. Table S1 summarizes the polymerization results. The polymerization carried out in the presence of $Pd(OAc)_2/ZnCl_2$ in DMAc and perfluorodecalin under atmospheric oxygen for 8 h could readily furnish poly(tetrasubstituted furan)s with high weight-average molecular weight (M_w) in high yield (Table S1, entry 4). Further prolonging the reaction time to 10 h led to a slight increase in M_w and yield of the product. In consideration of reaction efficiency, we chose 8 h as the preferable reaction time.

Second, the effect of temperature on the polymerization was investigated. We set 5 parallel experiments with different temperatures from 60 to 100 °C by 10 °C interval. The polymerization results showed that the reaction at 70 °C (Table S2, entry 2) could generate poly(tetrasubstituted furan)s with excellent molecular weight (M_w = 11 500) in high yield (82%). When the temperatures were elevated to 90 and 100 °C, the produced poly(tetrasubstituted furan)s are partially soluble, probably because higher reaction temperatures activate the reactivity of monomers and promote the generation of products with much higher M_w that are poorly soluble in the reaction solvent. Hence, 70 °C was considered as the optimal temperature.

Third, the effect of the concentration of $Pd(OAc)_2$ on the polymerization was studied. The experimental results showed that the M_w values of the products decreased from 11 500 to 5000 and the yields reduced from 82 to 53% when the concentration of $Pd(OAc)_2$ lowered from 20 to 5 mmol % (Table S3). Thus, we keep the original concentration of the catalyst for further polymerization.

Fourth, we checked the effect of the molar ratio of $Pd(OAc)_2$ and $ZnCl_2$ on the polymerization. As indicated in Table S4, the M_w values of the products increased from 6300 to 11 900 and the yields enhanced from 72 to 86% with the molar ratio of $Pd(OAc)_2$ and $ZnCl_2$ changing from 1:1 to 1:4. However, when the molar ratio is 1:4, the polydispersity index of the polymer broadened to 2.32. Therefore, we still keep their molar ratio at 1:3.

Finally, the effect of monomer concentration on the polymerization was investigated. When the concentrations of **1**(6) increased progressively from 0.05 to 0.20 M, both the yields and M_w values of the polymers were enhanced accordingly (Table S5, entries 1–4). Hence, the concentration of 0.20 M is the best one.

With these optimized polymerization conditions in hand, other diynes were subjected to polymerization with O_2 to test its universality. Table 1 summarizes the polymerization of other diynes and O_2 under optimal reaction conditions. The results show that all the polymerizations proceeded smoothly, furnishing their corresponding polymers P**1**(m) and P**2**–P**5** with high M_w values (up to 14 900) in satisfactory yields.

Table 1. Polymerization of 1(m), 2–5, and O_2 under Optimized Reaction Conditions[a]

entry	polymer	yield (%)	M_w[b]	$Đ$[c]
1	P**1**(4)	81	12 200	1.98
2	P**1**(6)	85	14 900	2.63
3	P**1**(8)	76	14 000	2.02
4	P**2**	74	11 600	2.29
5	P**3**	83	11 400	2.08
6	P**4**	76	13 100	2.56
7	P**5**	63	7 000	1.58

[a] Carried out in DMAc and perfluorodecalin (v/v = 1:1) at 70 °C under O_2 (balloon) atmosphere for 8 h in the presence of $Pd(OAc)_2$ and $ZnCl_2$. [M] = 0.2 M, [$Pd(OAc)_2$] = 0.04 M, and [$ZnCl_2$] = 0.12 M. [b] Estimated by advanced polymer chromatography (APC) in tetrahydrofuran (THF) on the basis of a polystyrene calibration. [c] $Đ$, polydispersity index (M_w/M_n).

Structural Characterization. All the polymers were fully characterized by Fourier transform infrared (FT-IR) and NMR spectroscopies, and satisfactory results corresponding to their molecular structures were achieved. Herein, the FT-IR and NMR spectra of P**1**(6) are given as examples. The FT-IR spectrum of P**1**(6) is shown in Figure 1. For comparison, the spectra of monomer **1**(6) and model compounds **4**–**6** are also given. The spectrum of P**1**(6) shows absorption peaks inherited from monomer **1**(6) and model compounds **4**–**6** excepting that at 2218 cm^{-1}, which is readily assignable to the C≡C group. These results indicate that the C≡C group of **1**(6) has been almost consumed by the O_2-involved alkyne-based polymerization.

