



# DBU-catalyzed CO<sub>2</sub> fixation in polypropargylamines under solvent-free conditions

Nam-Kyun Kim<sup>1</sup> · Hiromitsu Sogawa<sup>1,2</sup> · Mulyadi D. Felicia<sup>1</sup> · Toshikazu Takata<sup>1</sup>

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## Introduction

CO<sub>2</sub> is a useful and attractive C1 resource in polymer chemistry, given its direct applicability to polymer synthesis and modification. The use of CO<sub>2</sub> as a sustainable precursor of valuable polymers has aroused much interest, from both environmental and industrial perspectives. Thus far, research efforts have focused on the direct (co)polymerization of CO<sub>2</sub>, the polymerization of monomers synthesized from CO<sub>2</sub>, and the incorporation of gaseous CO<sub>2</sub> by postmodification approaches [1–4]. Among the most environmentally benign attempts is metal- and solvent-free CO<sub>2</sub> fixation in polymeric substrates under moderate conditions. However, this approach is hindered by the relatively low reactivity of CO<sub>2</sub> and the difficulty in performing polymer reactions in solvent-free conditions. Endo and coworkers reported an efficient base-catalyzed gas–solid phase reaction that incorporates CO<sub>2</sub> into oxirane-derived polymers [5–8], but current reports on this topic are limited. We have reported highly efficient CO<sub>2</sub> fixation in polypropargylamines with a 2-pyridyl group using 1,8-diazabicyclo [5.4.0]undec-7-ene (DBU) as a base catalyst [9]. Within a few minutes, the reaction yielded the corresponding polyoxazolidinone under atmospheric CO<sub>2</sub> and room temperature conditions. Owing to the highly reactive substrate, the reaction occurred even under conditions

with very low CO<sub>2</sub> concentrations in air. Herein, we report the efficient CO<sub>2</sub> fixation in polypropargylamines under solvent-free conditions. Two types of polymers with a propargylamine-repeating unit are synthesized: one with a main chain of repeating units and the other with side chains of repeating units. The side chain-type polypropargylamines are newly designed for the sake of simplification of copolymerization with other monomers in order to incorporate functional groups. Both types of polymers could be used for solvent-free CO<sub>2</sub> fixation. For side chain-type polymers, the effect of the incorporation of a tertiary amine moiety into the polymer chain was evaluated.

## Experimental procedure

### Materials and measurements

Commercially available solvents and reagents were used as received. (6-Bromo-pyridin-2-yl)methanol and *N*-benzyl-1,1-dimethylpropargylamine were synthesized as described in the literature [9]. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded by a Bruker Biospin AVANCE DPX-300 spectrometer and a Bruker AVANCEIIIHD500 using deuterated solvents. Spectra were calibrated using residual undeuterated solvent, tetramethylsilane as the internal standard. The IR spectra were recorded on a JASCO FT/IR-230 spectrometer. High-resolution mass spectrometry–electrospray ionization (HRMS–ESI) data were collected using a JEOL JMS-700 mass spectrometer at the Center for Advanced Materials Analysis, Tokyo Institute of Technology and are available on request. Size exclusion chromatography (SEC) was carried out at 30 °C in dimethylformamide (DMF) (5 mM LiBr, 0.85 mL/min) using a JASCO PU-2080 system equipped with a set of TOSOH TSKgel G2500H and G4000H columns. The number average molecular weight ( $M_n$ ), weight average molecular weight ( $M_w$ ), and polydispersity index (PDI) of the obtained polymers were calculated based on a polystyrene calibration. The 5% and

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✉ Toshikazu Takata  
ttakata@polymer.titech.ac.jp

<sup>1</sup> Department of Chemical Science and Engineering, Tokyo Institute of Technology, 2-12-1 (H-126), Ookayama, Meguro-ku, Tokyo 152-8552, Japan

<sup>2</sup> Present address: Biomacromolecules Research Team, RIKEN Center for Sustainable Resource Science, 2-1, Hirosawa, Wako-shi, Saitama 351-0198, Japan

10% weight decomposition temperatures  $T_{d5}$  and  $T_{d10}$ , at which the polymers lose 5% and 10% of their weight, respectively, were determined by thermogravimetric analysis (TGA). The TGA was carried out on a Shimadzu TGA-50 instrument under  $N_2$  atmosphere (flow rate 50 mL/min) at a heating rate of 10 °C/min. The glass transition temperatures ( $T_{gs}$ ) of the polymers were determined by differential scanning calorimetry (DSC) using a Shimadzu DSC-60 instrument in  $N_2$  atmosphere (flow rate 50 mL/min) with liquid  $N_2$  as a refrigerant. The DSC heating rate was 10 °C/min.

