Green Monomer of CO$_2$ and Alkyne-based Four-component Tandem Polymerization toward Regio- and Stereoregular Poly(aminoacrylate)s

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Electronic Supplementary Information

Abstract  Green monomers, such as carbon dioxide (CO$_2$), are closely related to our daily life and highly desirable to be transferred to functional polymers with diverse structures and versatile properties because they are abundant, cheap, nontoxic, renewable, and sustainable. However, the polymerizations based on these green monomers are to be further developed. In this work, a facile CO$_2$ and alkyne-based one-pot, two-step, four-component tandem polymerization was successfully established. The polymerization of CO$_2$, diynes, alkyl dihalides, and primary/secondary amines can proceed under mild reaction conditions and regio- and stereoregular poly(aminoacrylate)s with good solubility and thermal stability were obtained in high yields (up to 95%). Notably, distinctly different stereoregularity of resultant poly(aminoacrylate)s was realized via using primary or secondary amines. Using the former would readily generate polymers with 100% Z-isomers, whereas the latter furnished products with over 95% E-isomers. Through different monomer combination, the polymers with tunable structures and properties were obtained. Moreover, the tetraphenylethene units containing poly(aminoacrylate)s, showing the unique aggregation-induced emission characteristics, could function as a fluorescent probe for sensitive explosive detection. Thus, this work not only develops a facile CO$_2$ and alkyne-based multicomponent tandem polymerization but also provides a valuable strategy to fine-tune the polymer structures and properties, which could be potentially applied in diverse areas.

Keywords Carbon dioxide; Multicomponent tandem polymerization; Aggregation-induced emission; Green monomer

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INTRODUCTION

Multicomponent reactions (MCRs), in which three or more starting materials react together to form a product, are significant for living organisms. Various MCRs take place all the time in our bodies for the synthesis of DNA, RNA, proteins and so on. Nowadays, a great number of MCRs have been developed such as Mannich, Passerini, and Ugi reactions, which play important roles in organic synthesis.[1−3] Recently, multicomponent polymerizations (MCPs) as an emerging direction of synthetic polymer chemistry have been well-studied and inherit the advantages of multicomponent reactions such as structural diversity, high efficiency, mild reaction condition, high atom economy, and simple operation.[6−17] Very recently, efficient catalyst-free MCPs of sulfur, amines, and alkynes/isocyanides/acids have been developed and sulfur-containing polymers were prepared.[18−20] Compared with the sulfur monomer, one of the major byproducts from the petroleum industry, green monomers, such as oxygen (O$_2$), carbon dioxide (CO$_2$), and water (H$_2$O), are more closely related to our daily life and highly desirable to be used for MCPs because all of them are abundant, cheap, nontoxic, renewable, and sustainable. A few MCPs based on green monomers have been established. For example, a facile polymerization of H$_2$O, isocyanides, and bromoalkynes has been reported and functional polyamides were produced.[21] Afterwards, an efficient three-component polymerization involving benzoxazines, isocyanides, and H$_2$O was also developed to generate polyamides.[22] Similarly, O$_2$ was also firstly used in the alkyne-based polymerization, readily furnishing poly(tetrasubstituted furan) with versatile properties and potential applications in optoelectronic and biological fields.[23] Recently, several direct polymerizations of CO$_2$, diynes/diamines, and dihalides under very mild reaction conditions and normal CO$_2$ pressure have also been developed, and functional polymers were yielded.[24−28]

Besides MCRs, the tandem reactions, in which multiple
steps could be combined into one synthetic operation, have also drawn much attention because they can simplify experimental procedures, save time, and enable us to synthesize structurally complex compounds from simple and readily available substrates compared with traditional “step-by-step” operations. Thus, combining tandem reactions and MCTPs to develop efficient multicomponent tandem polymerizations (MCTPs) based on green monomers is very attractive.

A prominent advantage of MCTPs is structural control and diversity of resultant polymers. There are two main approaches to control the structure and expand the diversity of polymers via MCTPs. One is to change the type of third/fourth monomers to control the stereoregularity of polymers. The other is to alter the monomer combinations to control the backbone and side chains of polymers.

