Direct Conversion from Carbon Dioxide to Luminescent Poly(β-alkoxyacrylate)s via Multicomponent Tandem Polymerization-Induced Emission

*Bo Song,[†] Xiangyi Li,[†] Anjun Qin,*[,†] Ben Zhong Tang*[,†,‡]*

[†] State Key Laboratory of Luminescent Materials and Devices, Guangdong Provincial Key Laboratory of Luminescence from Molecular Aggregates, AIE Institute, Center for Aggregation-Induced Emission, South China University of Technology, Guangzhou 510640, China.

[‡] Shenzhen Institute of Aggregate Science and Technology, School of Science and Engineering, The Chinese University of Hong Kong, Shenzhen, Guangdong 518172, China.

ABSTRACT: Using carbon dioxide (CO_2) as a feedstock to synthesize various polymers has drawn much attention. One-pot multicomponent tandem polymerization (MCTP) with great synthetic simplicity and efficiency is a powerful strategy for the synthesis of new CO_2-based luminescent polymers. In this work, we successfully developed a new one-pot MCTP combining three sequential carboxylation-cyclization-esterification reactions of CO_2, diynes and alkyl dihalides to direct fixing CO_2 into luminescent polymers with aggregation-enhanced emission (AEE) property. This MCTP could be facilely carried out in *N,N*-dimethylacetamide in the presence of a cheap catalyst CuI and an organic base 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene under atmospheric pressure. A series of poly(β-alkoxyacrylate)s with well-defined structures, high molecular weights (M_w up to 15 400) were obtained in high yields (up to 96%). The resultant polymers possess good thermal stability with high decomposition temperature and high char yield. Due to polymerization-induced emission (PIE) behavior, the non-luminescent monomers could be converted to luminescent poly(β-alkoxyacrylate)s with AEE features. Thus, this work provides a new pathway to directly transform CO_2 into luminescent polymers via a one-pot MCTP strategy.

Introduction

Fixing carbon dioxide (CO_2) into polymeric materials has attracted wide attention nowadays, because CO_2 is a cheap, abundant, non-toxic and sustainable C1 feedstock. Except the most well-known poly(propylene carbonate)s generated from the CO_2/propylene oxide copolymerization,[1-8] some new CO_2-based polymers are generated in the past few years via a "step-by-step" strategy.[9] Non-isocyanate poly(hydroxyl urethane)s are typical ones obtained from CO_2 through two separate steps (Scheme 1A).[10] In many reported works, bis(cyclic carbonate)s (bis-CCs) were firstly prepared from CO_2 and diepoxides, then diamines were introduced to react with bis-CCs via non-regioselective ring opening reactions to obtain poly(hydroxyl urethane)s.[11-13] To solve the regioselectivity issue, Detrembleur et al. synthesized bis(α-alkylidene cyclic carbonate)s (bis-αCCs) from CO_2 and bis(propargylic alcohol)s, which could further react with nucleophiles such as diamines, diols and dithiols via regioselective ring opening reactions to generate poly(urethane)s, poly(carbonate)s and poly(thiocarbonate)s, respectively (Scheme 1B).[14,15] Jian et al. synthesized a highly reactive trivinyl methacrylate-type monomer from CO_2 and 1,3-butadiene via a three-step procedure. Then the monomer was used for the copolymerization with ethylene toward a new class of ester-functionalized polyethylenes (Scheme 1C).[16] Lu et al. also reported crystalline polyesters from CO_2 and 2-butyne via a five-step procedure (Scheme 1D).[17] All these reported works are significant for enriching the family of CO_2-based polymers. However, the "step-by-step" strategy needed more time for tedious separation and purification of intermediates. Thus, a new simple and efficient strategy for the synthesis of CO_2-based polymers is highly desirable.
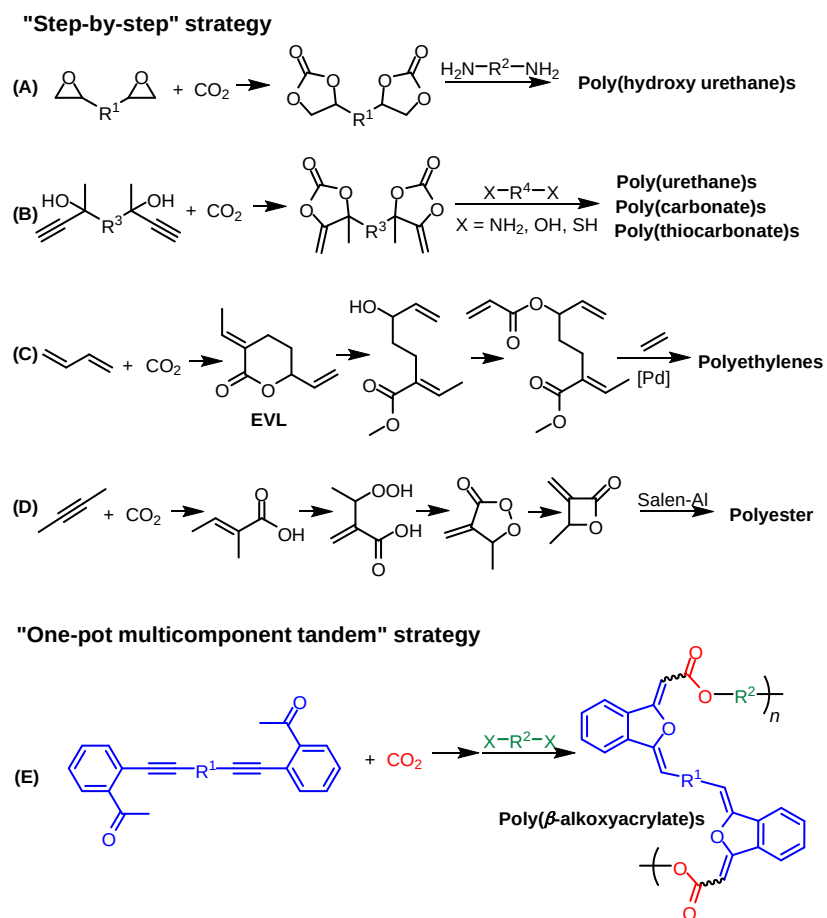
Scheme 1. The "step-by-step" and "one-pot multicomponent tandem" strategies for incorporating CO_2 into polymers.