## Synthesis of monomer 2

A solution of methacryloyl chloride (1.33 g, 12.7 mmol) in  $CH_2Cl_2$  (5.0 mL) was slowly added to a solution of (6-bromo-pyridin-2-yl)methanol (2.00 g, 10.6 mmol) and triethylamine (1.80 mL, 12.7 mmol) in  $CH_2Cl_2$  (20 mL) at 0 °C and stirred at room temperature for 18 h. The resulting mixture was filtered to remove the insoluble part, and the filtrate was washed with 5% NaOH aq., sat.  $NH_4Cl$  aq., and water. The organic layer was dried over anhydrous  $MgSO_4$ , and filtered and evaporated at reduced pressure. The residue was purified by silica gel column chromatography using *n*-hexane/ethyl acetate = 20/1 (v/v) as the eluent to give **A** (2.19 g, 80%). M.p. 32.4–34.0 °C;  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$  7.57 (t,  $J$  = 7.8 Hz, 1 H), 7.43 (dd,  $J$  = 7.9, 0.6 Hz, 1 H), 7.33 (dd,  $J$  = 7.5, 0.8 Hz, 1 H), 6.23 (q,  $J$  = 1.1 Hz, 1 H), 5.66 (q,  $J$  = 1.6 Hz, 1 H), 5.28 (s, 2 H), 2.00 (q,  $J$  = 0.8 Hz, 3 H) ppm;  $^{13}C$  NMR (126 MHz,  $CDCl_3$ )  $\delta$  166.69, 157.50, 141.55, 139.03, 135.75, 127.16, 126.45, 120.11, 66.05, 18.32 ppm; HRMS-ESI (m/z)  $[M^+HNa]^+$  calculated for  $[C_{10}H_{10}BrNO_2Na]^+$  277.9787; found: 277.9781; IR (neat) 2921 (C-H), 1719 (C=O), 1156 (C-N)  $cm^{-1}$ .

*N*-Benzyl-1,1-dimethylpropargylamine (0.31 g, 1.76 mmol),  $Pd(PPh_3)_2Cl_2$  (11 mg, 0.016 mmol), CuI (6 mg, 0.03 mmol), and  $Et_3N$  (890  $\mu$ L, 6.4 mmol) were added to a THF solution of **A** (0.21 g 0.80 mmol) under Ar atmosphere. The mixture was stirred at 50 °C for 2 h and diluted with  $CHCl_3$ . The organic layer was washed with  $NH_4Cl$  aq. and  $NaHCO_3$  aq., dried over anhydrous  $Na_2SO_4$ , and filtered and evaporated under reduced pressure. The residue was purified by silica gel column chromatography eluted with EtOAc/Hex = 1/4 (v/v) to give **2** as a yellow solid (0.27 g, 98%). m.p. 33.7–35.7 °C;  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$  7.67 (t,  $J$  = 7.8 Hz, 1 H), 7.38 (t,  $J$  = 6.6 Hz, 3 H), 7.32 (q,  $J$  = 7.4 Hz, 3 H), 6.23 (t,  $J$  = 1.2 Hz, 1 H), 5.65 (t,  $J$  = 1.5 Hz, 1 H), 5.33 (s, 2 H), 3.97 (s, 2 H), 2.01 (q,  $J$  = 0.8 Hz, 3 H), 1.54 (s, 6 H) ppm;  $^{13}C$  NMR (126 MHz,  $CDCl_3$ )  $\delta$  166.84, 156.51, 143.05, 140.53, 136.82, 135.91, 128.42, 128.36, 126.93, 126.38, 126.25, 120.20, 95.11, 81.77, 66.79, 50.57, 49.11, 29.39, 18.35 ppm; HRMS-ESI (m/z)  $[M]^+$  calculated

for  $[C_{22}H_{25}N_2O_2]^+$  349.1911; found: 349.1905; IR (neat) 3282 (N-H), 2978 (C-H), 2208 (C $\equiv$ C), 1719 (C=O), 1156 (C-N)  $cm^{-1}$ .

## Radical polymerization of monomer 2

Azobisisobutyronitrile (AIBN; 4.5 mg, 4 mol%) was added to a solution of **2** (238 mg, 0.68 mmol) in toluene (850  $\mu$ L, 0.8 M) under an Ar atmosphere. The reaction mixture was heated at 70 °C for 6 h and then cooled to room temperature and concentrated under reduced pressure. The residue was redissolved in  $CHCl_3$  (1 mL). The precipitate was collected by pouring  $CHCl_3$  (1 mL) solution into *n*-hexane (30 mL) and was dried under reduced pressure to give **P2AU** as a white solid (0.22 g, 90%).  $^1H$  NMR and FT-IR data are described in the ESI.

