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Synthesis and Postfunctionalization of Acrylate-Appended Poly(cyclohexene carbonate)s: Modulation of Properties of CO_2-Based Polymers

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Cite This: *Macromolecules* 2025, 58, 1571−1577 Read Online

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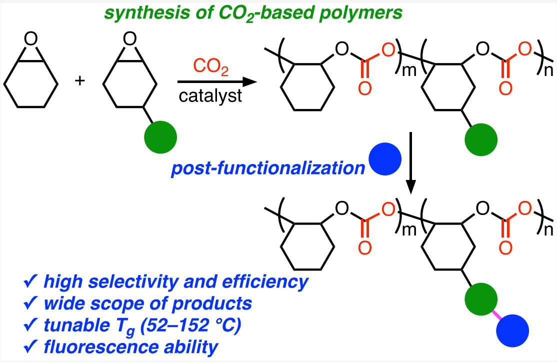
ABSTRACT: Functional CO_2-based polycarbonates are expected to be sustainable materials. Herein, a bifunctional aluminum porphyrin catalyzed the terpolymerization of cyclohexene oxide (CHO), acrylate-appended CHO, and CO_2 to provide poly(cyclohexene carbonate)s (PCHCs) with acrylate groups. Postfunctionalization of PCHCs via Michael addition or Heck reaction enabled the incorporation of thiol, amine, and aromatics into PCHCs with high selectivity and efficiency. PCHCs with the flexible long alkyl chains showed a glass-transition temperature (T_g) of down to 52 °C, which was much lower than that of PCHC (127 °C). In sharp contrast, PCHCs with rigid pyrenyl groups showed T_g values of up to 152 °C and fluorescence emission. Thus, a wide range of polymers were obtained by robust and sustainable synthetic methods, and the functional groups modulated the properties of the CO_2-based polycarbonates.



■ INTRODUCTION

A variety of CO_2-based materials have been developed to construct carbon-recycling systems.[1−12] Synthesis of polycarbonates from epoxides and CO_2 is one of the most ideal and sustainable technologies with one-step catalysis and high atom efficiency.[13−35] In particular, poly(cyclohexene carbonate)s (PCHCs), prepared from cyclohexene oxide (CHO) and CO_2, have attracted considerable attention because of the high CO_2 content (31 wt %) and good physical properties such as high glass-transition temperature and tensile strength. Recently, functional polycarbonates have been extensively synthesized via the copolymerization of well-designed epoxides and CO_2[36−38] or the terpolymerization using different comonomers[39−55] to provide CO_2-based polycarbonates with unique properties. When comonomers such as cyclic anhydrides or lactones are employed, however, the CO_2 contents of the terpolymers decrease with increasing amounts of the comonomers (Scheme 1a). On the other hand, postfunctionalization is an alternative method to obtain a variety of desired functional polymers without a significant decrease in the CO_2 content (Scheme 1b). For example, polycarbonates with alkenyl, alkynyl, formyl, and epoxide groups were synthesized, and late-stage functionalization was demonstrated.[56−67] However, it is still difficult to prepare rigid polycarbonates compared with flexible polycarbonates.