Multicomponent tandem polymerization (MCTP) was proposed recently as a powerful strategy to combine multiple steps in a one-pot procedure to synthesize functional polymers. Such "one-pot" strategy has great synthetic simplicity and efficiency and could avoid the isolation and purification of the reactive intermediates, enabling synthesis of complex polymers from simple monomers.[18] Could this powerful strategy be used to make new CO_2-based polymers? We found that the answer is "yes". Nozaki et al. have reported a new "one-pot, two-step" MCTP toward CO_2-based polymers. They firstly synthesized a metastable lactone intermediate by a palladium-catalyzed condensation of CO_2 and olefins. Then they added the radical initiator to trigger free-radical polymerization of the lactone intermediate to afford

polymers without any isolation and purification.[19] This is an elegant work but still has some drawbacks, such as unavoidable side reactions during MCTP, low yields, and high CO_2 pressure. Compared to olefins, alkynes possess higher reactivity, enabling various reactions with CO_2.[20-26] Thus, we would like to explore a new robust and efficient MCTP based on alkynes and CO_2 under mild conditions.

Lu and Yamada et al. reported a sequential carboxylation-cyclization reaction of *o*-alkynyl acetophenone with CO_2, which was featured with high efficiency, broad scope of substrates, mild conditions. The resultant products could be further esterified by alkyl halides via "one-pot" strategy.[27-29] Inspired by these reported works, we try to combine three sequential carboxylation-cyclization-esterification reactions in a one-pot procedure to develop a new MCTP for synthesizing CO_2-based polymers (Scheme 1E).

Following this idea, in this work, we successfully developed a Cu(I)-catalyzed MCTP of CO_2, diynes and alkyl dihalides. This MCTP could be facilely carried out in *N,N*-dimethylacetamide (DMAc) under atmospheric pressure. A series of poly(β-alkoxyacrylate)s with high weight-average molecular weights (M_ws) were obtained in high yields (Scheme 2). The resultant polymers possess good thermal stability, and due to polymerization-induced emission (PIE) behavior, the non-luminescent monomers could be converted to luminescent poly(β-alkoxyacrylate)s with aggregation-enhanced emission (AEE) features.