Attracted by the advantages of MCTPs, in this work, we succeeded in developing a facile and efficient one-pot, two-step, four-component tandem polymerization of CO\(_2\), diynes, alkyl dihalides, and primary/secondary amines (Scheme 1). The MCTP could propagate smoothly under mild conditions and normal CO\(_2\) pressure, and soluble, thermally stable, regio- and stereoregular poly(amineacrylate)s could be furnished in high yields. It is worth noting that using primary or secondary amine can cause distinctly different stereoregularities of resultant poly(amineacrylate)s. Moreover, through different combinations of monomers, the polymers with tunable structures and properties could be obtained. In addition, the tetraphenylenethene (TPE) units containing poly(amineacrylate) show unique aggregation-induced emission (AIE) characteristics and could be applied in sensitive explosive detection.

**EXPERIMENTAL**

**Materials**

All manipulations involving air- and/or water-sensitive compounds were carried out in a glove box or with the standard Schlenk techniques under dry nitrogen. CO\(_2\) (99.995%) was purchased from Guangzhou Ke Ming Gases Co., Ltd. and used as received. Monomers 1a, 1b, and 5 were prepared according to our previous procedures. 1,8-Dibromo-octane 2, benzylamine 3a, n-butylamine 3b, n-hexylamine 3c, diethylamine 4a, morpholine 4b, 1-bromooctane 6, 1,3-bis(aminomethyl)benzene 7, Ag\(_2\)WO\(_4\), Cs\(_2\)CO\(_3\), and N,N-dimethylacetamide (DMAc) were purchased from Sigma-Aldrich, Energy Chemical, TCI, Aladdin and used without further purification.

**Instruments**

\(^1\)H- and \(^13\)C-NMR spectra were measured on a Bruker Avance 500 MHz NMR spectrometer using deuterated dichloromethane as solvent and tetramethylsilane (TMS, \(\delta=0\)) as internal reference. FTIR spectra were recorded on a Bruker Vector 33 FTIR spectrometer. High resolution mass spectrometry measurements were performed on a GCT premier CAB 048 mass spectrometer. The number- \(M_n\) and weight-average \(M_w\) molecular weights and polydispersity indices (\(\text{PDI} = M_w/M_n\)) of polymers were estimated by a Waters advanced polymer chromatography (APC) system with a photo-diode array (PDA) detector, and THF was used as an eluent at a flow rate of 0.5 mL/min. A set of monodispersed linear polystyrenes covering the \(M_n\) range of \(10^3\)–\(10^7\) g/mol were utilized as standards for molecular weight calibration. Thermogravimetric analysis was carried out on a Shimadzu TGA-50 analyzer under a nitrogen atmosphere at a heating rate of 20 °C/min. UV-Vis absorption spectra were recorded on a Shimadzu UV-2600 spectrophotometer. Fluorescence spectra were recorded on a Horiba Fluoromax-4 spectrofluorometer.

**Polymerization**

All the polymerization reactions were carried out under CO\(_2\) atmosphere with normal pressure using the standard Schlenk technique. A typical polymerization procedure of 1a, 2, CO\(_2\), and 3a is given below as an example.

Into a 10 mL dried Schlenk tube equipped with a magne-

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**Scheme 1**  Polymerizations of CO\(_2\), diynes 1, alkyl dihalide 2, and primary amines 3, or secondary amines 4.

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tic stirrer were placed 1a (58.7 mg, 0.2 mmol), Ag$_2$WO$_4$ (9.3 mg, 0.02 mmol), and C$_5$H$_4$CO$_2$ (390.0 mg, 1.2 mmol) under CO$_2$ (balloon). Dried DMAC (1 mL) was injected into the tube by a syringe. The resultant mixture was stirred at 80 °C under CO$_2$ atmosphere for 12 h. Afterward, 3a (88 μL, 0.8 mmol) was injected. The mixture was stirred for additional 4 h in air. After cooled to room temperature, 4 mL of THF was added to dilute the mixture. Then the solution was added dropwise into 200 mL of methanol via a cotton filter under stirring. The precipitate was allowed to stand overnight and then collected by filtration. The polymer was washed with methanol and dried under vacuum at room temperature to a constant weight. A yellow solid of polymer P1a/2/3a/CO$_2$ was obtained in 86% yield (Table 1, entry 1). M$_n$ = 1.05×10$^4$ g/mol, M$_w$/M$_n$ = 1.80. FTIR (KBr disk, u, cm$^{-1}$): 3369, 3276, 3062, 3025, 2924, 2848, 1713, 1649, 1596, 1483, 1317, 1278, 1167, 1135, 1070, 1021, 924, 834, 790, 730, 694. 1H-NMR (500 MHz, CD$_2$Cl$_2$, δ, TMS, ppm): 8.84, 7.53–6.76, 4.66, 4.33, 4.03, 1.61, 1.32. 13C-NMR (125 MHz, CD$_2$Cl$_2$, δ, TMS, ppm): 170.69, 164.85, 148.77, 147.20, 140.23, 130.36, 129.93, 129.46, 128.95, 127.54, 127.30, 126.05, 124.68, 123.33, 86.32, 63.34, 48.84, 29.67, 29.42, 26.40. Table 1 Polymerization results of CO$_2$, dynes, alkyl dihalide, and primary/secondary amines. $^a$