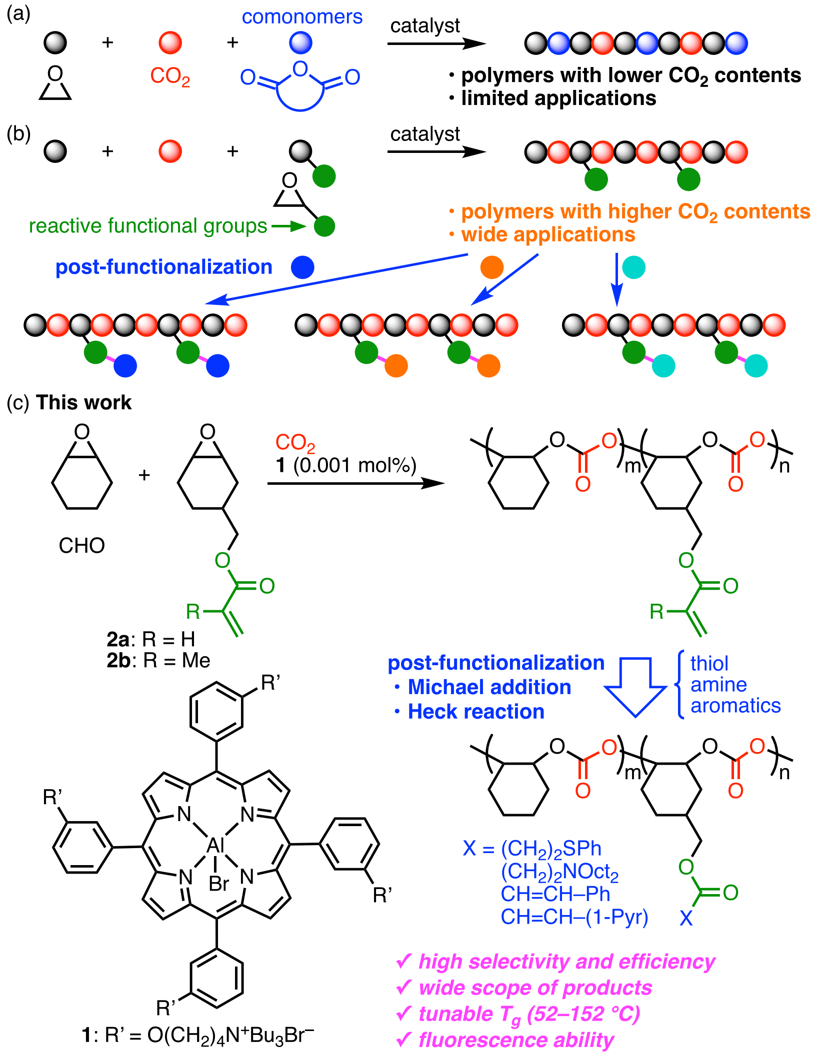
We have developed highly active bifunctional metalloporphyrin catalysts for the reactions of cyclic ethers with CO_2 to produce cyclic carbonates[68−72] and polycarbonates.[73−77] Bifunctional aluminum porphyrins catalyzed the copolymerization of CHO and CO_2 to give PCHC selectively.[73] Interestingly, the catalytic activity was dependent on the methylene chain length, and catalyst **1** with tetramethylene chains (Scheme 1c) was found to be the best catalyst, allowing for the synthesis of cross-linked PCHCs[75] and the terpolymerization with isocyanates or isothiocyanates.[76]

In this study, we synthesized acrylate-functionalized PCHCs and demonstrated late-stage functionalization of the acrylate groups (Scheme 1c). To the best of our knowledge, there are no reports on the synthesis of acrylate-functionalized PCHCs although acrylate-appended CHOs such as (3,4-epoxycyclohexyl)methyl acrylate (**2a**) and (3,4-epoxycyclohexyl)methyl methacrylate (**2b**) are commercially available. Although it seemed to be difficult to suppress side reactions of the reactive acrylate moieties, our highly active bifunctional catalyst **1** achieved terpolymerization quite selectively. Herein, we report the terpolymerization of CHO, acrylate-appended CHO **2**, and CO_2 using bifunctional aluminum porphyrin catalyst **1**. Postfunctionalization of the acrylate-functionalized PCHCs via the Michael addition or the Heck reaction allowed for the efficient incorporation of thiol,

Received: November 21, 2024
Revised: January 22, 2025
Accepted: January 28, 2025
Published: February 3, 2025

https://doi.org/10.1021/acs.macromol.4c02881
Macromolecules 2025, 58, 1571−1577

Scheme 1. (a) Terpolymerization of Epoxides, CO_2, and Comonomers; (b) Synthesis and Postfunctionalization of CO_2-Based Polycarbonates; (c) Synthesis and Postfunctionalization of Acrylate-Appended PCHCs



