



Polymeric aluminum porphyrin: Controllable synthesis of ultra-low molecular weight CO₂-based polyols

Chunwei Zhuo^a, Han Cao^a, Xiaoshen Wang^{a,b}, Shunjie Liu^{a,b,*}, Xianhong Wang^{a,b,*}

^a Key Laboratory of Polymer Ecomaterials, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, China

^b University of Science and Technology of China, Hefei 230026, China

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ABSTRACT

Carbon dioxide-based polyols with ultra-low molecular weight (ULMW, $M_n < 1000$ g/mol) are emergent polyurethane precursors with economic and environmental benefits. However, the lack of effective proton-tolerant catalytic systems limits the development of this field. In this work, the polymeric aluminum porphyrin catalyst (PAPC) system was applied to the copolymerization of CO₂ and propylene oxide, where sebacic acid, bisphenol A, poly(ethylene glycol), and water were used as chain transfer agents to achieve the controlled synthesis of CO₂-polyols. The molecular weight of the resulting CO₂-polyols could be facilely regulated in the range of 400–930 g/mol at low catalyst loadings, fully demonstrating its catalytic advantages of high activity, high product selectivity, and excellent proton tolerance of PAPC. Meanwhile, the catalytic efficiency of PAPC could reach up to 2.1–5.2 kg/g under organic CTA conditions, even reaching 1.9 kg/g using water as the CTA. The cPC content could be controlled within 1.0 wt% under the optimized conditions, indicating the excellent controllability of the PAPC system. ULMW CO₂-polyols combines the advantages of low viscosity (~3000 mPa s at 25 °C), low glass transition temperature (~-73 °C), and high carbonate unit content (~40%), which is important for the development of high-performance polyurethanes.

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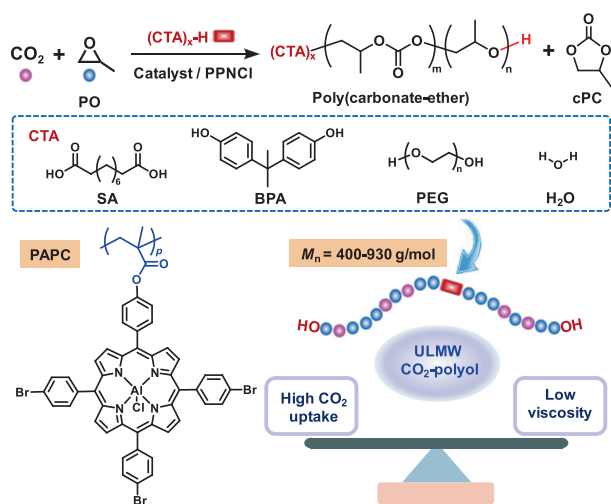
In recent years, CO₂-based polyols (CO₂-polyols) with low molecular weight ($M_n = 1000$ –6000 g/mol) derived from CO₂ and propylene oxide (PO) [1] has received increasing attention globally [2–9]. Compared with traditional polyether polyols, CO₂-polyols can reduce polyurethane production costs (10%–20%) [8] and greenhouse gas emissions (11%–19%) [3,10], which is in line with the Chinese green development goals of carbon peaking and carbon neutrality. Given the carbonate/ether coexisting structure of CO₂-polyols, the as-prepared polyurethanes have special properties [11–15] and important commercial value [7,16–18]. However, the viscosity and glass transition temperature (T_g) of CO₂-polyols increased significantly with the carbonate unit (CU) content in the chain structure. In particular, alternating CO₂-polyols (CU > 99%) prepared from SalenCo systems were solid at room temperature and had a T_g of >20 °C [19–23]. For the preparation of polyurethane foams, the high-viscosity CO₂-polyols suffer from low reaction efficiency, reduced mass transfer capability, and poor compatibility, which in turn adversely affects product performance

[7]. Therefore, it is important to develop high-performance CO₂-polyols with low viscosity, low T_g and high CU content (~40%).