| Entry | Polymer | Yield (%) | M$_w$ g/mol | B$^c$ |
|-------|---------|-----------|-------------|------|
| 1$^a$ | P1a/2/3a/CO$_2$ | 86 | 1.05×10$^4$ | 1.80 |
| 2$^a$ | P1a/2/3a/CO$_2$ | 91 | 1.13×10$^4$ | 1.86 |
| 3$^a$ | P1a/2/3b/CO$_2$ | 85 | 8500 | 1.64 |
| 4$^a$ | P1a/2/3c/CO$_2$ | 92 | 9300 | 1.77 |
| 5$^a$ | P1a/2/4a/CO$_2$ | 85 | 8100 | 1.54 |
| 6$^a$ | P1a/2/4b/CO$_2$ | 95 | 1.13×10$^4$ | 1.45 |
| 7$^a$ | P1a/2/4b/CO$_2$ | 87 | 1.25×10$^4$ | 1.82 |

$^a$ Carried out in N,N-dimethylacetamide (DMAc) at 80 °C under CO$_2$ (balloon) in the presence of Ag$_2$WO$_4$ and C$_5$H$_4$CO$_2$. $^b$ Carried out in DMAc at 80 °C under CO$_2$ (balloon) in the presence of Ag$_2$WO$_4$ and C$_5$H$_4$CO$_2$. $^c$ Carried out in DMAc at 80 °C under CO$_2$ (balloon) in the presence of Ag$_2$WO$_4$ and C$_5$H$_4$CO$_2$. $^d$ Carried out in DMAc at 80 °C under CO$_2$ (balloon) in the presence of Ag$_2$WO$_4$ and C$_5$H$_4$CO$_2$. $^e$ Carried out in DMAc at 80 °C under CO$_2$ (balloon) in the presence of Ag$_2$WO$_4$ and C$_5$H$_4$CO$_2$.  

P1b/2/3a/CO$_2$: A yellow solid was obtained in 91% yield (Table 1, entry 2). M$_n$ = 1.13×10$^4$ g/mol, M$_w$/M$_n$ = 1.86. FTIR (KBr disk, u, cm$^{-1}$): 3285, 3056, 3025, 2924, 2851, 1739, 1717, 1650, 1594, 1486, 1448, 1291, 1168, 1141, 1071, 1018, 929, 862, 836, 790, 764, 698. 1H-NMR (500 MHz, CD$_2$Cl$_2$, δ, TMS, ppm): 8.81, 7.41–6.75, 4.60, 4.18, 4.02, 1.59, 1.31. 13C-NMR (125 MHz, CD$_2$Cl$_2$, δ, TMS, ppm): 170.58, 164.85, 145.09, 143.41, 141.50, 140.07, 134.46, 131.62, 131.53, 128.92, 128.20, 127.75, 127.51, 127.37, 122.72, 86.57, 63.48, 48.61, 29.66, 29.40, 26.39. Table 2 Polymerization results of different monomer combination. $^a$

| Entry | Polymer | Yield (%) | M$_w$ g/mol | B$^c$ |
|-------|---------|-----------|-------------|------|
| 1$^a$ | P1a/6/7/CO$_2$ | 56 | 5000 | 1.40 |
| 2$^a$ | P5/2/7/CO$_2$ | 75 | 7200 | 1.56 |

