Polymer Chemistry

ROYAL SOCIETY OF CHEMISTRY

COMMUNICATION

View Article Online
View Journal | View Issue

Cite this: *Polym. Chem.*, 2020, **11**, 4699

Received 12th June 2020,
Accepted 12th July 2020

DOI: 10.1039/d0py00850h

rsc.li/polymers

Synthesis of terpyridine-containing polycarbonates with post polymerization providing water-soluble and micellar polymers and their metal complexes†

Gulzar A. Bhat, ‡ Ahmed Z. Rashad‡ and Donald J. Darensbourg *

Carbon dioxide based polymers synthesized from the metal-catalyzed copolymeriation of epoxides and CO_2 containing the terpyridine ligand as an end group are reported. The strategy used was to carry out the polymerization in the presence of a carboxylic acid derivative of terpyridine, 4′-(4-carboxyphenyl)-2,2′:6′,2″-terpyridine (HL), as a chain transfer agent. The epoxide monomer possessing a vinyl substituent, allyl glycidyl ether (AGE), was copolymerized with CO_2 employing a (salen)Co(III) catalyst to afford a polycarbonate which upon the addition of mercaptoacetic acid across the double bond, followed by deprotonation, yielded a water soluble polymer. In a similar manner, the sequential formation of a diblock terpolymer produced from propylene oxide, AGE, and CO_2 provided a amphiphilic polycarbonate which self-assembled upon addition to water to form micelle nanostructures. The molecular weights of these CO_2-derived polycarbonates were shown to be easily controlled by the quantity of chain transfer agent used. These polymeric ligands were demonstrated to provide a modular design for synthesizing a wide variety of metal complexes as illustrated herein for zinc and platinum derivatives.

Introduction

The strong π-acceptor ligand, 2,2′:6′,2″-terpyridine (terpy), has been widely used to generate transition and rare earth metal complexes ranging from discrete to polymeric species.[1–6] These metal complexes have applications in numerous areas, including materials science (*e.g.* photovoltaics and optoelectronics),[7–9] biomedicinal chemistry (*e.g.* DNA intercalation and biomemitics),[10–13] and catalysis, inclusive of organometallic catalysis, organo-catalysis, and photocatalysis.[6,14,15] Terpyridine metal complexes have also been employed in artificial photosynthesis (water splitting),[16] and as photosensitizers in dye-sensitized solar cells (DSSCs) due to their rich intrinsic photophysical properties.[3,11,17] Pendant terpyridine ligands have also been introduced into polymers to achieve characteristic applications.[18–20] Various approaches have been utilized to conjugate the terpyridine moieties into polymeric materials.[21,22] These include, controlled radical polymerization processes such as nitroxide-mediated radical polymerization (NMP) and reversible addition–fragmentation chain transfer polymerization (RAFT). Using these pathways it has been possible to prepare polymers with controlled molecular weights and molar percentage of terpy ligands in the polymers.[23] By way of contrast, controlled radical polymerization *viz* atom transfer radical polymerization (ATRP) was unsuccessful at incorporating terpy into polymer chains due to competing complexation of catalyst by the terpy groups.[24]