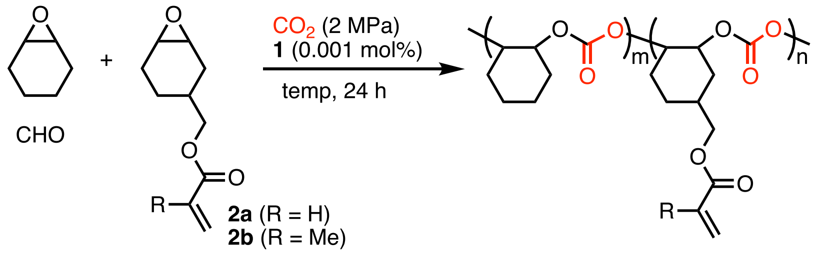
amine, and aromatics into PCHCs, and the functional PCHCs exhibited a glass-transition temperature (T_g) in the range of 52−152 °C and fluorescence emission.

■ RESULTS AND DISCUSSION

Initially, we conducted the terpolymerization of CHO, **2a** with the acrylate group, and CO_2 (2 MPa) at a ratio of 95000:5000:1 (CHO:**2a**:**1**) at 120 °C (Table 1, entry 1). The ^{1}H NMR spectrum of the reaction mixture suggested the formation of the terpolymers, while large amounts of insoluble polymers formed probably because polymerization of the acrylate moieties also occurred. Therefore, the terpolymerization was conducted at a lower temperature and proceeded well even at 80 °C, whereas the conversion was somewhat lower at 60 °C (entries 2−3).[78] When the ratio of **2a** to CHO was changed, the use of 0.3−2% of **2a** to CHO produced the terpolymers without any formation of insoluble products (entries 4−7).[79] Although insoluble products increased with an increase in the content of **2a**, the addition of 4-methoxyphenol (0.5 mol % of **2a**) as a radical scavenger allowed for the preparation of soluble terpolymers with the acrylate contents of 7−31% (entries 8−10). However, the molecular weight decreased with an increase in the amount of 4-methoxyphenol (entry 10). Therefore, we conducted the reaction at a ratio of 80:20 (CHO:**2a**) using 0.1 mol % 4-methoxyphenol at 70 °C (entries 11 and 12), which gave the terpolymers with the M_n of 45 kg/mol in 60% after 48 h (entry 12).[80] Methacrylate-appended CHO **2b** also underwent terpolymerization to furnish the methacrylate-appended PCHCs (entries 13−15 and Table S1 in the Supporting Information). PCHC was also obtained under otherwise identical reaction conditions (entry 16). It should be noted that cyclic carbonates were produced in less than 1% yield and that no ether linkages were observed, which indicated the high selectivity for the polycarbonate linkage formation.

The crude products were precipitated with $CHCl_3$/MeOH to obtain the purified terpolymers, which were characterized by means of NMR and IR spectroscopy (Supporting Information). The ^{1}H NMR spectrum of the polymer (Table 1, entry 8) confirmed the peaks for the acrylate moieties at 6.39, 6.11, and 5.82 ppm.[81] DOSY NMR spectrum showed a single diffusion coefficient (D) of 5.8×10^{-7} cm^2/s, indicating that both **2a** and CHO were incorporated into the same polymer chains. In addition, IR spectra confirmed new peaks at 3046 cm^{-1} for the unsaturated C−H stretching of the acrylate groups, 1711 cm^{-1} for the C═O stretching of the ester groups,