$^a$ Carried out in DMAc at 80 °C under CO$_2$ (balloon) in the presence of Ag$_2$WO$_4$ and C$_5$H$_4$CO$_2$. Alkynes, haloalkanes, and CO$_2$ were allowed to react for 2 h prior to the addition of amines. $^b$ Estimated by APC using THF as an eluent on the basis of a polystyrene calibration. $^c$ D = polydispersity index (M$_w$/M$_n$). M$_w$ = weight-average molecular weight, M$_n$ = number-average molecular weight. $^d$ $[1a] = 0.20$ mol/L, $[6] = 0.40$ mol/L, $[1a]/[Ag_2WO_4]/[C_5H_4CO_2] = 1:0.2:1/6$. $^e$ $[7] = 0.20$ mol/L, t$_2$ = 24 h. $^f$ [5] = 0.40 mol/L, $[2] = 0.20$ mol/L, $[5]/[Ag_2WO_4]/[C_5H_4CO_2] = 2/1:0.1/6$. $^g$ [7] = 0.20 mol/L, t$_2$ = 24 h.
CO2 (Balloon) (Balloon) Ag2WO4, Cs2CO3 DMAc Ag2WO4, Cs2CO3 + B1 + CO2 + C2 A1 + B2 + CO2 + C2

4.64, 4.31, 3.98, 1.57, 1.30. (Table 2, entry 2).

23.07, 14.29.

Model Reaction

Into a 10 mL dried Schlenk tube equipped with a magnetic stirrer were placed 5 (269.4 mg, 1.0 mmol), 1-bromooctane 6 (231.7 mg, 1.2 mmol), Ag2WO4 (23.2 mg, 0.05 mmol), and Cs2CO3 (977.5 mg, 3.0 mmol) under CO2 (balloon). Dried DMAc (3 mL) was injected into the tube by a syringe. The resultant mixture was stirred at 80 °C under CO2 atmosphere for 12 h. Afterward, 3a (163.8 µL, 1.5 mmol) was injected. The mixture was stirred for additional 4 h in air. Then the reaction mixture was cooled to room temperature and extracted with DCM (60 mL×3). The organic layer was washed with water (100 mL×3) and dried over Na2SO4. After purification by silica gel column chromatography using petroleum ether (PE)/EA mixture as the eluent, a yellow solid of compound 8 (479 mg) was obtained in 90% yield. FTIR (KBr disk, ν, cm⁻¹): 3369, 3276, 3059, 3032, 2929, 2854, 1737, 1653, 1592, 1486, 1320, 1297, 1165, 1073, 1024, 838, 793, 752, 697. 1H-NMR (500 MHz, CDCl3, δ, TMS, ppm): 8.81, 7.49−6.66, 4.64, 4.31, 3.98, 1.57, 1.30. 13C-NMR (125 MHz, CDCl3, δ, TMS, ppm): 170.66, 164.98, 149.33, 147.62, 140.65, 129.78, 129.28, 129.18, 126.07, 125.83, 125.42, 123.98, 122.18, 86.41, 63.27, 49.47, 29.71, 29.00, 29.41, 26.41.

RESULTS AND DISCUSSION

Multicomponent Tandem Polymerization

Encouraged by our previous work that the poly(alkynoate)s obtained from MCP of CO2, diyynes, and alkyl dihalides could be postfunctionalized by benzylamine,[23] we would like to combine them to develop a CO2 and alkyn-based one-pot, two-step, four-component tandem polymerization using the monomers 1a, 1b, and 2−4. The polymerization of triphenylamine (TPA)-containing diyne 1a, 1,8-dibromooctane 2, primary amine 3a, and CO2 was first investigated as an example. This polymerization was conducted in two steps. First, 1a, 2, and CO2 were polymerized to afford poly(alkynoate) intermediate, and then, the intermediate was directly reacted with the fourth component 3a via amino-yne click reaction without separation and purification.[31] When the reaction time of the second step (t2) reached 4 h, the poly(aminooacrylate) with a weight-average molecular weight (Mw) of 1.05×10⁴ g/mol was obtained in a high yield (86%).