Decreasing the molecular weight of the polyol is one of the effective solutions to decrease the viscosity [18,24]. Therefore, lowering the molecular weight, *i.e.*, controlled synthesis of CO₂-polyols with ultra-low molecular weight (ULMW, $M_n = 500$ –1000 g/mol), should be an effective strategy to improve its viscosity while maintaining high CO₂ insertion. CO₂-polyols were prepared through the immortal copolymerization of CO₂ and PO using a catalyst and a chain transfer agent (CTA) containing active hydrogen. According to the mechanism, the high loading of CTA is necessary for the controlled synthesis of ULMW CO₂-polyols, which poses a great challenge to the proton tolerance of the catalytic system. The representative zinc–cobalt double metal cyanide (DMC) catalyst suffers from the formation of dominated cyclic propylene carbonate (cPC) by-products under high loading of CTA [25–27]. For example, Wang *et al.* reported that DMC-initiated CO₂/PO copolymerization could not occur at a PO:CTA molar ratio of (5–10):1 (target $M_n < 1200$ g/mol) [28]. Alternatively, the well-defined homogeneous bifunctional SalenCo(III)X and cobalt(III)–potassium(I) heteronuclear bimetallic catalytic systems relied on restricting monomer conversion (<30%) to afford CO₂-polyols with low M_n (1300 g/mol) [29,30]. Therefore, it remains challenging to develop

* Corresponding authors at: Key Laboratory of Polymer Ecomaterials, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, China.

E-mail addresses: sjliu@ciac.ac.cn (S. Liu), xhwang@ciac.ac.cn (X. Wang).



Scheme 1. The schematic illustration of the synthetic route to ULMW CO₂-polyols using PAPC as the catalyst and protic compounds as CTAs.

efficient catalytic systems with high proton tolerance to the controllable synthesis of ULMW CO₂-polyols.

The cooperative effect between catalyst active units is considered a key element to promote the efficiency of CO₂/PO copolymerization, which has led to the recent development of binary and bifunctional systems [20,31–38]. In 2019, Wang *et al.* proposed the concept of polymeric catalyst design based on an in-depth understanding of the cooperative catalytic mechanism, *i.e.*, polymerizing mono-molecular aluminum porphyrin into aluminum porphyrin polymers [39]. The resulting polymeric aluminum porphyrin catalyst (PAPC) maintained high catalytic activity and product selectivity (>99%) at dilute conditions ([PO]:[Al]=100,000) due to the multicenter cooperative effect of the side-group porphyrin units derived from the spatial constraints of the polymeric backbone. The synthesized copolymers had a carbonate/ether coexisting chain structure and the CU could be adjusted in the range of 30%–70% [39–41]. In 2021, Cao *et al.* prepared itaconic acid-based diols using polymeric aluminum porphyrin, which showed great application potential in the controlled synthesis of CO₂-polyols [9].

Herein, we reported the synthesis of ULMW CO₂-polyols using PAPC as the catalyst and protic compounds such as sebacic acid (SA), bisphenol A (BPA), polyethylene glycol (PEG-200), and water (H₂O) as CTAs (Scheme 1). The molecular weight of the resulting CO₂-polyols could be facilely regulated in the range of 400–930 g/mol, fully demonstrating catalytic advantages of high activity, high product selectivity, and excellent proton tolerance of PAPC. Meanwhile, the catalytic efficiency of PAPC could reach up to 2.1–5.2 kg/g under organic CTA conditions, even reaching 1.9 kg/g using water as the CTA. The cPC content could be controlled within 1.0 wt% under the optimized conditions, indicating the excellent controllability of the PAPC system. This study provides an efficient catalytic system with high proton tolerance for the controllable synthesis of ULMW CO₂-polyols.

Catalysts are the core driving force for chemical reactions. To achieve the controlled synthesis of ULMW CO₂-polyols, PAPC was used as the catalyst in this work. PAPC is mainly characterized by the introduction of porphyrin ligands modified with bromine substituents and short linkage chains between the porphyrin active unit and the main chain (Scheme 1). The characterization results reveal the well-defined polymer structure of PAPC (Figs. S1–S8 in Supporting information), with a main-chain polymerization degree (*p*) of about 12. PAPC is an ideal catalytic system for the controllable synthesis of CO₂-polyols, with the advantages

of high activity and high selectivity for CO₂/PO copolymerization. The poly (carbonate-ether) prepared by PAPC has an adjustable molecular weight with a narrow distribution. Oligomeric diols with a well-defined linear structure are conventional and highly demanded polyol species in the polyurethane industry. In this study, protonic compounds such as SA, BPA, PEG-200 and H₂O were used as the CTAs. ULMW diols were efficiently and controllably synthesized under different CO₂/PO copolymerization conditions (Table 1).