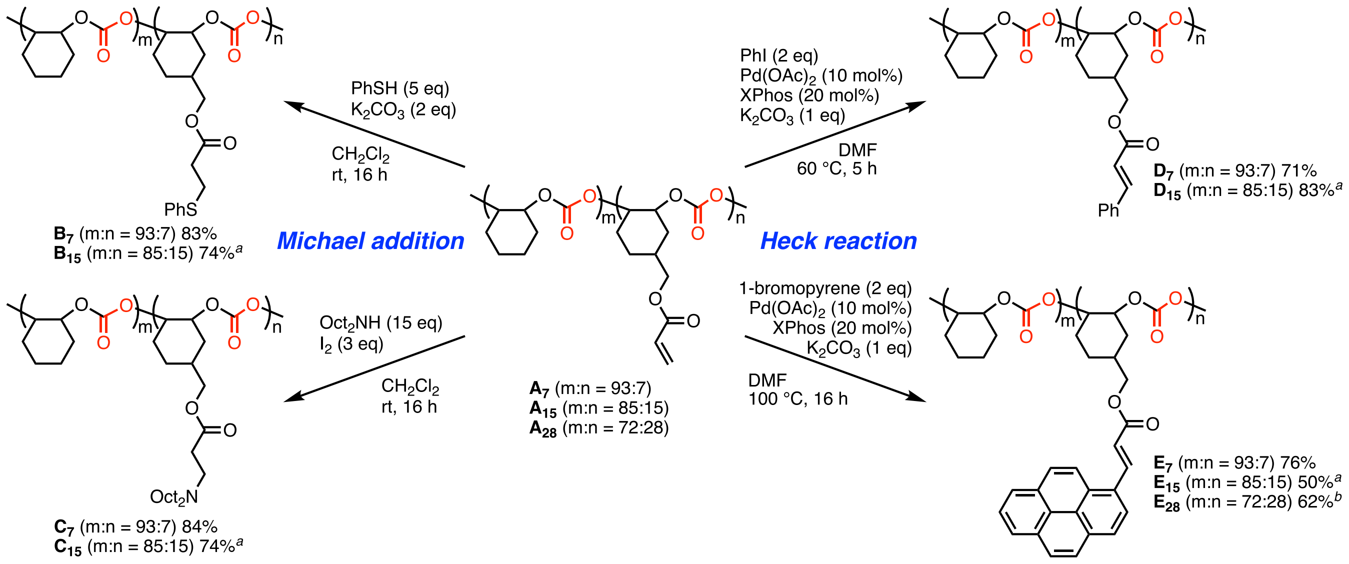
Table 1. Terpolymerization of CHO, 2, and CO_2 Using Bifunctional Aluminum Porphyrin Catalyst 1[a]



entry	2	CHO/2	temp. (°C)	conv. (%)[b,c]	yield (%) (m:n)[b,d]	M_n (kg/mol) (PDI)[e]
1[f]	**2a**	95/5	120	66	34 (95:5)	71/31 (1.2/1.0)
2[f]	**2a**	95/5	80	73	64 (94:6)	74/33 (1.1/1.0)
3	**2a**	95/5	60	29	29 (94:6)	38/18 (1.1/1.0)
4	**2a**	98/2	80	50	50 (97:3)	61/30 (1.0/1.0)
5	**2a**	99/1	80	64	64 (99:1)	54/26 (1.0/1.0)
6	**2a**	99.5/0.5	80	54	54 (99.2:0.8)	83/39 (1.1/1.0)
7	**2a**	99.7/0.3	80	53	53 (99.5:0.5)	83/38 (1.1/1.1)
8[g]	**2a**	95/5	80	55	55 (93:7)	66/31 (1.1/1.1)
9[g]	**2a**	90/10	80	55	55 (85:15)	51/22 (1.1/1.1)
10[g]	**2a**	80/20	80	52	52 (69:31)	28/14 (1.1/1.1)
11[h]	**2a**	80/20	70	40	39 (68:32)	49/23 (1.1/1.0)
12[h,i]	**2a**	80/20	70	60	60 (72:28)	45/21 (1.1/1.0)
13	**2b**	95/5	60	40	40 (94:6)	55/24 (1.1/1.0)
14[g]	**2b**	90/10	60	44	44 (85:15)	50/23 (1.0/1.0)
15[g]	**2b**	80/20	60	35	32 (70:30)	27/11 (1.1/1.0)
16		100/0	80	58	58 (100:0)	106/53 (1.0/1.0)

[a] Reaction conditions: CHO + **2** (20 mmol), **1** (0.2 μmol), CO_2 (2.0 MPa), 24 h, in a 30 mL stainless autoclave. [b] Determined by ^{1}H NMR spectroscopy using mesitylene as an internal standard. [c] Conversion based on the total amount of unreacted CHO and **2**. [d] Yields and ratios of the soluble polymers. [e] Determined by SEC analysis. [f] Insoluble polymers formed. The ratios of soluble to insoluble polymers were 52:48 (entry 1) and 88:12 (entry 2). [g] 4-Methoxyphenol (0.5 mol % of **2**) was used as a radical scavenger. [h] 4-Methoxyphenol (0.1 mol % of **2**) was used. [i] 48 h.