Results and Discussion

Polymerization. In order to develop the one-pot MCTP of CO_2, diynes and alkyl dihalides, monomer **1** was designed and synthesized (Scheme S1) to polymerize with CO_2 and commercially available monomer **2**. The polymerization of CO_2, **1** and **2** was carried out in the

presence of Ag(I)/Cu(I) catalysts and organic bases under normal CO_2 pressure. In the first step, monomer **1** was reacted with CO_2 for 3 h, and **2** was then added in the second step to proceed with the esterification for 1 h to afford poly(β-alkoxyacrylate)s.
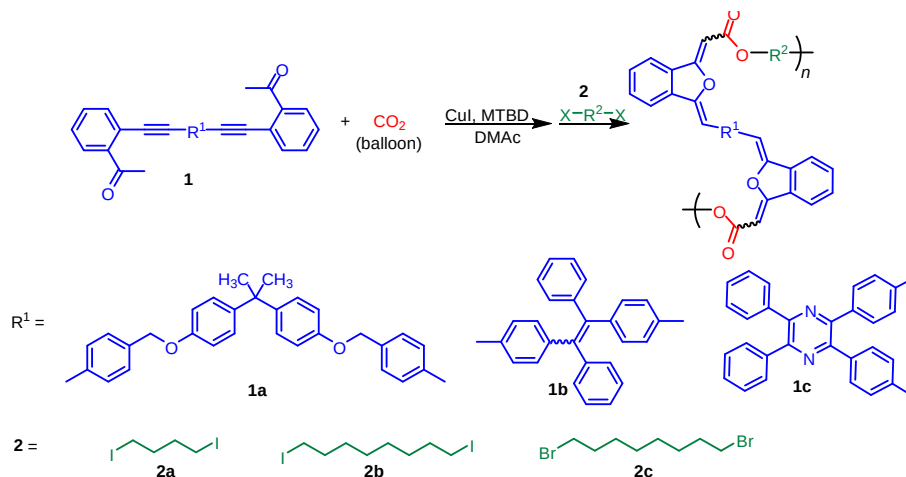
Scheme 2. Cu(I)-catalyzed MCTP of CO_2, **1** and **2**.

Table 1. Effect of catalysts on the polymerization of **1a**, **2a** and $CO_2{}^{a}$

entry	catalyst	yield (%)	$M_w{}^{b}$	$Đ^{c}$
1	AgOAc	83	4000	1.12
2	AgNO$_3$	92	4600	1.15
3	AgBF$_4$	80	5200	1.28
4	CuI	93	6100	1.36

[a] Carried out in *N,N*-Dimethylformamide (DMF) at 80 °C under CO_2 (balloon) for 4 h in the presence of different catalyst and DBU. [**1a**] = [**2a**] = 0.05 M, [**1a**]/[**2a**]/[Catal.]/[DBU] = 1:1:0.4:8. Monomer **1a** and CO_2 was reacted for 3 h prior to the addition of **2a**. [b] Estimated by gel permeation chromatography (GPC) in DMF on the basis of a polymethyl methacrylate calibration. [c] $Đ$ = polydispersity index (M_w/M_n, M_w = Weight-average Molecular Weight, M_n = Number-average Molecular Weight).

The catalyst and base are key factors for successful establishment of this MCTP. Herein, we used CO_2, **1a** and **2a** as model monomers to explore the effect of different catalysts and bases. First, we tried various catalysts like AgOAc, AgNO$_3$, AgBF$_4$, and CuI for the MCTP. As shown

in Table 1, the MCTP catalyzed by CuI showed the best results both in yields and M_ws of polymers. Secondly, we explored the effect of different bases for the MCTP, 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (MTBD) brought better results than 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (Table 2) during the polymerization. Thus, we chose CuI and MTBD as the catalyst and base for this MCTP.

Table 2. Effect of bases on the polymerization of **1a**, **2a** and CO_2[a]

entry	Base	yield (%)	M_w[b]	Đ[c]
1	DBU	89	6400	1.36
2	MTBD	91	8600	1.55

[a] Carried out in DMF at 80 °C under CO_2 (balloon) for 4 h in the presence of CuI and different base. [**1a**] = [**2a**] = 0.05 M, [**1a**]/[**2a**]/[CuI]/[base] = 1:1:0.4:8. Monomer **1a** and CO_2 was reacted for 3 h prior to the addition of **2a**. [b] Estimated by GPC in DMF on the basis of a polymethyl methacrylate calibration. [c] Đ = polydispersity index (M_w/M_n).