Given that PAPC can maintain high catalytic performance at low catalyst concentrations, the catalyst loading was first set at a [PO]:[Al] molar ratio of 50,000:1, and an equimolar amount of bis(triphenylorthophosphino)ammonium chloride (PPNCl) was used as the co-catalyst ([PAPC]:[PPNCl]=1:1). As shown in entry 1, the PO conversion was above 99% and the turnover frequency (TOF) reached 4200 h⁻¹ at 80 °C, 4.0 MPa, and [PO]:[SA]=10:1 after 12 h, while the catalytic efficiency reached 4.7 kg/g when calculated as the mass of polymer synthesized per gram of catalyst ($m_{\text{polyol}}/m_{\text{PAPC}}$). PAPC efficiently synthesized CO₂-polyols with M_n of 760 g/mol ($\mathcal{D}=1.07$), similar to the theoretical molecular weight ($M_{n,\text{theo}}=880$ g/mol), exhibiting good controllability in polymerization. It is normally observed that the polymer selectivity decreases with an increase in protic CTA loading [19,31]. It is worth mentioning that PAPC still had excellent product selectivity with only 2.5 wt% of cPC. Meanwhile, CO₂-polyols, with a CU content of 28% is a typical poly(carbonate-ether). PAPC was also effective in the preparation of CO₂-polyols without PPNCl, with a TOF of 3500 h⁻¹ (Table 1, entry 2), indicating the strong intermolecular cooperative effect of the polymeric catalytic system. However, the selectivity was significantly lower, with a W_{polyol} of 93.7% and CU content of 16.5%. In sharp contrast, mono-molecular aluminum porphyrin (Mono-Al, Figs. S9–S13 in Supporting information) could not initiate the copolymerization at the same SA loading (Table S1 in Supporting information, entry 1). Similarly, the DMC catalyst could not effectively catalyze CO₂/PO copolymerization due to the blunting effect of high-loading SA on the active center. Moreover, the polymerization reaction was uncontrolled due to explosive polymerization when increasing the amount of DMC (Table S1, entries 2 and 3). Altogether, the above results demonstrated the excellent proton tolerance of PAPC, which is particularly suitable for the synthesis of ULMW CO₂-polyols.

The effect of reaction conditions (temperature, pressure, CTA ratio, *etc.*) on the CO₂/PO copolymerization was further investigated. It is strange that the TOF of PAPC at 100 °C (4300 h⁻¹) was similar to that at 80 °C (4200 h⁻¹), possibly owing to the interference of high-loading CTA (Table 1, entry 3). In addition, CO₂-polyols with a CU content of 34.6% and a M_n of 730 g/mol was prepared by increasing the pressure to 6.0 MPa (Table 1, entry 4), demonstrating a positive CO₂ pressure effect. At a relatively low temperature of 60 °C, PAPC still maintained high activity with a TOF value and catalytic efficiency of 2460 h⁻¹ and 4.6 kg/g, respectively, producing CO₂-polyols with a M_n of 690 g/mol (Table 1, entry 5). The W_{polyol} and CU content were 99.5% and 38.1%, indicating an excellent control on polymerization. On the other hand, the loading of CTA is a key factor in controlling the molecular weight and is a criterion used to measure the proton tolerance of the catalyst. By controlling the [PO]:[SA] molar feeding ratio between 6:1 and 12:1, the precise control of M_n in the range of 520–850 g/mol with narrow molecular weight distributions ($\mathcal{D}\sim 1.07$) was achieved, indicating the excellent proton tolerance of PAPC (Table 1, entries 5–8). In addition, the loading of CTA can hardly affect the activity and selectivity of the catalyst, giving 4.6–5.2 kg/g catalytic efficiency, >99% product selectivity, and ~40% CU content (Figs. 1a and b). The relation between the [PO]:[SA] molar ratio to M_n showed a good linear fit with a correlation coefficient of $R^2=0.99$ based on the *pseudo*-living polymerization characteristics (Fig. 1c).

Table 1
Controlled Synthesis of ULMW CO₂-polyols using PAPC^a.