## Radical copolymerization of monomer 2 and 2-(*N,N*-diethylamino)ethyl methacrylate (DEAEMA)

Compound **2** and DEAEMA were fused by radical copolymerization, varying the feed ratio of the two monomers in a manner similar to the process for the polymerization of **2**. The products were **P3AU**, **P4AU**, and **P5AU**. The  $^1H$  NMR and FT-IR data of **P3AU**, **P4AU**, and **P5AU** are described in the ESI.

## Solvent-free CO<sub>2</sub> fixation in P1AU

To prepare the polymer film, **P1AU** solution in  $CHCl_3$  and DBU (200 mol% per repeating unit) was placed in Teflon® Petri dishes (80 mm diameter). The solvent was allowed to evaporate under Ar conditions for 3 days and under vacuum conditions for 1 day. The prepared film was placed into a glass vial. After purging with  $CO_2$ , the glass vial was incubated at 60 °C, and the reaction was monitored by  $^1H$  NMR spectroscopy. Once the reaction had finished, the reaction mixture was poured into 5%  $H_2O/MeOH$  (v/v). The resulting precipitates were collected by filtration and dissolved in  $CHCl_3$  (1 mL), and the solution was again poured into 5%  $H_2O/MeOH$  (v/v). The resulting precipitates were collected by filtration, giving **P1OZ** at 86% yield.

$^1H$ -NMR (500 MHz,  $DMSO-d_6$ )  $\delta$  7.78 (br, 1 H), 7.68 (br, 1 H), 7.29–7.21 (m, 2 H), 7.03–6.90 (br, 3 H), 6.28–5.92 (br, 1 H), 5.13 (br, 2 H), 4.42 (br, 2 H), 1.60–1.13 (m, 6 H) ppm; IR (neat) 2971 (C-H), 1780 (C=O), 1585 (aromatic C=C), 1683 (C=C)  $cm^{-1}$ .

## Solvent-free CO<sub>2</sub> fixation in P2AU–P5AU

The general method was as follows. A polymer film was prepared by charging a solution of **P2AU** (40 mg) in  $CHCl_3$

and DBU (20 mol% per repeating unit) in a round-bottomed flask and allowing the solvent to evaporate in vacuo. After purging with CO<sub>2</sub>, the flask was heated at 60 °C, and the reaction was monitored by <sup>1</sup>H NMR spectroscopy. Once the reaction had finished, the reaction mixture was dissolved in CHCl<sub>3</sub> (1 mL) and washed with aq. NaHCO<sub>3</sub> (1 mL x 3) and brine (1 mL). The organic layer was dried over Na<sub>2</sub>CO<sub>3</sub> and concentrated under reduced pressure to give **P2OZ** (34 mg).

The characterization of the formed polymers (**P2OZ**–**P5OZ**) is described in the ESI.

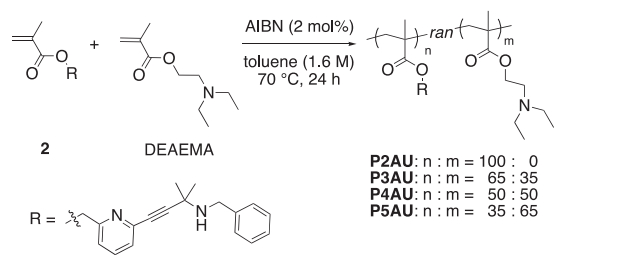
## Results and discussion

### Synthesis and characterization of the polymers

The main-chain type polypropargylamine **P1AU** was synthesized as described in the literature [9], namely, by the Sonogashira–Hagihara coupling of the AB-type monomer (**1**). The corresponding polymer was obtained at 71% yield (scheme S1). From the SEC result, the number average molecular weight ( $M_n$ ) and PDI of **P1AU** were estimated to be 38,600 and 2.21, respectively. The vinyl polymer **P2AU** was synthesized via the typical free-radical polymerization of the vinyl monomer with the