Table 3. Effect of solvents on the polymerization of **1a**, **2a** and CO_2[a]

entry	solvent	yield (%)	M_w[b]	Đ[c]
1	DMF	90	7600	1.42
2	DMAc	95	8700	1.48
3	DMSO[d]	86	6100	1.30

[a] Carried out in different solvents at 80 °C under CO_2 (balloon) for 4 h in the presence of CuI and MTBD. [**1a**] = [**2a**] = 0.05 M, [**1a**]/[**2a**]/[CuI]/[MTBD] = 1:1:0.4:8. Monomer **1a** and CO_2 was reacted for 3 h prior to the addition of **2a**. [b] Estimated by GPC in DMF on the basis of a polymethyl methacrylate calibration. [c] Đ = polydispersity index (M_w/M_n). [d] Dimethyl sulfoxide.

Then the solvent, temperature, monomer concentration and catalyst loading were carefully investigated (Tables 3-6). All the factors exerted much effects on the polymerizations. When the polymerization was carried out in DMAc under normal CO_2 pressure in the presence of CuI and MTBD at 90 °C for 4 h ([**1a**] = [**2a**] = 0.10 M, [**1a**]/[**2a**]/[CuI]/[MTBD] = 1:1:0.3:8), the poly(*β*-alkoxyacrylate)s with a M_w of 15 400 was produced in a 95% yield, showing the best results.

Table 4. Effect of temperature on the polymerization of **1a**, **2a** and CO_2[a]

entry	T (°C)	yield (%)	M_w[b]	$Đ$[c]
1	80	93	8400	1.55
2	90	92	9500	1.57
3	100	84	8300[d]	1.52

[a] Carried out in DMAc under CO_2 (balloon) for 4 h in the presence of CuI and MTBD. [**1a**] = [**2a**] = 0.05 M, [**1a**]/[**2a**]/[CuI]/[MTBD] = 1:1:0.4:8. Monomer **1a** and CO_2 was reacted for 3 h prior to the addition of **2a**. [b] Estimated by GPC in DMF on the basis of a polymethyl methacrylate calibration. [c] $Đ$ = polydispersity index (M_w/M_n). [d] Soluble part.

Table 5. Effect of monomer concentration on the polymerization of **1a**, **2a** and CO_2[a]

entry	[**1a**] (M)	yield (%)	M_w[b]	$Đ$[c]
1	0.025	86	5500	1.23
2	0.050	94	9100	1.52
3	0.100	95	10 500	1.60

[a] Carried out in DMAc at 90 °C under CO_2 (balloon) for 4 h in the presence of CuI and MTBD. [**1a**]/[**2a**]/[CuI]/[MTBD] = 1:1:0.4:8. Monomer **1a** and CO_2 was reacted for 3 h prior to the addition of **2a**. [b] Estimated by GPC in DMF on the basis of a polymethyl methacrylate calibration. [c] $Đ$ = polydispersity index (M_w/M_n).

To test the universality of this MCTP, we polymerized other monomers under the above-mentioned optimal conditions. The MCTP of CO_2, **1a-1c**, and **2a-2c** generally proceeded smoothly and polymers with satisfactory M_w (9400-15 400) could be obtained in good to excellent yields (80-96%; Table 7), further demonstrating the robustness of our developed MCTP. Notably, alkyl dibromide **2c** also showed high reactivity compared with alkyl diiodide **2b**, greatly expanding the scope of the monomers.

Table 6. Effect of catalyst loading on the polymerization of **1a**, **2a** and CO_2[a]

entry	[CuI] (mM)	yield (%)	M_w[b]	$Đ$[c]
1	20	90	12 600	1.69
2	30	95	15 400	1.70
3	40	94	11 800	1.61

The possible mechanism of the polymerization was proposed in Scheme S2.[27,28] First, monomer **1** was carboxylated with CO_2 to produce intermediate **I** in the presence of MTBD. Second, intermediate **I** underwent keto–enol tautomerism and the enol oxygen atom attacked the copper(I)-activated alkyne moiety (intermediate **II**). Third, the cyclization with regio-selectivity took place to generate intermediate **III**. Finally, with adding alkyl dihalides, intermediate **III** was esterified to produce the polymers.