Entry	CTA	[PO]/[Al]/[PPNCl] ^b	[PO]/[CTA] ^b	T (°C)	t (h)	P (MPa)	Conv. ^c (%)	TOF ^d (h ⁻¹)	W _{polyol} ^e (wt%)	CU ^f (%)	M _{n-theo} ^g (g/mol)	M _{n-GPC} ^h (g/mol)	D ^h	Productivity ⁱ (kg/g)
1	SA	50,000/1/1	10	80	12	4.0	99	4200	97.5	28.0	880	760	1.07	4.7
2 ^j	SA	50,000/1/1	10	80	12	4.0	85	3500	93.7	16.5	730	640	1.07	4.0
3	SA	50,000/1/1	10	100	10	4.0	86	4300	91.0	22.0	750	660	1.09	4.0
4	SA	50,000/1/1	10	80	14	6.0	94	3370	96.4	34.6	870	730	1.06	4.7
5	SA	50,000/1/1	10	60	18	6.0	89	2460	99.5	38.1	860	720	1.07	4.6
6	SA	50,000/1/1	12	60	18	6.0	94	2610	99.3	41.3	1050	850	1.08	4.7
7	SA	50,000/1/1	8	60	26	6.0	88	1680	99.0	38.0	720	620	1.07	4.9
8	SA	50,000/1/1	6	60	26	6.0	82	1580	99.1	37.1	560	520	1.06	5.2
9	BPA	50,000/1/1	10	60	26	6.0	64	1220	99.1	33.3	680	590	1.09	3.6
10	BPA	50,000/1/1	6	60	26	6.0	71	1360	98.9	35.3	530	400	1.09	4.7
11 ^k	PEG	20,000/1/1	10	60	10	6.0	98	1950	99.0	53.1	980	930	1.13	2.1
12 ^k	PEG	20,000/1/1	6	60	10	6.0	88	1760	98.2	62.5	640	610	1.10	2.4
13	H ₂ O	20,000/1/1	15	60	10	6.0	91	1820	99.2	45.1	1070	870	1.12	1.8
14	H ₂ O	20,000/1/1	10	60	20	6.0	89	890	98.4	50.6	720	600	1.10	1.9

^a The polymerization reactions were carried out in a 75 mL autoclave with 40 mL PO in bulk using bis(triphenylphosphine)iminium chloride (PPNCl) as the co-catalyst, unless otherwise specifically noted.

^b Molar ratio.

^c Epoxide conversion, determined by ¹H NMR analysis of crude reaction mixture.

^d Turnover frequency, calculated by (mol PO conv.)/(mol Al × h).

^e The weight percentage of cPC, determined by ¹H NMR analysis.

^f The molar percentage of carbonate units (CU) in polyols, determined by ¹H NMR analysis.

^g Calculated from PO/CTA, PO conversion, W_{polyol} and CU.

^h Determined by gel permeation chromatography in CH₂Cl₂ at 35 °C, calibrated with polyethylene glycol standards.

ⁱ The mass of CO₂-polyols produced per gram of catalyst, calculated by m_{polyol}/m_{PAPC}.

^j The polymerization was carried out without PPNCl.

^k The CU% was an estimate due to the overlap of the characteristic peaks of PEG and polyether.

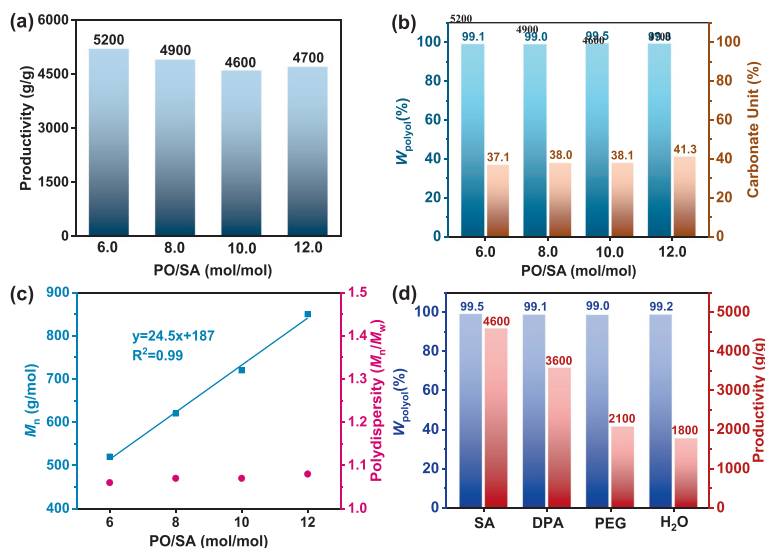


Fig. 1. Catalytic performance for ULMW CO₂-polyols. Control of (a) productivity, (b) selectivity, and (c) molecular weight by the feed ratio of PO/SA (Table 1, entries 5–8). (d) Comparing the catalytic performance of PAPC for CO₂/PO copolymerization using different CTAs (Table 1, entries 5, 9, 11 and 13).