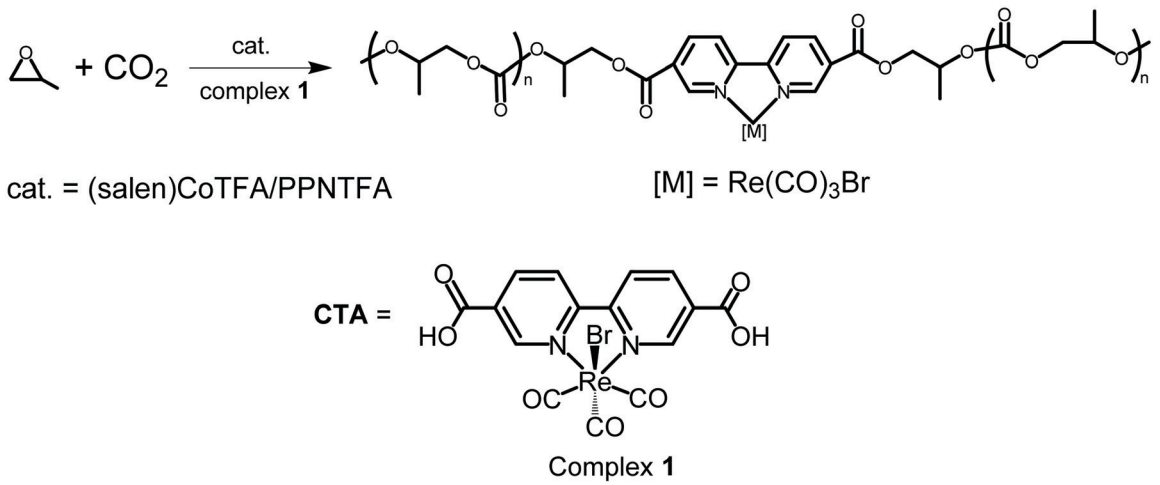
Recently, we have reported an alternative polymerization process for introducing a single ligand or its metal complex into the backbone or end-group of a polycarbonate or polymonothiocarbonate.[25,26] In this procedure, we employed an immortal polymerization pathway involving CO_2 or COS and epoxides in presence of the desired ligand or its metal complex serving as the chain-transfer agant (CTA). Thusfar, we have used mono- or bifunctional alcoholic or carboxylic acid as CTAs to synthesize di (AB)- or tri (ABA)-block copolymers, where the ligand or metal complex is contained in the B block. This process is illustrated in Scheme 1 with the commonly employed dicarboxylic acid functionalized metal complex as chain-transfer agent.

In this report we have copolymerized CO_2 with allyl glycidyl ether (AGE) using this approach in the presence of a terpyridine derived chain-transfer agent to synthesize polycarbonates with terpyridine end groups. Furthermore, upon employing thiol–ene click chemistry to functionalize the vinyl substituents of AGE with mercaptoacetic acid, these polycarbonates could be made water soluble. Additionally in a one-pot, two step process, triblock terpolymers of propylene oxide, AGE, and CO_2 were prepared which upon functionalization with carboxylic acid thiols afforded amphiphilic polycarbonates. These

Department of Chemistry, Texas A&M University, College Station, Texas 77843, USA. E-mail: djdarens@chem.tamu.edu

†Electronic supplementary information (ESI) available: Experimental details, including all synthesis and characterization data, *i.e.*, ^{1}H and ^{13}C NMR spectra. See DOI: 10.1039/d0py00850h

‡GAB and AZR contribute equally for this work.