Scheme 2. Postfunctionalization of Acrylate-Appended PCHCs



[a] Gram-scale reactions. [b] $Pd(OAc)_2$ (20 mol %), XPhos (40 mol %), 90 °C.

and 1620 cm^{-1} for the C═C stretching, which are not seen in PCHC. The formation of the terpolymers was additionally confirmed by means of mass analysis. Electrospray ionization (ESI) mass spectra of the reaction mixture showed main peaks with both 142- and 226-mass intervals corresponding to the repeating units of PCHC and the acrylate-appended PCHC, respectively (Figure S2 in the Supporting Information). The terpolymers prepared from **2b** were also characterized by NMR and IR spectroscopy.

We then investigated the postfunctionalization of terpolymers **A_7** and **A_{15}** with acrylate contents of 7% and 15%, respectively (Table 1, entries 8 and 9). We found that the Michael addition with benzenethiol or dioctylamine efficiently proceeded to give the corresponding functional PCHCs

(Scheme 2, $\mathbf{B}_7$, $\mathbf{B}_{15}$, $\mathbf{C}_7$, and $\mathbf{C}_{15}$). On the other hand, the Heck reaction with aryl halides such as iodobenzene and 1-bromopyrene allowed the preparation of PCHCs $\mathbf{D}_7$, $\mathbf{D}_{15}$, $\mathbf{E}_7$, and $\mathbf{E}_{15}$ with the aryl-acrylate groups. These functionalized PCHCs were characterized by NMR and IR spectroscopy (Supporting Information). Importantly, the ^{1}H NMR spectra of the polymers confirmed the peaks for the pendant groups whose contents were almost unchanged from the acrylate content of the parent polymers $\mathbf{A}_7$ and $\mathbf{A}_{15}$, indicating the quantitative conversions of the postfunctionalizations. It should be noted that $\mathbf{A}_{15}$ contains ca. 40 acrylate groups in one polymer chain, almost all of which were converted into these functional groups.[82] We also confirmed that these postfunctionalizations took place on a gram-scale, and the purified samples were isolated in up to 83% yield.

Thermal properties of the functional PCHCs as well as PCHCs were investigated by means of thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurements (Table 2 and Figure 1). TGA profiles of PCHC showed a 50% weight loss temperature (T_{50}) of 316 °C, while these functional PCHCs showed higher T_{50} values than PCHC. The 5% weight loss temperatures (T_5) of functional PCHCs **B**, **D**, and **E** were 290−302 °C, which were also higher than that of PCHC (284 °C). On the other hand, **C7** and **C15** showed T_5 values of 255 and 278 °C, respectively, suggesting that the amino groups were somewhat thermally unstable. DSC measurements revealed that the glass-transition temperature (T_g) was highly dependent on the structure and content of the functional groups. PCHC showed a T_g of 127 °C, while polymers $\mathbf{B}_7$, $\mathbf{B}_{15}$, $\mathbf{C}_7$, and $\mathbf{C}_{15}$ with flexible aliphatic ester groups showed lower T_g values of 106, 95, 83, and 52 °C, respectively. Although polymers $\mathbf{D}_7$ and $\mathbf{D}_{15}$ with the phenyl acrylate groups showed somewhat lower T_g of 117 and 121 °C, respectively, polymers $\mathbf{E}_7$ and $\mathbf{E}_{15}$ with the rigid conjugated pyrenyl groups showed the T_g of 133 and 139 °C, respectively. The high T_g values encouraged us to prepare polymer $\mathbf{E}_{28}$ with the higher pyrenyl content of 28% from the corresponding acrylate-appended PCHC $\mathbf{A}_{28}$ (Table 1, entry 12). $\mathbf{E}_{28}$ showed an even higher T_g of 152 °C, which was one of the highest values for PCHC-based terpolymers.[83] Importantly, all of the polymers retain the CO_2 contents of over 20 wt %, and the present postfunctionalization is a useful method without the significant loss of the CO_2 contents.[84]