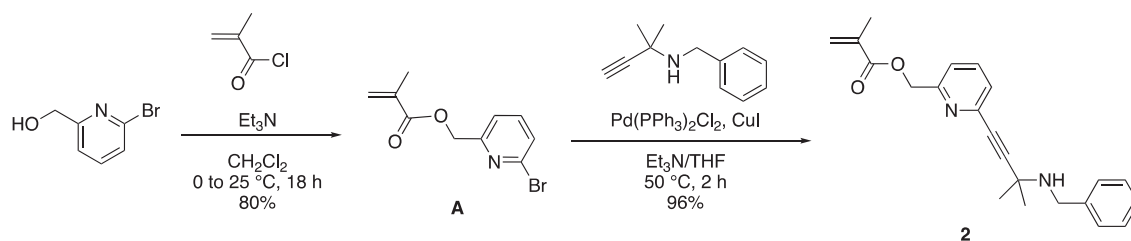
propargylamine moiety (**2**). The reaction was initiated by AIBN in toluene (Table 1). The preparation of **2** is described in Scheme 1. **P2AU** with a moderate  $M_n$  and PDI (15,500 and 2.71, respectively) was isolated by reprecipitation in *n*-hexane. All **P2AU** signals in <sup>1</sup>H NMR were assignable, indicating that the radical polymerization proceeded without damaging the propargylamine scaffold. The random copolymers **P3AU**–**P5AU** were prepared by varying the feed ratio of **2** and DEAEMA. Given the high CO<sub>2</sub>-capturing ability of its tertiary amine moiety [10, 11], the DEAEMA comonomer was expected to accelerate the rate of CO<sub>2</sub> fixation to the propargylamine moiety. The composition ratios of the comonomer in **P3AU** to **P5AU** almost coincided with the feed ratios based on the integral ratios in the <sup>1</sup>H NMR spectra, indicating similar polymerizability of these two monomers. The  $M_n$  and thermal properties of **P1AU**–**P5AU** are summarized in Table 2. Unexpectedly, the DSC measurements yielded almost identical  $T_g$  values for **P1AU** and **P2AU**. Each copolymer in the **P3AU**–**P5AU** series exhibited a single  $T_g$  peak, which shifted to the lower temperature side (33 → 24 → 0 °C) as the DEAEMA content increased. The  $T_g$  of a DEAEMA homopolymer prepared by the same procedure ( $M_n$  10,900, PDI 1.98) appeared at –22 °C (see ESI), so these results are entirely reasonable. No obvious melting peak was observed over the measurement range in all cases.

**Table 1** Synthesis of **P2AU**–**P5AU**



Code	Feed (%)		Yield (%) <sup>a</sup>	Composition (%) <sup>b</sup>		$M_n^c$	PDI <sup>c</sup>
	<b>2</b>	DEAEMA		<b>2</b>	DEAEMA		
<b>P2AU</b>	100	0	90	100	0	15,500	2.71
<b>P3AU</b>	65	35	87	65	35	15,200	2.83
<b>P4AU</b>	50	50	91	50	50	19,300	2.51
<b>P5AU</b>	35	65	61	33	67	18,200	2.33

<sup>a</sup>*n*-Hexane-insoluble part. <sup>b</sup>Determined by the <sup>1</sup>H NMR integration ratio. <sup>c</sup>Estimated by SEC (5 mM LiBr in DMF, PSt standards, detected by UV).



**Scheme 1** Synthesis of monomer **2**

### Solvent-free CO<sub>2</sub> fixation in **P1AU**

A **P1AU** film containing DBU (200 mol%) was prepared by the slow evaporation of CHCl<sub>3</sub> solution under a 0.1 MPa CO<sub>2</sub> atmosphere. At room temperature, which was tried initially, the reaction failed to complete even after prolonged reaction times (25% conversion in 288 h), in spite of the results in DMSO solution (100% conversion in 5 min) [9]. After raising the reaction temperature to 60 °C, which is slightly higher than the  $T_g$  of **P1AU**, the conversion rate was 90% after 120 h (Fig. 1). The decreased benzyl peaks of **P1AU** (b and c) and the appearance of double-bond peaks at ~5.8–6.2 ppm in the <sup>1</sup>H NMR spectra strongly suggest the formation of the oxazolidinone moiety **P1OZ**. The ratio of *Z*- to *E*-isomers (89:11) almost coincided with that of the solution reaction in DMSO.

**Table 2**  $M_n$  and thermal properties of polymers

Code	$M_n^a$	PDI <sup>a</sup>	$T_g$ (°C) <sup>b</sup>	$T_{d5}$ (°C) <sup>c</sup>
<b>P1AU</b>	38,600	2.21	41	260
<b>P1OZ</b>	8400	3.93	143	348
<b>P2AU</b>	15,500	2.71	42	250
<b>P2OZ</b>	18,300	2.71	106	302
<b>P3AU</b>	15,200	2.83	33	233
<b>P3OZ</b>	15,800	2.63	87	276
<b>P4AU</b>	19,300	2.51	24	249
<b>P4OZ</b>	20,800	2.61	73	275
<b>P5AU</b>	18,200	2.33	0	231
<b>P5OZ</b>	17,800	2.47	49	275