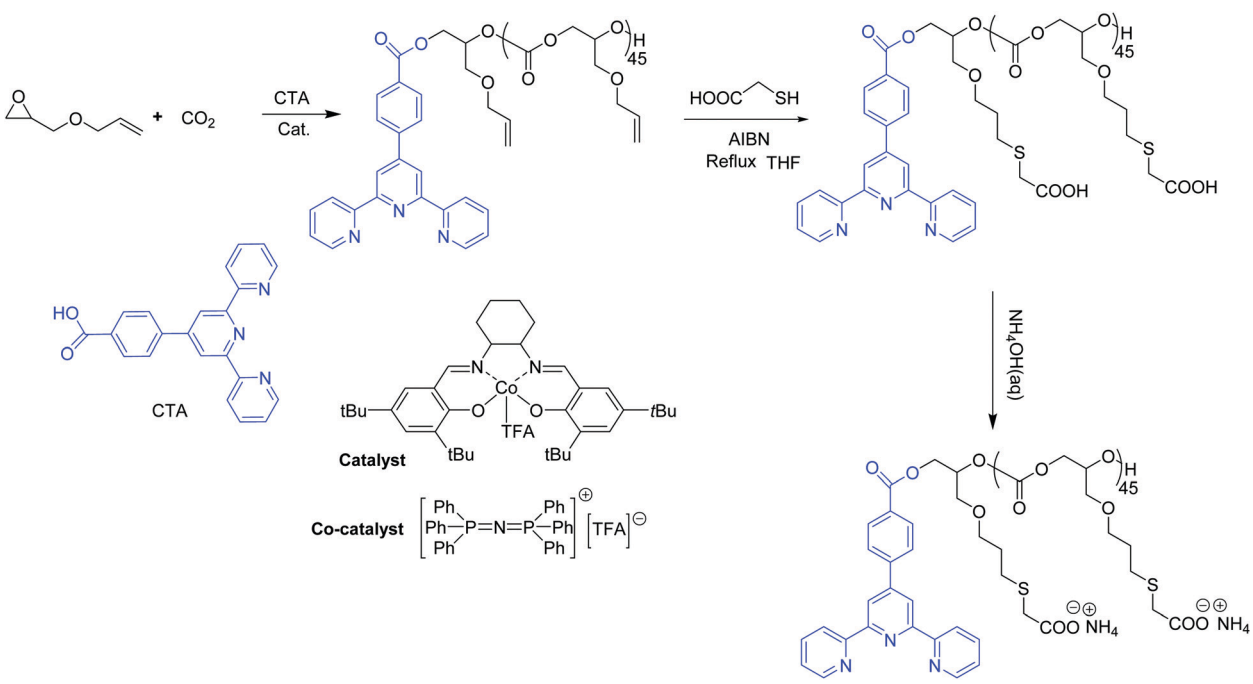


Scheme 1 Formation of an ABA triblock copolymer *via* immortal polymerization.

polycarbonates have been shown to self-assemble in water to provide spherical nanostructural micelles that can incorporate important platforms for human diagnostic or therapeutic functions, as well as, appropriate media for performing micellar metal-catalyzed transformations. The designed terpyridine terminated polycarbonates can be used in a modular procedure to synthesize a variety of metal complexes.

Results and discussion

The successful immortal copolymerization of allyl glycidyl ether (AGE) and CO_2 using the versatile chelating 4′-(4-carboxyphenyl)-2,2′:6′,2″-terpyridine (HL) ligand as chain-transfer agent occurs readily at ambient temperature (Scheme 2). The HL ligand was choosen due to its high binding affinity towards a range of transition metal ions and varied applications of its metallated complexes in the field of catalysis, self healing materials, photo physical, electrochemical and biological studies.[9,15,20] As indicated in the reaction Scheme 2, the efficient binary (salen)CoX/PPNX catalyst system was employed in this copolymerization process. The vinyl substituents in these copolymers were further functionalized by using thiol–ene click chemistry, and the resulting polymers on deprotonation became water soluble with accessible chelating binding sites in the backbone. We attribute this position of HL in the



Scheme 2 Copolymerization of AGE and CO_2 with HL as CTA, followed by functionalization of vinyl substituents using thiol–ene click chemistry.

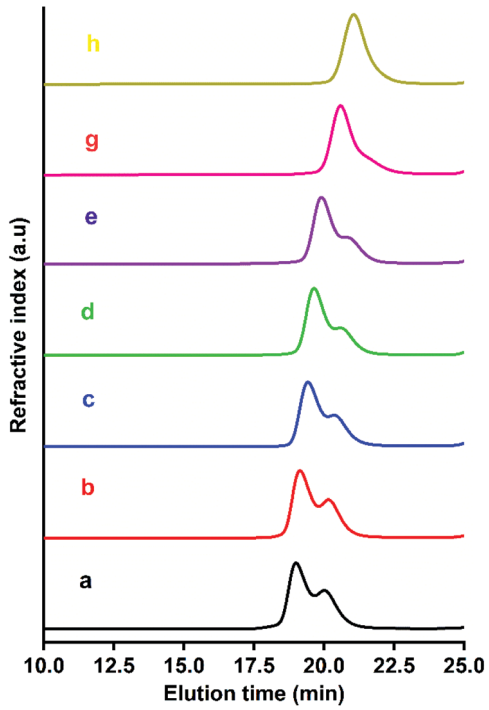


Fig. 1 GPC traces of the copolymerization process as a function of added CTA: (a) one equivalent, (b) two equivalents, (c) three equivalents, (d) four equivalents, (e) five equivalents, (g) six equivalents, and (h) seven equivalents of (salen)CoTFA/PPNTFA/CTA.