Table 2. Thermal Properties of Functional PCHCs

polymer	m:n	T_{50} (°C)[a]	T_5 (°C)[a]	T_g (°C)[b]	CO_2 content (wt %)
PCHC	100:0	316	284	127	31
$\mathbf{B}_7$	93:7	325	297	106	28
$\mathbf{B}_{15}$	85:15	327	302	95	26
$\mathbf{C}_7$	93:7	324	255	83	27
$\mathbf{C}_{15}$	85:15	324	278	52	23
$\mathbf{D}_7$	93:7	324	294	117	29
$\mathbf{D}_{15}$	85:15	323	295	121	27
$\mathbf{E}_7$	93:7	326	293	133	27
$\mathbf{E}_{15}$	85:15	332	299	139	24
$\mathbf{E}_{28}$	72:28	335	290	152	20

[a] Temperature at 50% decomposition (T_{50}) and 5% decomposition (T_5) determined by TGA. [b] Glass-transition temperature determined by DSC.

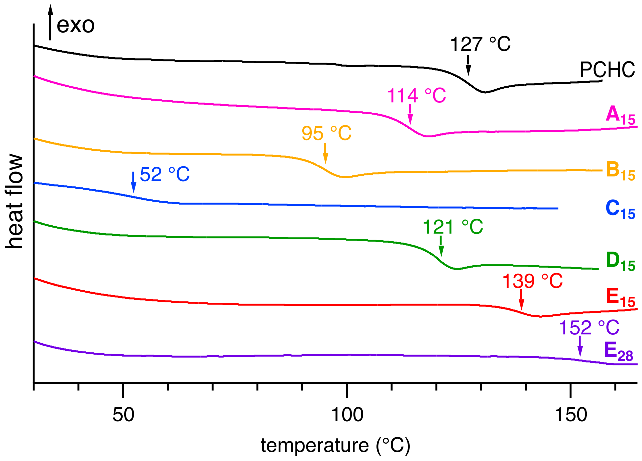


Figure 1. DSC Profiles of Functional PCHCs.

Finally, the photophysical properties of polymers $\mathbf{E}_7$, $\mathbf{E}_{15}$, and $\mathbf{E}_{28}$ containing pyrenyl groups were investigated along with ethyl (*E*)-3-(1-pyrenyl)acrylate (**3**) as a model compound (Figure 2). Both polymers and **3** showed absorption bands at 370 and 400 nm typical for pyrenyl groups, while only polymers showed weak bands at 450 nm. In addition, fluorescence spectra broadened with an increase in the pyrenyl contents, suggesting the intramolecular interaction of the pyrenyl groups in the polymers in the excited state. Thus, we tuned the photophysical and thermal properties by the functional groups.