To test the generality of this four-component tandem polymerization, we polymerized other monomers. As listed in Table 1, all the polymerizations propagated smoothly, and soluble poly(aminooacrylate)s were produced in high yields (up to 95%). These results demonstrate that this polymerization has wide monomer scope, which will greatly enrich the structures and functionality of the obtained poly(aminooacrylate).

The high efficiency and the multicomponent reaction nature of this polymerization enable us to use versatile monomer combination such as “A2+B2+CO2+C2”, “A2+B2+CO2+C2”, and “A1+B1+CO2+C1” to construct polymers with different main-chains and properties, where, A, B, and C represent alkynyl, bromoalkyl, and amino monomers, respectively. As shown in Scheme 2, the reaction of diyne 1a, 1-bromooctane 6, and CO2 in the first step could produce a new alkynoate monomeric intermediate with 100% conversion, in which the diamine in the first step could produce a new alkynoate monomeric intermediate with 100% conversion, in which the diamine 7 was added readily furnished poly(aminooacrylate) P1a/6/7/CO2 with alkyl side chains and Mw of 5000 g/mol in a yield of 56%. Similarly, the polymerization of monoyne 5, dibromooctane 2, CO2, and diamine 7 could be used to generate the poly(aminooacrylate) P5/2/7/CO2 with different main-chains and Mw of 7200 g/mol in a yield of 75%. The yields and Mw of P1a/6/7/CO2 and P5/2/7/CO2 are both lower than those of P1a/2/3a/CO2, probably due to the poor solubility of diamine 7 in DMAc when the monomer concentration reached 0.2 mol/L, which further resulted in incomplete conversion of diamine 7 and stoichiometric imbalance of monomers during the polymerization (Table 2).
Structural Characterization

To facilitate the characterization of polymer structures, a model compound 8 was synthesized through a similar one-pot, two-step, four-component tandem reaction in 90% yield (Scheme 3). All the monomers, model compound, and polymers were fully characterized by standard spectroscopic techniques, and satisfactory analysis data corresponding to their expected molecular structures were obtained. The FTIR spectra of monomer 1a, model compound 8, and polymer P1a/2/3a/CO2 are provided in Fig. 1 as an example. The absorption bands of 1a associated with \( \equiv \text{C} \equiv \text{H} \) and \( \text{C} \equiv \text{C} \) stretching vibrations could be observed at 3290 and 2099 cm\(^{-1}\), respectively. These bands, however, could not be observed in the spectra of P1a/2/3a/CO2 and 8. Meanwhile, a new band associated with C=O stretching vibrations appeared at 1649 cm\(^{-1}\), revealing the occurrence of the polymerization. Similar results were obtained in the FTIR spectra of other polymers (Figs. S1–S8 in ESI).

As shown in Fig. S9 (in ESI), the stereoregularity of resultant poly(amineacrylate)s was totally different. As shown in Fig. S9 (in ESI), the \( E \)- and \( Z \)-vinyl protons could be readily distinguished at 4.91 and 4.70 ppm in the spec-

![Scheme 3Synthetic route to model compound 8.](image)

Fig. 1 FTIR spectra of (a) monomer 1a, (b) model compound 8, and (c) polymer P1a/2/3a/CO2.

To gain more structural details, \(^1\)H-NMR spectra of the monomers, 8, and P1a/2/3a/CO2 in DCM-\( d_2 \) were compared and analyzed (Fig. 2). The ethynyl protons of 1a, CH\(_2\) protons adjacent to the Br atom of 2, and NH\(_2\) protons of 3a resonated at 3.08, 3.40, and 1.84 ppm, respectively, which could not be found in the spectra of 8 and P1a/2/3a/CO2. Meanwhile, four new signals at 8.84, 4.66, 4.33, and 4.03 ppm, assigned to the resonances of the NH proton, ethynyl proton, CH\(_2\) protons next to the N and O atoms, respectively, appeared in the spectra of 8 and P1a/2/3a/CO2. Only one resonance signal of ethynyl proton could be observed and the N=H resonance was located at downfield in the \(^1\)H-NMR spectra of 8 and P1a/2/3a/CO2, indicative of the formation of an intramolecular hydrogen bond between the N=H and C=O, which has been confirmed by X-ray single crystal analysis and density functional theory (DFT) calculations in our previous reports. Thus, the newly formed vinyl group was confirmed to be a \( Z \)-isomer in 8 and P1a/2/3a/CO2, suggesting that this polymerization is highly regio- and stereoselective (Scheme 1). The stereoregularity of P1a/2/3a/CO2 is better than those of poly(amineacrylate)s obtained from primary amine and ester-activated terminal alkyne monomers (\( Z/E = 61/39 \)). However, when the secondary amines were used as the comonomers instead of primary ones, the stereoregularity of resultant poly(amineacrylate) was totally different. As shown in Fig. S9 (in ESI), the \( E \)- and \( Z \)-vinyl protons could be readily distinguished at 4.91 and 4.70 ppm in the spec-