copolymers to the mechanism of chain transfer chemistry in polycarbonates which we have discussed in detail in our previous contributions.[25,26] That is, the incipent growing polymer chain initiated by the $CF_3CO_2^-$ (TFA) anion is terminated upon protonation by the CTA resulting in a metal bound carboxylate intermediate which initiates a new polymer chain. This process installs the terpyridine ligand as the end group of a new growing polymer chain. As expected, the molecular weights of the afforded polycarbonates are inversely propotional to an increase in the quantitiy of added CTA (Fig. 1 and 2), Table 1. Table 1 contains a summary of the copolymerization of AGE and carbon dioxide in the presence of various quantities of the chain-transfer agent, HL. The purified copolymers

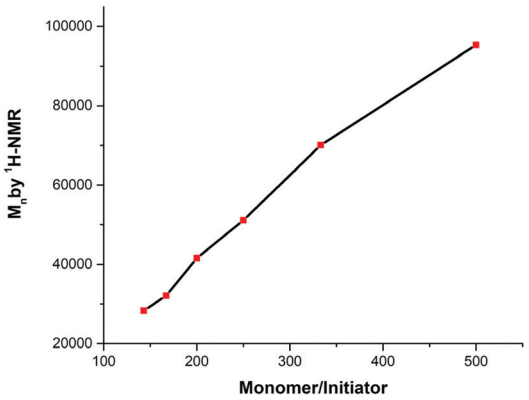


Fig. 2 Copolymer's measured molecular weight (M_n) *versus* [monomer]/[initiator] Loading.

with HL capped end groups were confirmed by ^{1}H NMR spectroscopy, where the peaks of HL in the copolymers exhibit down field shifts compared to those of the free HL (see ESI† for more details).

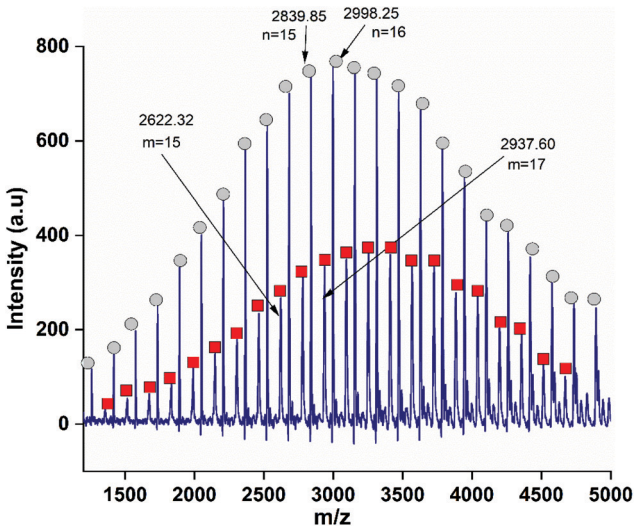


Fig. 3 MALDI-ToF spectrum of copolymer produced from CO_2 and AGE. Mol. wt. of polymer I (■) = $M_{[CF_3CO_2^-]} + nM_{[AGE + CO_2]} + M_{[Na^+]}$ and mol. wt. of polymer II (●) = $M_{[CTA]} + nM_{[AGE + CO_2]} + M_{[H^+]}$.

Table 1 Copolymerization of AGE and CO_2 in the Presence of HL as CTA[a]

Entry	Catayst/AGE/CTA[b]	Monomer/initiator	M_w	M_n (NMR)	M_n (GPC)	PDI	M_n(calcd.)[c]
1	1/1000/1	500	46 200	95 300	45 800	1.01	79 400
2	1/1000/2	333	42 400	70 000	41 500	1.02	53 000
3	1/1000/3	250	40 900	51 100	40 600	1.01	39 900
4	1/1000/4	200	31 600	41 600	31 300	1.01	32 000
5	1/1000/5	167	23 900	32 100	23 700	1.01	26 800
6	1/1000/6	143	12 200	28 200	11 800	1.03	23 000
7	1/1000/7	125	9100	16 300	9000	1.02	20 100