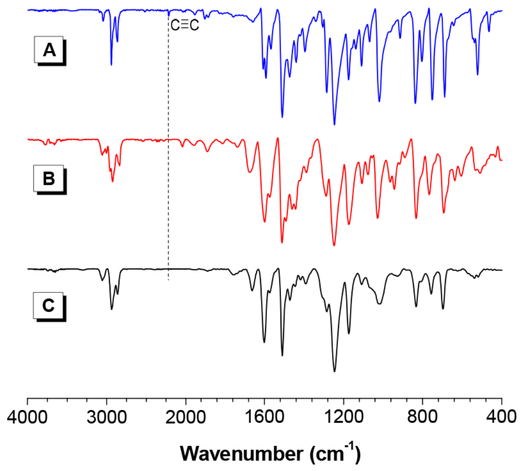


Figure 1. FT-IR spectra of (A) monomer **1**(6), (B) its model compounds **4**–**6**, and (C) polymer P**1**(6).

Their ^1H NMR spectra are also compared in Figure 2. The peaks at δ 7.63–5.93 in P**1**(6) were associated with the

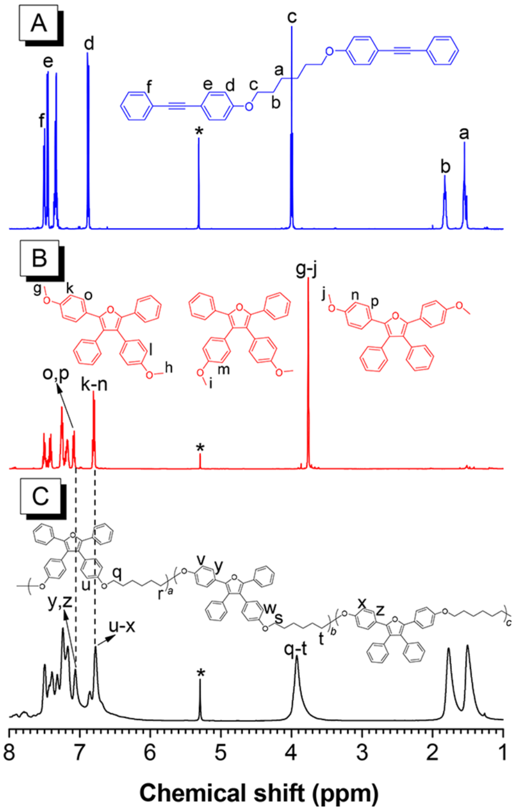


Figure 2. ^1H NMR spectra of (A) monomer **1**(6), (B) model compounds **4**–**6**, and (C) polymer P**1**(6) in DCM-d_2. The solvent peaks are marked with asterisks.

aromatic proton resonance, which are similar to that in model compounds **4**−**6**, confirming the occurrence of the polymerization and the expected polymer structure. The resonant peaks of P**1**(6) are much broader than those of compounds **4**−**6**, indicative of its polymeric nature. The ^{13}C NMR spectroscopy could also offer some informative analysis data (Figure 3). For example, the ^{13}C NMR spectrum of P**1**(6) exhibits no resonance peaks of acetylene carbon atoms of **1**(6) at δ 89.1 and 90.6. Furthermore, its spectral pattern largely resembles that of **4**−**6**, confirming the structure of P**1**(6) again. The FT-IR and NMR spectroscopical data of P**1**(4), P**1**(8), and P**2**−P**5** are summarized in the Supporting Information and all solidly confirm their respective structures (Figures S4−S21).

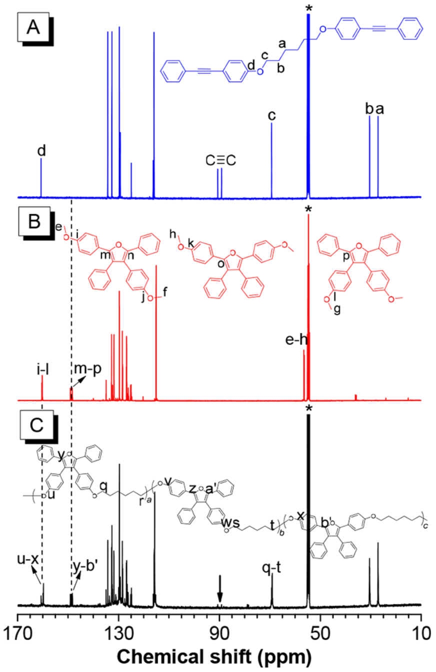


Figure 3. ^{13}C NMR spectra of (A) monomer **1**(6), (B) model compounds **4**−**6**, and (C) polymer P**1**(6) in DCM-d_2. The solvent peaks are marked with asterisks.