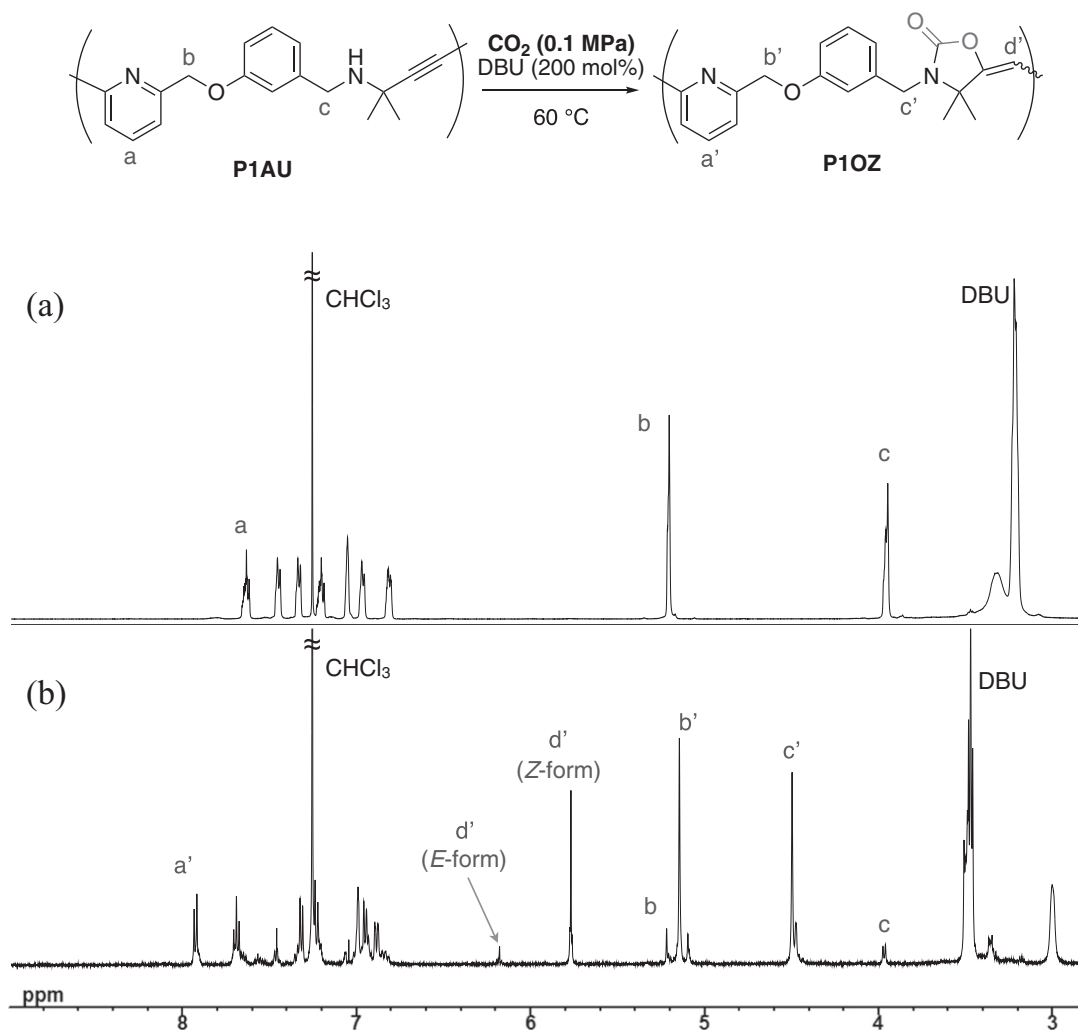
<sup>a</sup>Estimated by SEC (5 mM LiBr in DMF, PSt standards, detected by UV)

<sup>b</sup>Determined by DSC (2nd heating, heating rate at 10 °C/min, N<sub>2</sub> flow)