[a] All crude ^{1}H NMR spectra of copolymers showed CTA loading was 100%. [b] Reaction conditions: cat./PPNTFA/AGE/CTA = 1 : 1 : 1000:CTA, where CTA was 1, 2, 3, 4, 5, 6 and 7. Ambient temperature in DCM/toluene at 2.5 MPa for 22 h. [c] Calculation based on number of initiators = no. of CTAs + 1. The initial chain is initiated by TFA^- ion and does not contain the CTA, hence the M_n calculated are approximate only.

In order to better understand the nature of the polymers produced during this polymerization, copolymer samples were subjected to MALDI-ToF analysis. The MALDI-ToF spectrum (Fig. 3) of the low molecular weight fraction of the copolymer produced in entry 5 of Table 1 shows two series of peaks indicative of a bimodal molecular weight distribution as observed in the GPC traces (Fig. 1). Each series of peaks showed a separation of 158 m/z which correspond to the repeated addition of AGE/CO_2 units. Among the possible end groups expected from this immortal copolymerization process as indicated in Fig. 3 and 4, polymer **II** was shown to be the major component. The minor series of peaks are assigned to the copolymer initiated by the $CF_3CO_2^-$ anion.

For the purpose of preparing amphiphlic polycarbonates, a one-reactor, two-step synthesis of a triblock terpolymer of propylene oxide, allyl glycidyl ether, and carbon dioxide was carried out in the presence of HL using the (salen)CoTFA/PPNTFA binary catalyst system (Scheme 3). Following thiol–ene click chemistry of the ABA triblock polycarbonates with mercaptoacetic acid, and deprotonation with NH_4OH the terpolymer was found to self-assemble in water into nanoparticles.

The deprotonated polymer was dispersed in deionized water by sonication at ambient temperature, and the morphology of the resulting material was characterized by dynamic light scattering (DLS) and transmission electron microscopy (TEM) studies. The results of DLS and TEM measurements of the negatively charged triblock amphiphilic polycarbonate polymer are displayed in Fig. 5. These measurments revealed that the amphiphilic polymer self assembles in deionized water to form more stable nanoparticles with good uniformity in size, providing an intensity-averaged hydrodynamic diameter of 172 ± 59 nm. The morphology of these nano-