The pervasiveness of CTA is another important criterion for catalyst proton tolerance. We then carried out the copolymerization of CO₂/PO using four types of hydroxyl-containing compounds: organic carboxylic acids, phenols, oligomers, and water. Existing catalytic systems (e.g., DMC) typically exhibit varying degrees of reduced activity and selectivity under hydroxyl-typed CTAs (strong coordination to metal center). In contrast, PAPC displayed excellent CTA pervasiveness, achieving the efficient and controllable synthesis of ULMW CO₂-polyols using BPA, PEG, or H₂O. As shown in entries 9 and 10, the highest loading of CTA/PCPA reached 8300:1, effectively synthesizing 400–590 g/mol of CO₂-polyols with high product selectivity (99%) using phenolic hydroxyl BPA as the CTA. Although the TOF value (~1300 h⁻¹) decreased by ~20% compared to that of SA, the catalytic efficiency remained at 3.6–4.7 kg/g. When PEG (M_n ~200 g/mol) was used as the CTA,

the nearly quantitative conversion of PO was achieved within 10 h, while the cPC content was controlled within 1.0 wt% under [PO]:[CTA]:[Al] = 20,000:1, 600:1. Increasing the amount of PEG (PO:PEG = 6:1) resulted in a slight decrease of PO conversion, while the M_n could be controlled in the range of 610–930 g/mol with high efficiency of 2.1–2.4 kg/g (Table 1, entries 11 and 12). Water is a natural and efficient CTA but can significantly deactivate the catalytic center [40]. As shown in entries 14 and 15, PAPC could stably provide CO₂-polyols with M_n of 600–870 g/mol under high loading amounts of H₂O and very low catalyst concentrations (PO:H₂O = 10–15:1; PO:Al = 20,000:1). The PO conversion reached 90%, while the CTA loading (H₂O: Al) was as high as 1942. The above experiments demonstrated excellent proton tolerance, high loading capacity, and a wide CTA range for PAPC. In general, PAPC could synthesize ULMW CO₂-polyols with 1.8–5.2 kg/g produc-