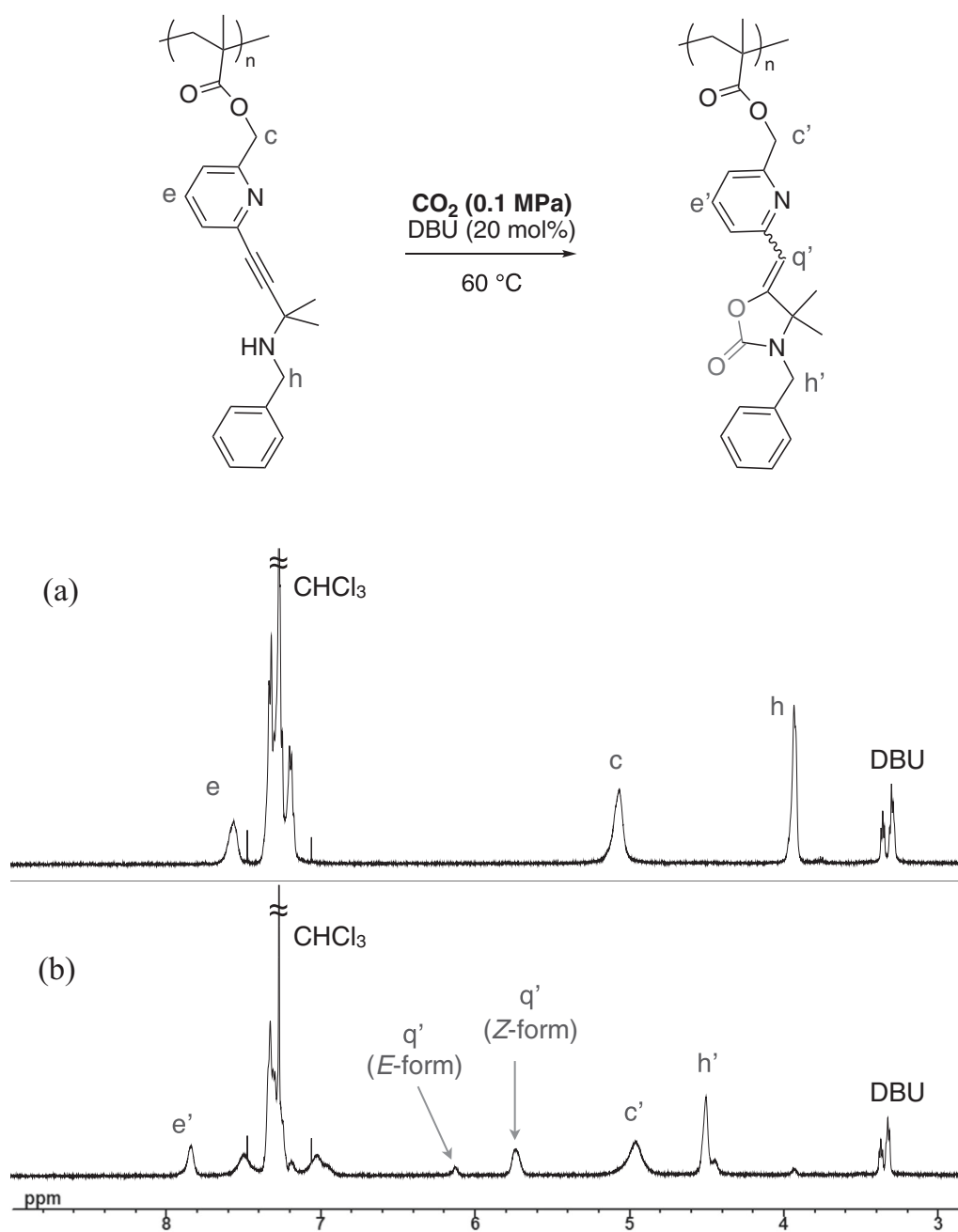
<sup>c</sup>Determined by TGA (heating rate at 10 °C/min, N<sub>2</sub> flow)

## Solvent-free CO<sub>2</sub> fixation in P2AU–P5AU

Each polymer film of the side-chain-type polymers **P2AU**–**P5AU** was prepared by removing CHCl<sub>3</sub> from a solution of mixed polymer and DBU in vacuo. Because self-standing films of this type are difficult to form, thin films were prepared on the flask wall. To fabricate homogeneous films, we also reduced the DBU content from 200 mol% to 20 mol%. Note that the  $T_g$  of **P2AU** decreased from 42 to –2 °C upon the addition of DBU, probably because DBU behaved as a plasticizer for the polymer. The CO<sub>2</sub>-fixation reaction at 60 °C transformed both the homopolymer **P2AU** and the copolymers **P3AU**–**P5AU** into their corresponding poly-oxazolidinones (**P2OZ**–**P5OZ**) at high conversion rates (Fig. 2 and ESI). Figure 3 shows the time-conversion curves, and Table 3 summarizes the results of the solvent-free CO<sub>2</sub>-fixation reaction. The reaction rate increased at higher DEAEMA compositions, as expected from its basic nature. Namely, the times to near-quantitative conversion



**Fig. 1** Partial <sup>1</sup>H NMR of **P1AU** (a) before and (b) after the solvent-free CO<sub>2</sub>-fixation reaction at 60 °C for 120 h (500 MHz, 298 K, CDCl<sub>3</sub>)



**Fig. 2** Partial <sup>1</sup>H NMR spectra of **P2AU** (a) before and (b) after the solvent-free CO<sub>2</sub>-fixation reaction at 60 °C for 22 h (500 MHz, 298 K, CDCl<sub>3</sub>)