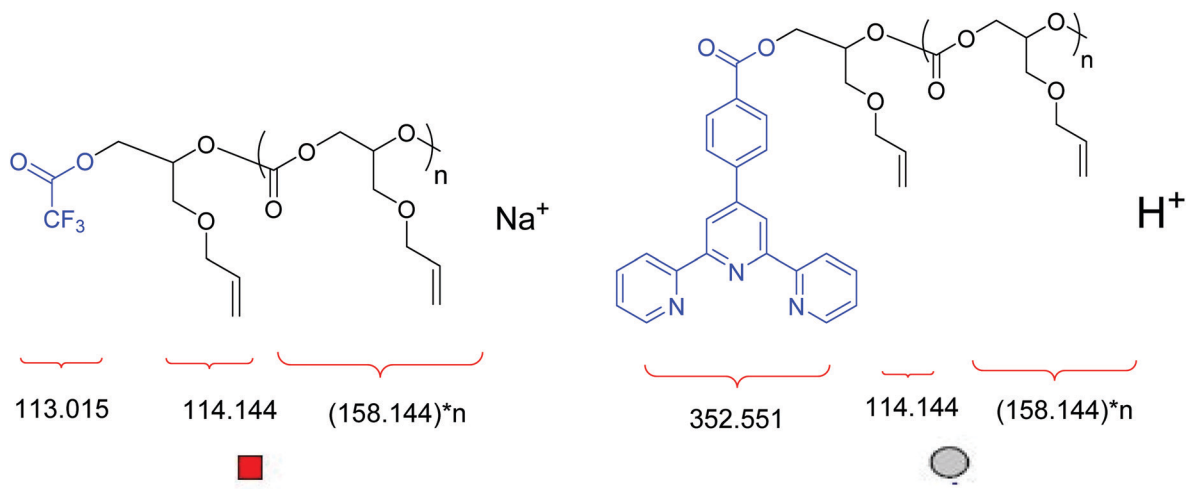
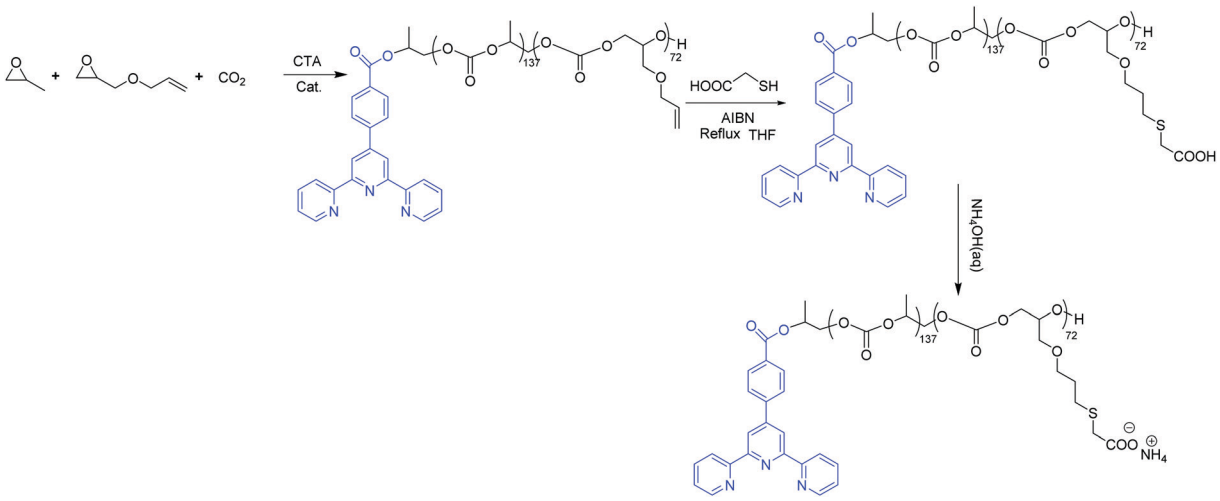


Fig. 4 Possible copolymer architectures afforded by the copolymerization of AGE and CO_2 in the presence of HL using the (salen)Co(CF_3CO_2)/[PPN][CF_3CO_2] catalyst system.



Scheme 3 Synthesis of triblock polycarbonate having free chealating ligand and postpolymerization functionalization for making nanostructures.

particles confirmed by TEM is spherical in nature as shown in Fig. 5b.

Postpolymeriation metalation of the terpyridine ligand in the copolymer obtained from AGE and CO_2 (Table 1, entry 7) was attempted using $ZnCl_2$ and K_2PtCl_4. To this polymer containing a single terpyridine ligand per polymer chain (mol. wt. ≈9000 g mol^{-1}) in dichloromethane or THF was added 10 equivalents of either $ZnCl_2$ or K_2PtCl_4 in methanol or H_2O,