Table 7. Polymerization results of different monomers[a]

entry	polymer	yield (%)	M_w[b]	$Đ$[c]
1	P**1a**/**2a**/CO_2	95	15 400	1.70
2	P**1b**/**2a**/CO_2	89	10 500	1.62
3	P**1c**/**2a**/CO_2	85	9700	1.56
4	P**1a**/**2b**/CO_2	96	10 300	1.75
5	P**1a**/**2c**/CO_2	87	10 400	1.72
6	P**1b**/**2b**/CO_2	84	9400	1.53
7	P**1c**/**2b**/CO_2	80	10 700	1.60

Scheme 3. Model reaction of CO_2, **1a** and *n*-iodobutane.

Structural Characterization. All resultant polymers were fully characterized by Fourier transform infrared spectroscopy (FT-IR) and nuclear magnetic resonance (NMR) spectroscopies. To help the characterization of chemical structures of polymers, model compound **3** was designed and synthesized under the same conditions (Scheme 3). Herein, the FT-IR and NMR spectra of polymer **P1a/2a**/CO_2, its corresponding monomer **1a** and model compound **3** were shown as examples to prove the expected structure of the polymer. In the FT-IR spectra of **3** and **P1a/2a**/CO_2 (Figure 1), the absorption band related to the C≡C stretching vibration of **1a** at 2211 cm^{-1} disappeared, suggesting the total consumption of the C≡C bonds from monomer **1a** in the MCTP. Meanwhile, the C=O stretching vibration peak of monomer **1a** at 1690 cm^{-1} retained in the spectrum of **3** and **P1a/2a**/CO_2 and new peaks of the C=C stretching vibration of **3** and **P1a/2a**/CO_2 appeared at 1640 cm^{-1}, corresponding to the expected structures of **3** and **P1a/2a**/CO_2. In the FT-IR spectra of other polymers, similar results were observed (Figures S1-S5).
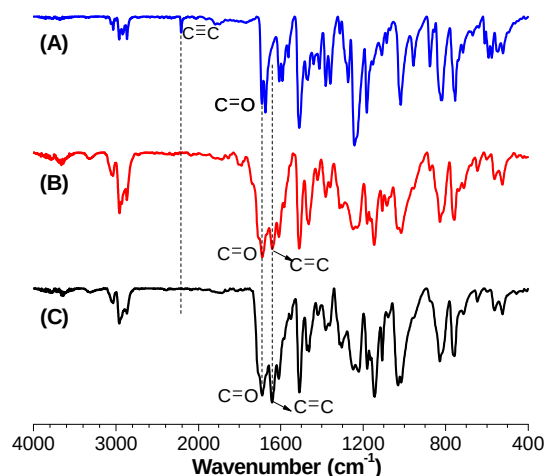
Figure 1. FT-IR spectra of (A) monomer **1a**, (B) model compound **3** and (C) polymer P**1a**/**2a**/CO_2.