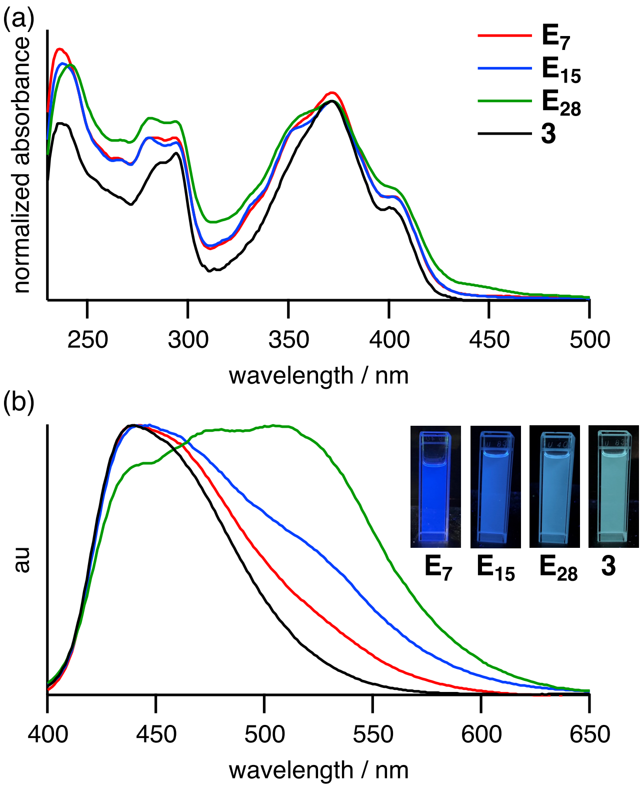


Figure 2. (a) UV/vis and (b) fluorescence spectra in CH_2Cl_2 (λ_{ex} = 365 nm). Photographs of CH_2Cl_2 solutions under black light (λ = 365 nm) are also shown.

■ CONCLUSIONS

In summary, we succeeded in the terpolymerization of CHO, acrylate-appended CHO **2**, and CO_2 using bifunctional aluminum porphyrin catalyst **1** (0.001 mol %). 0.5−32% of **2** was successfully incorporated into the terpolymers, as confirmed by NMR, IR, and mass spectroscopy. Postfunctionalization of the terpolymers was conducted via the Michael addition or the Heck reaction, and functional groups with both flexible and rigid frameworks were introduced with high selectivity and efficiency. The functional PCHCs with the flexible groups showed a lower T_g of down to 52 °C than PCHC (127 °C), while those with the rigid conjugated pyrenyl groups showed a higher T_g of up to 152 °C. Notably, we prepared a variety of functional PCHCs with different thermal properties from the same polymers containing the acrylate groups without the significant loss of the CO_2 contents, which demonstrated the usefulness and sustainability of the postfunctionalization. In addition, the Heck reaction allows facile introduction of aromatics, including fluorescence units. The functional PCHCs with pyrenyl groups also showed fluorescence dependent on the pyrenyl content, and the photophysical properties could also be tuned by the functional groups. Further investigation on the development of CO_2-based functional polycarbonates is currently investigated in our laboratory.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.macromol.4c02881.

Experimental procedures and compound data (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the Takahashi Industrial and Economic Research Foundation. The authors thank Dr. Y. Aoki and Ms. E. Sato (Mitsubishi Chemical Corporation) for the helpful discussion on terpolymerization.

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(78) The SEC charts at 60 and 80 °C showed a bimodal distribution, suggesting a chain transfer process, while that at 120 °C showed a multimodal distribution (Scheme S1 in Supporting Information). The molecular weights of the resultant polymers are lower than that of the theoretical values, which is due to the chain transfer process. The SEC charts of faster fractions in multimodal peaks suggests a production of cross-linked polycarbonates.

(79) The reactivity ratios of **2a** and CHO were determined by the Fineman−Ross plots to be 1.74 and 0.46, respectively (Figure S1 in Supporting Information).

(80) The time-course experiments revealed that the acrylate contents were somewhat higher at the shorter reaction times and that acrylate-appended CHO **2a** was slightly more reactive than CHO under the present terpolymerization conditions (Scheme S2 in Supporting Information). The methyl acrylate group might induce the reactive conformation of the cyclohexane ring of **2a**.

(81) The ^{1}H NMR spectra of the terpolymers confirmed only the repeating units of PCHC and the acrylate-appended PCHC, which indicated that the ester groups were inert under the terpolymerization.

(82) The postfunctionalization of the acrylate groups allows the Michael addition or the Heck reaction almost quantitively, which cannot be achieved with simple vinyl groups.

(83) PCHC derivatives showing the T_g of over 150 °C are quite rare, and only a few examples have been reported; poly(limonene) dicarbonate showed the T_g of 180 °C,[61] and cross-linked polymers with the T_g of 157−194 °C were obtained via the olefin cross-metathesis of vinyl functionalized PCHCs.[56]

(84) Terpolymerization of CHO, phthalic anhydride, and CO$_2$ produced poly(ester−carbonate)s showing the T_g of 135 °C, while the CO$_2$ content is only 10 wt%.[47]