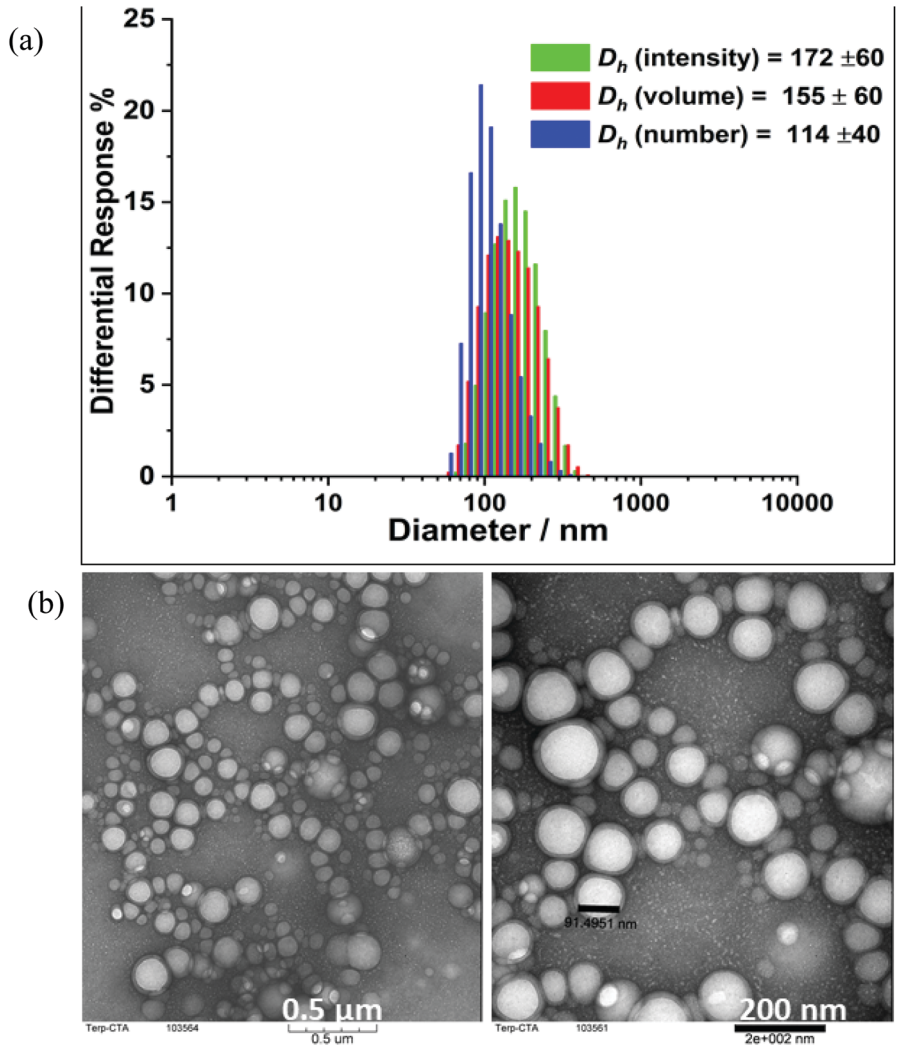
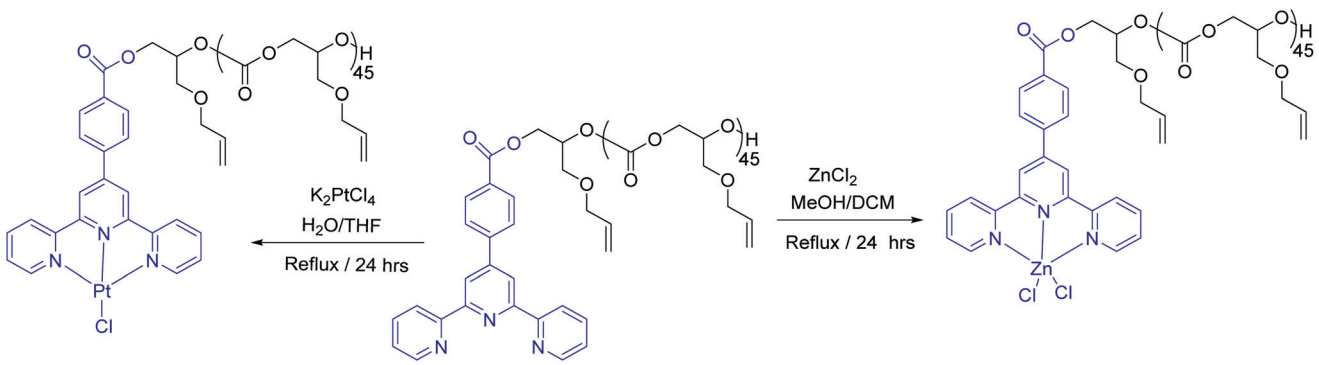


Fig. 5 (a) DLS results of anionic nanoparticles of deprotonated polymer in water. (b) TEM images of anionic nanoparticles.