Solubility and Thermal Stability. Because of the irregular distribution of the repeating tetrasubstituted furan units, the polymers exhibit good solubility in common organic solvents, such as DCM, chloroform, THF, and toluene, and could be fabricated into high-quality films by spin-coating or static-casting processes. In addition, the decomposition temperatures of P**1**(m) and P**2**−P**5** at 5% weight loss are in the range of 253−379 °C under nitrogen, making them suitable for general applications (Figure S22).

Photophysical Properties. After their structures were confirmed, the ultraviolet−visible absorption and photoluminescence (PL) of all resultant poly(tetrasubstituted furan)s were investigated (Figure S23 and Table S6). The maximum absorption and emission of P**1**(4), P**1**(6), and P**1**(8) are located at 329 and 396 nm, respectively, which are similar to those of tetraphenylfuran.[25] The absolute PL quantum yield measurement showed that P**1**(6) possesses the highest value of 35.4%. P**2**−P**5** are conjugated polymers, so their THF solutions exhibit redder absorption and emission. P**2** shows green emission (517 nm), and P**3** and P**4** exhibit deep blue emission (444 and 449 nm). Because of the incorporated electron-accepting cyano and pyrazine groups of P**5**, its emission is red-shifted with a maximum peak at 564 nm, which is much redder than other polymers.

Explosive Detection. Sensors based on fluorescent polymers have attracted much attention because of their amplified response and superior sensitivity to analytes compared with their low molar mass congeners. The conjugated structure and high Φ_F value of P**1**(6) in THF solution enable us to explore its potential application as a chemosensor for explosive detection in antiterrorism implications. Picric acid (PA) was used as a model explosive because of its commercial availability. The quenching behavior of THF solution of P**1**(6) was studied by monitoring their PL changes with addition of PA (Figure 4). The PL quenching can be clearly identified at a PA concentration as low as 0.1 μg/mL. The PL of P**1**(6) dissolved in THF was weakened gradually with increasing the amount of explosives (Figure 4A). At a PA concentration of 0.65 mM, no emitting curve could be recorded by the spectrofluorometer. The Stern−Volmer plot of relative PL intensity ($I_0/I - 1$) versus the PA concentration gave an upward bending curve instead of a linear one (Figure 4B), indicative of a superamplification quenching effect.[26] It is

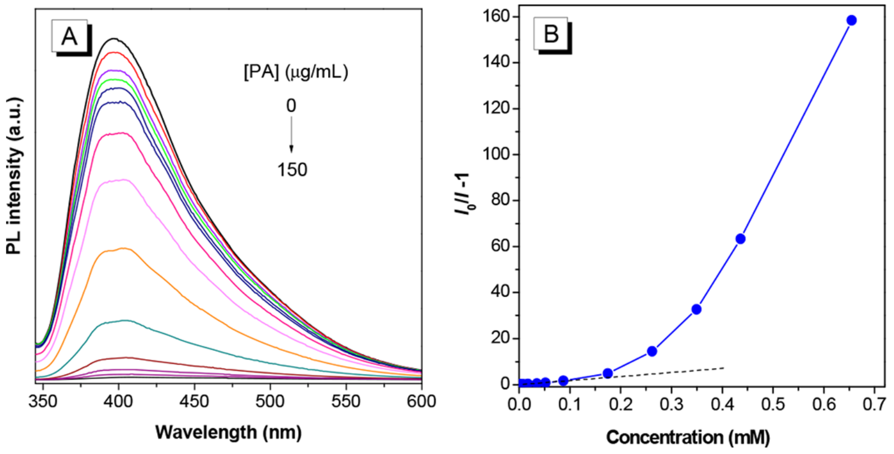


Figure 4. (A) PL spectra of P**1**(6) in THF containing different amounts of PA. (B) Stern−Volmer plot of ($I_0/I - 1$) values versus PA concentrations in THF of P**1**(6). I_0, peak intensity at [PA] = 0 M; concentration, 10 μM; excitation wavelength, 329 nm.