![Fig. 2 \(^1\)H-NMR spectra of (A) diyne 1a, (B) dibromoocante 2, (C) monoamine 3a, (D) model compound 8, and (E) polymer P1a/2/3a/CO2 in DCM-\( d_2 \). The solvent signals are marked with asterisks.](image)
trum of P1a/2/4b/CO2, respectively. From the peak integrals at these signals, the ratio of E- and Z-isomers in P1a/2/4b/CO2 was calculated to be 97/3, indicative of a high stereoregularity of resultant poly(aminocarboxylate). Notably, this regioregularity is consistent with previous report because the E-isomers are more stable than the Z-ones with an energy difference of 22.6 kJ/mol via DFT calculation.\[33,34\]

The 13C-NMR spectra further confirmed the success of this four-component tandem polymerization. As shown in Fig. 3, the resonant signals of ethynyl carbons of 1a at 83.86 and 76.94 ppm were absent in the 13C-NMR spectra of 8 and P1a/2/3a/CO2. Meanwhile, the new signals associated with the resonances of ester carbon, vinyl carbons, and CH2 carbons adjacent to the generated ester group emerged at 170.69, 164.85, 86.32, and 63.34 ppm in 8 and P1a/2/3a/CO2, respectively. Similar conclusions could be drawn by analysis of the 1H- and 13C-NMR spectra of other polymers (Figs. S9–S24 in ESI).

**Solubility and Thermal Stability**

Due to the flexible structures of the resultant polymers, they all enjoyed good solubility in commonly used organic solvents, such as DCM, chloroform, THF, and DMAC, and could be fabricated into high-quality films by spin-coating process. The polymers were also thermally stable as evaluated by thermogravimetric analysis (TGA).

As shown in Fig. 4, the temperatures of 5% weight loss (T_d) are in the range of 240–324 °C under nitrogen. It is noteworthy that the poly(aminocarboxylate)s with different mainchains showed different thermal stability as concluded from the T_d values of P1a/2/3a/CO2, P1a/6/7/CO2, and P5/2/7/CO2. When the backbones of polymers become rigid, their T_d values increase correspondingly. Hence, tunable T_d values can be achieved via different monomer combination.

![Fig. 4 TGA thermograms recorded under nitrogen at a heating rate of 20 °C/min.](https://doi.org/10.1007/s10118-020-2454-2)

**Photoluminescence Properties**

The incorporation of tetraphenylethene (TPE), a typical moiety featuring the aggregation-induced emission (AIE) characteristics,\[37−41\] into the polymer skeletons of P1b/2/3a/CO2 and P1b/2/4b/CO2 made them AIE-active, too. Their photoluminescence (PL) spectra obtained in THF/water solutions with different water fractions (w) were then investigated to study their AIE behaviors (Fig. 5a, Figs. S25 and S26 in ESI). The PL curves of their THF solutions are almost a flat line parallel to the abscissa, indicating that the polymers were virtually non-emissive in the solutions. Gradual addition of water as the poor solvent into the THF solution led to aggregation of the polymer chains, which induced the emission intensified slowly. From the photographs of P1b/2/3a/CO2 taken in THF and a THF/water mixture with a f_w of 90% (insets of Fig. 5b), we can find that the former emits faintly, while the latter fluoresces intensely. The highest PL intensities of P1b/2/3a/CO2 and P1b/2/4b/CO2 were recorded for the THF/water mixtures with f_w of 90%, which are 41- and 7-folds higher than those in THF solutions, respectively (Fig. 5b). Such PL behaviors further confirm that P1b/2/3a/CO2 and P1b/2/4b/CO2 are AIE-active. Notably, the PL enhancement of P1b/2/3a/CO2 is higher than that of P1b/2/4b/CO2 because when P1b/2/3a/CO2 is dissolved in good solvents, the large free volumes enable the phenyl rings of TPE units to rotate.