The ^{1}H NMR spectra of **1a**, **2a**, model compound **3**, and P**1a**/**2a**/CO_2 could provide more detailed information (Figure 2A-D). The methyl protons adjacent to the carbonyl groups of **1a** which resonated at δ 2.75 (b) disappeared in the spectra of **3** and P**1a**/**2a**/CO_2, while the peak from the methylene protons of **1a** at δ 5.06 (c) was retained. Most importantly, new peaks emerged at δ 6.37 (k), 5.71 (j) and 4.26 (i) in the spectra of **3** and P**1a**/**2a**/CO_2, representing two newly generated alkenyl protons adjacent to phenyl and ester groups and methylene protons adjacent to ester groups, respectively. Notably, a weak peak at δ 6.02 (j) in the spectra of **3** and P**1a**/**2a**/CO_2, corresponding to alkenyl protons adjacent to the ester groups from *E*-isomer, was also observed.[27,28,30] Since the chemical shifts of the stereoisomers are largely different, the *Z*/*E* ratio in P**1a**/**2a**/CO_2 could be calculated using their integrals, which was deduced to be 90/10. The ratios of the *Z*-isomers of other polymers could be also obtained by this calculation, which are all higher than 88% (Figure S6-S10), demonstrating the good stereo-selectivity of the MCTP.
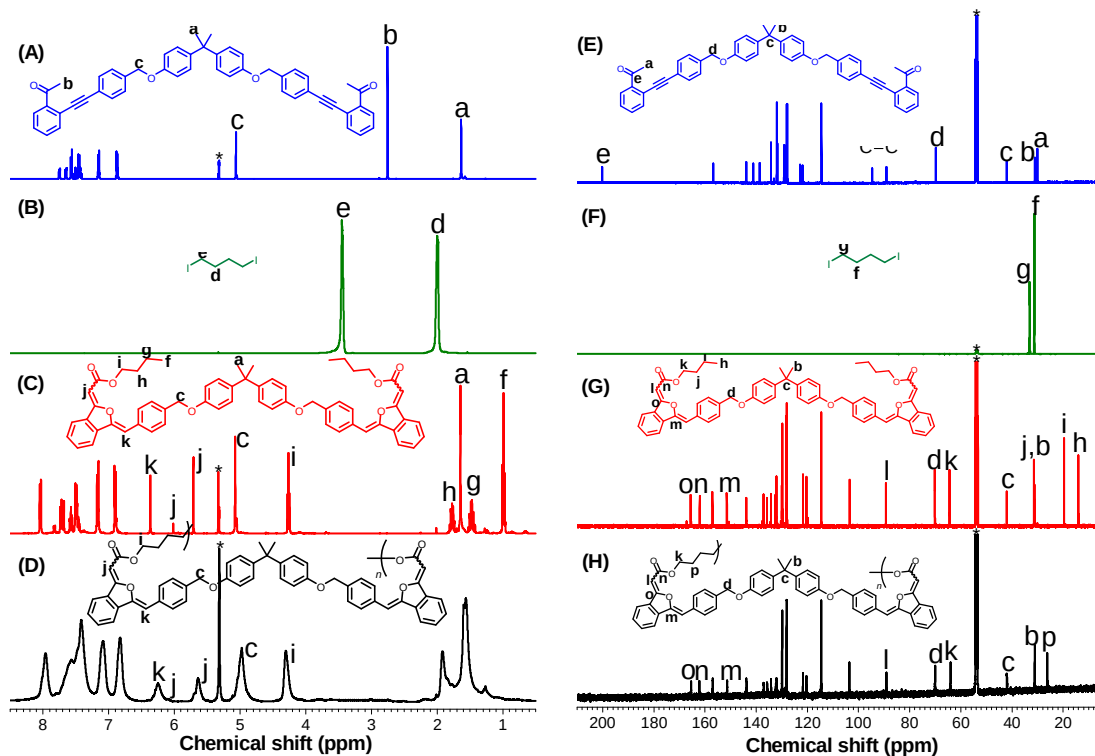
Figure 2. ^1H NMR spectra of (A) monomer **1a**, (B) **2a**, (C) model compound **3**, (D) polymer P**1a**/**2a**/CO_2 and ^{13}C NMR spectra of (E) **1a**, (B) **2a**, (C) **3**, (D) P**1a**/**2a**/CO_2 in dichloromethane (DCM)-d_2. The solvent peaks are marked with asterisks.

The ^{13}C NMR spectra could also offer some informative analysis data. As shown in Figure 2E-H, the ethynyl carbons resonated at δ 94.69 and 89.05 and the carbonyl carbons resonated at δ 200.19 (e) of monomer **1a**, which could not be found in the spectra of **3** and P**1a**/**2a**/CO_2. Furthermore, several new peaks associated with the resonances of ester carbons, methylene and alkenyl carbons adjacent to the ester groups appeared at δ 162.20 (n), 64.05 (k), 165.42 (o) and 89.07 (l), respectively, in the spectra of **3** and P**1a**/**2a**/CO_2. These results again confirmed the structure of P**1a**/**2a**/CO_2 and the success of this MCTP. Similar results were also observed in the ^{13}C NMR spectra of other polymers (Figure S11-S15).