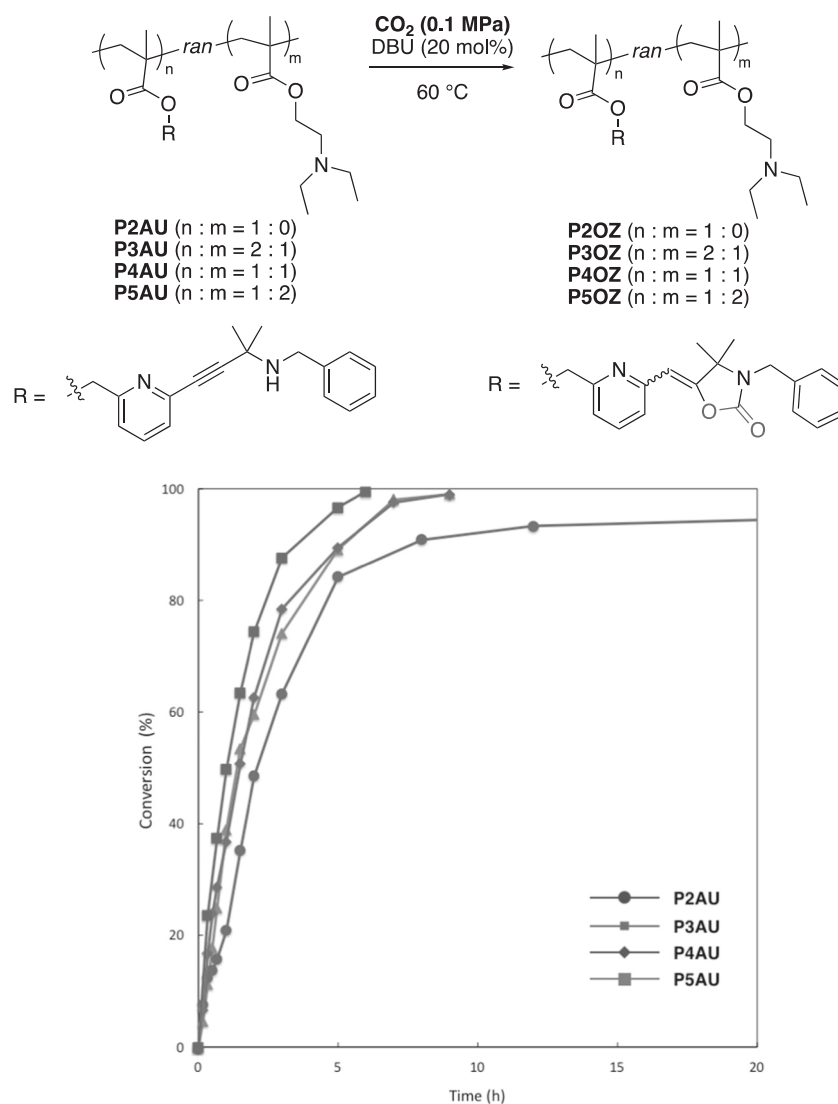
were shorter for **P3AU** (9 h), **P4AU** (9 h), and **P5AU** (6 h) than for **P2AU** (22 h). As shown in the time-conversion curve profile, **P2AU** did not reach full conversion even after a prolonged reaction time. Note that the CO<sub>2</sub> fixation in **P3AU–P5AU** did not proceed without DBU, indicating that the tertiary amine moiety of the DEAEMA unit could not catalyze the reaction alone. It can be concluded that the competitive effect of DBU and DEAEMA accelerated the CO<sub>2</sub> fixation even under solvent-free conditions. *Z*-isomers were preferentially formed in all cases. Because both the DBU contents and preparation procedures differed between

**P1AU** and **P2AU–P5AU**, comparing the isomer ratios among these polymers is of low significance, although **P1AU** gave the highest *Z*-isomer ratio. On the other hand, the *Z*-selectivities of **P2AU–P5AU** slightly decreased with increasing DEAEMA content for reasons that are unclear at present.

### Physical properties of the polymers

The *M<sub>n</sub>* of **P1OZ** was lower than that of **P1AU**, whereas **P2OZ–P5OZ** exhibited *M<sub>n</sub>* values similar to those of

**Fig. 3** Time-dependent curves of the CO<sub>2</sub>-fixation reactions of **P2AU–P5AU**



**Table 3** Results of solvent-free CO<sub>2</sub>-fixation of **P1AU–P5AU**<sup>a</sup>

Code	Time (h)	Conversion (%) <sup>a</sup>	Ratio (%) <sup>b</sup>	
			Z	E
<b>P1AU</b>	120	90	89	11
<b>P2AU</b>	22	94	87	13
<b>P3AU</b>	9	99	78	22
<b>P4AU</b>	9	99	74	26
<b>P5AU</b>	6	99	73	27

<sup>a</sup>DBU content: 200 mol% for **P1AU** and 20 mol% for **P2AU–P5AU**

<sup>b</sup>Determined by NMR

**P2AU–P5AU** (Table 2). The  $M_n$  values clearly depend on the position of the reactive group (SEC charts of the polymers are shown in the ESI). This phenomenon can be explained as follows. The formation of a cyclic structure

would shrink the main chain to some extent, decreasing the hydrodynamic volume of **P1OZ**, although main-chain scission cannot be ruled out. On the other hand, **P2OZ–P5OZ** were produced by modifying only the side chains of the vinyl polymer; the main chain was unchanged. Finally, the thermal stabilities of the polymers were investigated by TGA analysis. The  $T_{d5}$  values of **P1OZ–P5OZ** were higher than those of **P1AU–P5AU**, owing to the thermally stable oxazolidinone moiety formed in the former [12]. Notably, the  $T_{d5}$  values of the **P1OZ** and **P2OZ** homopolymers were 88 °C and 66 °C higher than those of **P1AU** and **P2AU**, respectively. Both the  $T_{d5}$  and  $T_g$  of **P1OZ–P5OZ** increased after CO<sub>2</sub> fixation, probably because the fixation increased the rigidity of the polymer structures. Consequently, the thermal stability was improved through the CO<sub>2</sub>-fixation reaction.