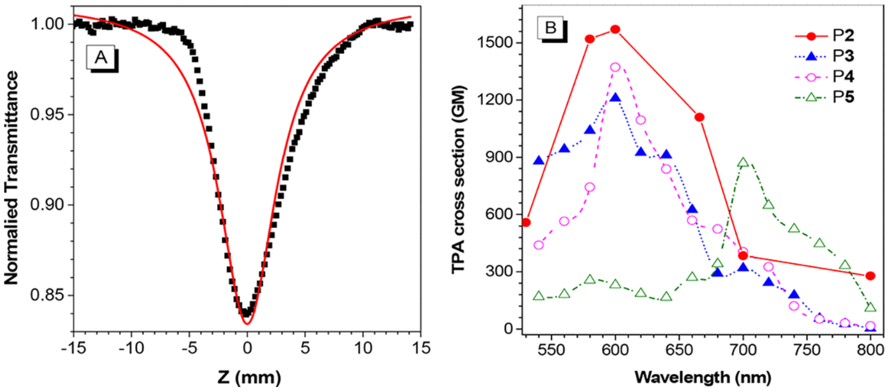


Figure 5. (A) Open-aperture Z-scan trace of P2 (scattered squares, experimental data; straight line, theoretical fitted data) in DCM at 600 nm excitation wavelength. (B) Two-photon absorption spectra of P2−P5 in DCM (concentration: ∼1 mM).

worth noting that the quenching behaviors of the resultant polyfurans are superior to that of polysiloles and polygermoles.[27]

To explain such quenching phenomena, we studied the absorption spectrum of PA and the PL spectrum of **P1**(6) (Figure S24). The obvious spectral overlap of the absorption of PA and emission of **P1**(6) in the range of 330−465 nm can be observed, greatly facilitating the energy transfer from the excited state of **P1**(6) to the ground state of PA. On the other hand, the electron-deficient PA is supposed to exert the strongest electric interaction with **P1**(6) because the furan moieties are electron-rich.[28]

Two-Photon Absorption Properties. Organic materials exhibiting large two-photon absorption (TPA) cross sections (σ) are of interest in applications in the areas including photodynamic therapy, optical pulse suppression, two-photon fluorescence microscopy, 3D microfabrication, 3D optical data storage, etc.[29] A variety of organic materials with the structure of donor−π−acceptor (D−π−A) and donor−π−donor (D−π−D) have been developed to realize large TPA cross sections.[30−33] Because **P2**−**P5** contain D−π−D or D−π−A conjugated structural motifs, we are curious to know whether they also possess large TPA cross sections. The TPA cross sections of **P2**−**P5** were thus measured by the open-aperture femtosecond Z-scan technique in DCM solutions with laser excitation in the range of 530−800 nm. Figure 5A shows the fitting curve of the open-aperture Z-scan of **P2** at 600 nm excitation wavelength as an example. The TPA cross section (σ) can be calculated by the equation $\sigma = h\nu\beta/N_0$, in which $N_0 = N_AC$ is the number density of the absorption centers, N_A the Avogadro constant, and C the solute molar concentration.[34−36] The largest TPA cross sections of **P2**−**P5** at different laser wavelength excitation (Figure 5B) were recorded to be 1570, 1208, 1371, and 868 GM, respectively, which are greater than those of conjugated polymers previously reported by our groups and others.[37−39]

CONCLUSIONS

In this work, we have developed a new facile O_2-involved alkyne-based polymerization under atmospheric oxygen. The polymerization could be performed in the presence of $Pd(OAc)_2/ZnCl_2$ in DMAc and perfluorodecalin at 70 °C, and poly(tetrasubstituted furan)s with high molecular weights were readily produced in high yields after 8 h. The resultant polymers are soluble and could be fabricated into high-quality films. By analyzing the components of model reaction products through HPLC, we unambiguously identified the ratios of isomeric repeating units of **P1**(m). Moreover, **P1**(6) can function as a fluorescent chemosensor for sensitive detection of explosive with superamplification quenching effect. Because of the conjugated structures of **P2**−**P5**, their TPA cross sections were measured to be as high as 1570, 1208, 1371, and 868 GM, respectively, showing great potential as two-photon absorption materials. Thus, this work not only first uses O_2 as a monomer in the alkyne-base polymerization but also furnishes poly(tetrasubstituted furan)s with versatile properties, which could be potentially applied in optoelectronic and biological fields, etc. We also believe that this polymerization will inspire polymerization with other green monomers.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macromol.8b01293.

Experimental details, reaction conditions optimization parameters, characterization data (TGA, FT-IR, NMR, UV, PL, PLQY) (PDF)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was financially supported by the National Natural Science Foundation of China (21788102, 21525417, and 21490571), the National Program for Support of Top-Notch Young Professionals, the Natural Science Foundation of Guangdong Province (2016A030312002), the Fundamental Research Funds for the Central Universities (2015ZY013), and the Innovation and Technology Commission of Hong Kong (ITC-CNERC14S01).

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DOI: 10.1021/acs.macromol.8b01293