Solubility and Thermal Stability. Due to the flexible structures of the resulting polymers, they showed good solubility in commonly used organic solvents, such as DCM, chloroform, DMF,

DMAc and DMSO. The thermal stability of resultant polymers was evaluated by thermogravimetric analysis (TGA). As shown in Figure 3, the temperatures of 5% weight loss (T_d) are in the range of 274-334 °C under nitrogen, indicating that all the polymers are thermally stable. Notably, **P1c/2a**/CO_2 and **P1c/2b**/CO_2 retain more than half of their original weights after being heated to 800 °C, showing high char yields.
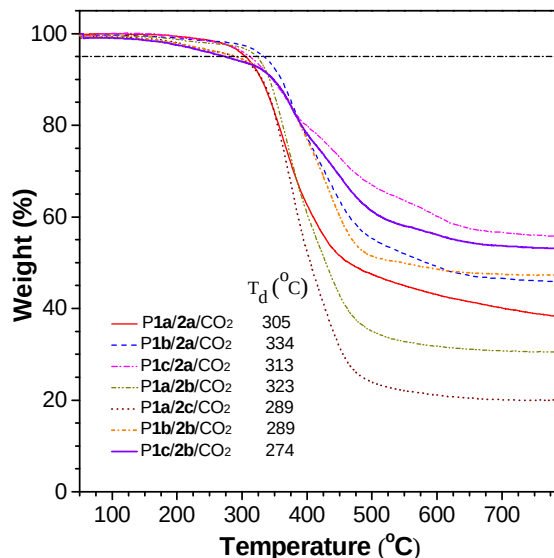

Figure 3. TGA thermograms recorded under nitrogen at a heating rate of 20 ^{o}C·min^{-1}.

Polymerization-Induced Emission (PIE). Luminescent polymers with aggregation-induced emission (AIE) properties have gained considerable attention due to their versatile applications in diverse areas, including fluorescent chemosensors, bioimaging, organic light-emitting diodes, etc.[31-34] Generally, AIE polymers are obtained by the polymerization of AIE monomers which must be designed and synthesized elaborately. PIE is an emerging powerful strategy that could transform non-luminescent monomers into luminescent polymers.[35-37] It could also expand the methodology library of AIE polymers.
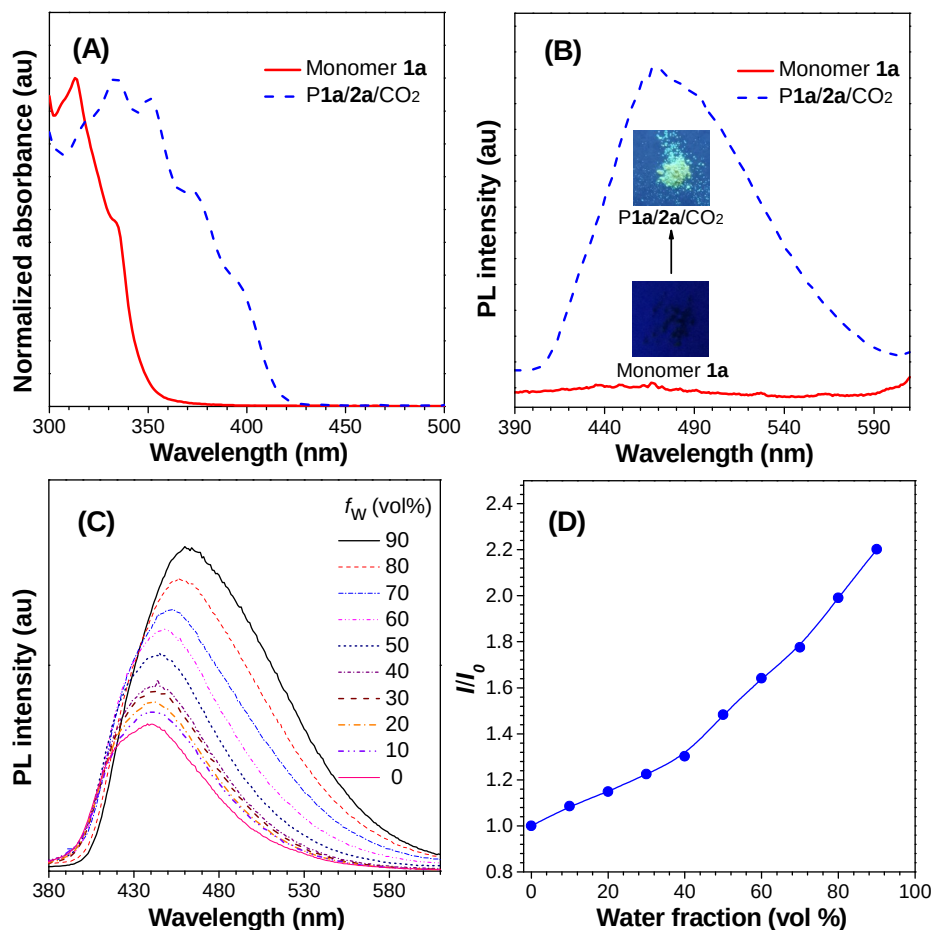
Figure 4. (A) Absorption spectra of monomer **1a** and P**1a**/**2a**/CO_2 in THF. Concentration: 10 μM. (B) PL spectra of monomer **1a** and P**1a**/**2a**/CO_2 in solid. λ_{ex}: 320 nm. Inset in panel B: photographs of monomer **1a** and P**1a**/**2a**/CO_2 under UV light. (C) PL spectra of P**1a**/**2a**/CO_2 in THF and THF/water mixtures. Concentration: 10 μM. λ_{ex}: 320 nm. (B) Plot of relative PL intensity versus water fraction in THF/water mixtures, where I = peak intensity in water mixtures and I_0 = peak intensity in pure THF.