![Fig. 3 13C-NMR spectra of (A) diyne 1a, (B) dibromooctane 2, (C) monoamine 3a, (D) model compound 8, and (E) polymer P1a/2/3a/CO2 in DCM-d2. The solvent signals are marked with asterisks.](https://doi.org/10.1007/s10118-020-2454-2)
Concentration: 10 µmol/L. Inset in panel b: photographs of P1b/2/3a/CO2 in THF and a THF/water mixture with 90% water fraction. Herein, the commercially available picric acid (PA) was used as a chemosensor for explosive detection, which is important for antiterrorism and homeland security. Thanks to its excellent fluorescent behaviors in the aggregate state, P1b/2/3a/CO2 was used as a model explosive, and the nanoaggregates of P1b/2/3a/CO2 with a Wf of 90% containing different amounts of picric acid (PA) were utilized as the probe. With gradual addition of PA into the system, the PL intensity of the aggregates of P1b/2/3a/CO2 progressively decreased (Fig. 6a). The quenching constant of P1b/2/3a/CO2 was deduced from the Stern-Volmer plots to be 1.45×10^4 L/mol (Fig. 6b) in the PA concentration range of 0–140 µmol/L and the limit of detection (LOD) was thus calculated to be 5.5×10^−6 mol/L according to the equation of LOD = 3SB/m [33]. In this equation, SB represents the standard deviation of the blank measurements and m is the slope of intensity versus sample concentration. This LOD value is comparable with those in the previous reports [44–46].

Fig. 5 (a) PL spectra of P1b/2/3a/CO2 in THF and THF/water mixtures. Concentration: 10 µmol/L, λex: 322 nm. (b) Plot of relative PL intensity versus water fraction in THF/water mixtures, where I = peak intensity in water mixtures and I0 = peak intensity in pure THF. inset in panel b: photographs of P1b/2/3a/CO2 in THF and a THF/water mixture with 90% water fraction.

Explosive Detection

Thanks to its excellent fluorescent behaviors in the aggregate state, P1b/2/3a/CO2 was used as a chemosensor for explosive detection, which is important for antiterrorism and homeland security. Thanks to its excellent fluorescent behaviors in the aggregate state, P1b/2/3a/CO2 was used as a chemosensor for explosive detection, which is important for antiterrorism and homeland security. Herein, the commercially available picric acid (PA) was used as a model explosive, and the nanoaggregates of P1b/2/3a/CO2 in THF/water mixtures with a Wf of 90% were utilized as the probe. With gradual addition of PA into the system, the PL intensity of the aggregates of P1b/2/3a/CO2 progressively decreased (Fig. 6a). The quenching constant of P1b/2/3a/CO2 was deduced from the Stern-Volmer plots to be 1.45×10^4 L/mol (Fig. 6b) in the PA concentration range of 0–140 µmol/L and the limit of detection (LOD) was thus calculated to be 5.5×10^−6 mol/L according to the equation of LOD = 3SB/m [33]. In this equation, SB represents the standard deviation of the blank measurements and m is the slope of intensity versus sample concentration. This LOD value is comparable with those in the previous reports [44–46].

CONCLUSIONS

In summary, we successfully developed a facile and efficient CO2 and alkyne-based one-pot, two-step, four-component tandem polymerization under mild reaction conditions. Regioregular and tunable stereoregular poly(aminooacrylate) could be generated in high yields. Through adjusting the monomer combination, such as “A1+2B2+CO2+2C1,” “A1+B2+CO2+2C2,” and “A1+B2+CO2+2C3,” the polymers with tunable structures and properties could be obtained. The resultant polymers possessed excellent solubility in organic solvents and thermal stabilities. The TPE units containing poly(aminooacrylate) showed the unique AIE characteristics, and their aggregates could function as the fluorescent probe for sensitive explosive detection. Thus, this work not only develops a facile CO2 and alkyne-based multi-component tandem polymerization but also provides a valuable strategy to construct polymers with diverse structures and versatile properties, which could potentially find wide applications in diverse areas.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of
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