## Conclusion

We successfully performed solvent-free CO<sub>2</sub> fixation into polymers having 2-pyridyl group-substituted propargylamine moieties in the main and side chains. Achieving polymer reactions under such conditions is notoriously difficult. The reactivity of the polymer films was improved by the inclusion of the pendant tertiary amine moiety in the reaction. Additionally, the CO<sub>2</sub>-fixation reaction clearly enhanced the thermal stability of the polymers. Polymer resins hardened by the incorporation of CO<sub>2</sub> can be fabricated by applying similar propargylamine moiety-containing polymers to cross-linked systems [13]. As the polyoxazolidinone backbone can be regarded as a new class of polyurethane and is actually used for thermoplastic materials [14], further studies focusing on the functions of the polyoxazolidinones will provide novel polymer materials.

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## Compliance with ethical standards

**Conflict of interest** The authors declare that they have no conflict of interest.

## References

1. Scharfenberg M, Hilf J, Frey H. Functional polycarbonates from carbon dioxide tailored epoxide monomers: degradable materials and their application potential. *Adv Funct Mater.* 2018;28:1704302.
2. Luo M, Li Y, Zhang Y-Y, Zhang X-H. Using carbon dioxide and its sulfur analogues as monomers in polymer synthesis. *Polym (Guildf).* 2016;82:406–31.
3. Qin Y, Sheng X, Liu S, Ren G, Wang X, Wang F. Recent advances in carbon dioxide based copolymers. *J CO2 Util.* 2016; 11:3–9.
4. Maeda C, Miyazaki Y, Ema T. Recent progress in catalytic conversion of carbon dioxide. *Catal Sci Technol.* 2014;4:1482–97.
5. Ochiai B, Iwamoto T, Endo T. Selective gas-solid phase fixation of carbon dioxide into oxirane-containing polymers: synthesis of polymer bearing cyclic carbonate group. *Green Chem.* 2006;8: 138–40.
6. Ochiai B, Endo T. Carbon dioxide and carbon disulfide as resources for functional polymers. *Prog Polym Sci.* 2005;30: 183–215.
7. Ochiai B, Iwamoto T, Miyazaki K, Endo T. Efficient Gas-Solid Phase reaction of Atmospheric Carbon Dioxide into Copolymers with Pendant Oxirane Groups. Effect of comonomer component and catalyst on incorporation behavior. *Macromolecules.* 2005; 38:9939–43.
8. Kihara N, Endo T. Self-Catalyzed Carbon Dioxide Incorporation System. The reaction of copolymers bearing an epoxide and a quaternary ammonium group with carbon dioxide. *Macromolecules.* 1994;27:6239–44.
9. Kim N-K, Sogawa H, Yamaoto K, Hayashi Y, Kawauchi S, Takata T. DBU-Mediated highly efficient CO<sub>2</sub>-Fixation to propargylamines and polypropargylamine. *Chem Lett.* 2018;47: 1063–6.
10. Darabi A, Jessop PG, Cunningham MF. CO<sub>2</sub>-responsive polymeric materials: synthesis, self-assembly, and functional applications. *Chem Soc Rev.* 2016;45:4391–436.
11. Zhang Q, Zhu S. Oxygen and carbon dioxide dual responsive nanoaggregates of fluoro- and amino-containing copolymer. *ACS Macro Lett.* 2014;3:743–6.
12. Kordomenos PI, Kresta JE. Thermal Stability of Isocyanate-Based Polymers. 1. Kinetics of the thermal diisociation of urethane, oxazolidone, and isocynaurate groups. *Macromolecules.* 1981;14: 1434–7.
13. Adewole JK, Ahmad AL, Ismail S, Leo CP. Current challenges in membrane separation of CO<sub>2</sub> from natural gas. *Int J Greenh Gas Control.* 2013;17:46–65.
14. Li M, Xia J, Mao W, Yang X, Xu L, Huang X, Li S. Preparation and properties of castor oil-based dual cross-linked polymer networks with polyurethane and polyoxazolidinone structures. *ACS Sustain Chem Eng.* 2017;5:6883–93.