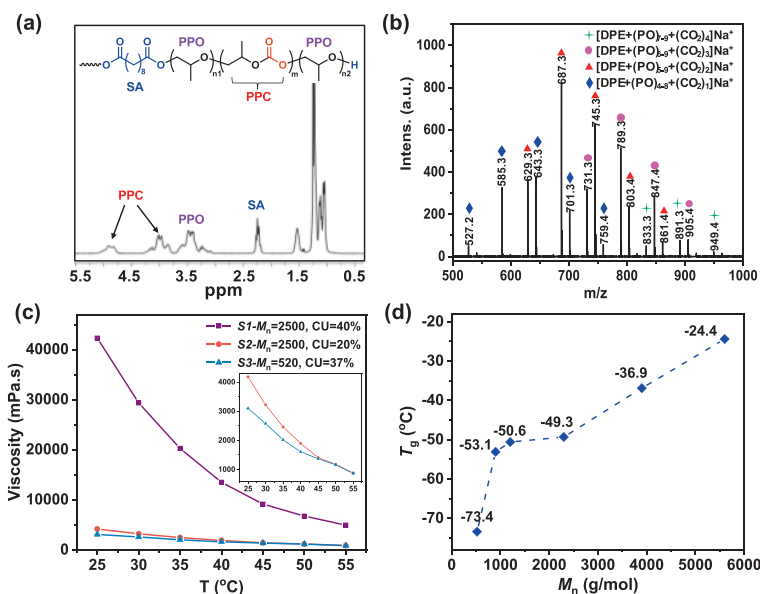


Fig. 2. Chemical structure and properties of ULMW CO₂-polyols. (a) ¹H NMR spectrum of SA-based CO₂-polyols in CDCl₃ (Table 1, entry 5). (b) MALDI-TOF-MS spectrum of BPA-based CO₂-polyols (Table 1, entry 9). (c) The plots of viscosity with temperature of three samples (Table S1, entries 4 and 5; Table 1, entry 8): S1 ($M_n = 2300$ g/mol, CU = 40%), S2 ($M_n = 2300$ g/mol, CU = 20%), and S3 ($M_n = 520$ g/mol, CU = 37%). (d) The plot of T_g with CO₂-polyols (CU ~40%), which the M_n were 520, 850, 1100, 2300, 3400, and 5600 g/mol (Table 1, entry 8; Table S1, entries 4 and 6–9).

tivity and 99% product selectivity under different CTA conditions (Fig. 1d).

The accurate characterization of the structure and properties of ULMW CO₂-polyols are of vital importance. The characteristic chemical shifts of the ¹H NMR spectra confirmed the successful insertion of different CTAs into the carbonate/ether chain structure of CO₂-polyols (Fig. 2a and Figs. S14–S17 in Supporting information). The matrix-assisted laser desorption/ionization time-of-flight mass spectrometry characterization (MALDI-TOF-MS) results further confirmed that the end-chain structure of the CO₂-polyols were all hydroxyl groups (Fig. 2b and Figs. S18–S21 in Supporting information). Although there are chloride ions that undergo chain initiation in the PAPC system, the mono-hydroxyl polymerization initiated by chlorine atoms is negligible due to the drastically higher content of CTA (>1000-fold). Meanwhile, we focused on the effect of M_n on viscosity and T_g . The viscosities of three representative samples, S1 ($M_n = 2300$ g/mol, CU = 40%), S2 ($M_n = 2300$ g/mol, CU = 20%), and S3 ($M_n = 520$ g/mol, CU = 37%), were determined (Table S1, entries 4 and 5; Table 1, entry 8). As shown in Fig. 2c, S1 displayed a viscosity of 41,750 mPa s at 25 °C while 4640 mPa s at 55 °C. S2 with reduced CO₂ insertion had good flowability at room temperature, showing a much lower viscosity of 4270 mPa s. The viscosity of S3 with an ultra-low molecular weight (3100 mPa s at 25 °C) was even lower than that of S2 while maintaining the CO₂ insertion amount, exhibiting low viscoelasticity similar to that of polyether polyols. Low viscosity is important for improving reaction efficiency, enhancing mass transfer, and improving compatibility in polyurethane synthesis, reflecting the good practicality of ULMW CO₂-polyols. In addition, T_g decreased with the molecular weight (Fig. 2d). Notably, when M_n decreased from 850 g/mol to 520 g/mol, T_g decreased sharply from –53.1 °C to –73.4 °C, which was far lower than the thermal performance of conventional CO₂-polyols. In conclusion, ULMW CO₂-polyols is a novel polyurethane precursor with low viscosity, low T_g and short chain structure. The prepared polyurethane is expected to have excellent mechanical strength and high temperature resistance, which will be the focus of subsequent work.

In conclusion, using PAPC as the catalyst and four structurally different carboxylic acids/alcohols (SA, DPA, PEG and H₂O) as

CTAs, the efficient and controlled synthesis of CO₂-polyols with ultra-low molecular weight was achieved, fully demonstrating the excellent proton tolerance of the polymeric catalyst system. The catalytic efficiency of PAPC exceeded 2.1 kg/g under different organic CTAs, even reaching 1.9 kg/g with water as the CTA, efficiently preparing CO₂-polyols with M_n of 400–930 g/mol. Among them, the productivity of PAPC reached 5.2 kg/g with high product selectivity (cPC = 0.9 wt%) for the SA-based diols. In addition, the selectivity was not affected by the loading amount or type of CTA and the cPC content was controlled within 1.0 wt% under the optimized conditions, demonstrating the excellent controllability of the PAPC system. ULMW CO₂-polyols have similar viscoelasticity to polyether polyols, with material properties of low viscosity (~3000 mPa s at 25 °C), low T_g (~–73 °C), and high CU content (~40%). The polymeric aluminum porphyrin system and ULMW CO₂-polyols reported in this study will provide new impetus for the development of CO₂-based polyurethanes.

Declaration of competing interest

The authors declare no competing financial interest.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.ccl.2022.108011.

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