The MCTP of CO_2, diynes and alkyl dihalides we developed exhibited PIE behavior. Herein, the ultraviolet-visible (UV) absorption and photoluminescence (PL) of the polymer P**1a**/**2a**/CO_2 and its corresponding monomer **1a** were investigated. As shown in Figure 4A, P**1a**/**2a**/CO_2 exhibited redder absorption than that of **1a**. More importantly, monomer **1a** showed non-luminescent but exhibited bright luminescent after MCTP (Figure 4B). Because P**1a**/**2a**/CO_2 possessed intense luminescence in solid state, it was expected to exhibit AIE feature. Therefore,

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its photoluminescence in THF and THF/water mixtures with different water fraction (f_w) were tested. As shown in Figure 4C, upon excitation by the wavelength of 320 nm, the THF solution of P**1a**/**2a**/CO_2 emitted gently with the peak at 441 nm. However, its emission intensity increased and red-shifted with addition of water due to the restriction of intramolecular motion. P**1a**/**2a**/CO_2 showed the highest fluorescence intensity with maximum peak at 462 nm, at the f_w of 90%, which was 2.2 times higher than that of its THF solution (Figure 4D), confirming its AEE features.

Conclusions

In this work, we successfully developed a new one-pot multicomponent tandem polymerization combining three sequential carboxylation-cyclization-esterification reactions of CO_2, diynes and alkyl dihalides to direct fix CO_2 into luminescent polymers with AEE property. This MCTP could be facilely carried out in DMAc in the presence of a cheap catalyst CuI and an organic base MTBD under atmospheric pressure. A series of poly(β-alkoxyacrylate)s with well-defined structures, high molecular weights (M_w up to 15 400) were obtained in high yields (up to 96%). The resultant polymers possess good thermal stability with high decomposition temperature and high char yield. Due to PIE behavior, the non-luminescent monomers could be converted into luminescent poly(β-alkoxyacrylate)s with AEE features. Thus, this work provides a new pathway to direct transform CO_2 into luminescent polymers with AEE property via a one-pot MCTP strategy. It inspired us to explore some advanced applications of these CO_2-based AEE polymers in the future.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Materials, instrumentation, experimental procedures, characterization data; ^{1}H and ^{13}C NMR and FT-IR spectra of monomers and polymers; possible mechanism (PDF)

AUTHOR INFORMATION

Corresponding Authors

* msqinaj@scut.edu.cn (A.J.Q.)

* tangbenz@cuhk.edu.cn (B.Z.T.)

Notes

The authors declare no competing financial interest.

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Table of content:

CO$_2$ and alkyne based three-component tandem polymerization

Polymerization-Induced Emission

√ Atmospheric pressure
√ High efficiency

√ Commercial catalyst
√ AEE property