Scheme 4 Postpolymerization metalation of polycarbonate copolymer with appended terpyridine in the backbone.

and the reaction mixtures were refluxed for 24 h. During this time, the reaction solution underwent a prominent color change from light yellow to bright yellow in the case of zinc or light orange in the case of platinum, indicative of metal-terpyridine binding (Scheme 4), see photos in Fig. S12.† Further evidene for metalation of the copolymer was ascertained upon comparing their ^{1}H NMR spectra which show a marginal downfield shift of the terpyridine peaks (Fig. S8 and S9 in ESI†). Similar peak shifts for discrete terpyridine metal complexes have been reported in the literature.[27–29] Subsequent to thiol–ene click chemistry with mercaptoacetic acid and deprotonation, these metallopolymers were made water soluble (see ESI†). In the isolated metal complexes, the zinc analog is shown to be a distorted trigonal bipyramidal,[27] and the platinium complex is square planar.[29]

Conclusions

In this report we have described the synthesis of polycarbonates *via* the immortal copolymerization of CO_2 and epoxides in the presence of a carboxylic acid derivative of terpyridine as a monofunctional chain transfer agent. By this strategy, the terpyridine ligand serves as the end-capping group of homocopolymers or diblock copolymers, where the molecular weight of these polymers can be controlled by the quantity of terpyridine ligand used in the copolymerization process. Particular attention has focused on the preparation of polycarbonates from the allyl glycidyl ether monomer which affords a vinyl group side chain for carrying out thiol–ene click chemistry. This feature provides the copolymers with the property of solubility or micellar self-assembly in water. Metallation of these polycarbonates was shown to be readily achieved as illustrated herein for the preparation of polymers containing zinc and platinum complexes. Therfore, a pathway for synthesizing in a modular process various metallopolymers for employment in a variety of applications. Furthermore, the general tactic of attaching ligands to low molecular weight copolymers of this type can serve as a method for preparing a wide variety of water soluble ligands and their metal complexes.

Conflicts of interest

The authors declare no competing financial interest.

Acknowledgements

We gratefully acknowledge the financial support of the National Science Foundation (CHE-1665258) and the Robert A. Welch Foundation (A-0923).

References

1 E. C. Constable, *Chem. Soc. Rev.*, 2007, **36**, 246–253.
2 R. Sakamoto, S. Katagiri, H. Maeda and H. Nishihara, *Coord. Chem. Rev.*, 2013, **257**, 1493–1506.
3 L. Flamigni, J.-P. Collin and J.-P. Sauvage, *Acc. Chem. Res.*, 2008, **41**, 857–871.
4 R. Sakamoto, K.-H. Wu, R. Matsuoka, H. Maeda and H. Nishihara, *Chem. Soc. Rev.*, 2015, **44**, 7698–7714.
5 H. Hofmeier and U. S. Schubert, *Chem. Soc. Rev.*, 2004, **33**, 373–399.
6 C. Wei, Y. He, X. Shi and Z. Song, *Coord. Chem. Rev.*, 2019, **385**, 1–19.
7 J. W. Xu, L. Toppare, Y. Li, C. Xu, E. Kim, Y.-W. Zhong, C. Zhang, A. Beneduci, M. Ak and S.-H. Hsiaob, *Electrochromic Smart Materials: Fabrication and Applications*, Royal Society of Chemistry, 2019.
8 C.-L. Ho and W.-Y. Wong, *Coord. Chem. Rev.*, 2011, **255**, 2469–2502.
9 V. Duprez, M. Biancardo, H. Spanggaard and F. C. Krebs, *Macromolecules*, 2005, **38**, 10436–10448.
10 G. A. Bhat, R. Maqbool, A. A. Dar, M. Ul Hussain and R. Murugavel, *Dalton Trans.*, 2017, **46**, 13409–13420.
11 J. P. Collin, S. Guillerez, J. P. Sauvage, F. Barigelletti, L. De Cola, L. Flamigni and V. Balzani, *Inorg. Chem.*, 1991, **30**, 4230–4238.
12 M. Mauro, A. Aliprandi, D. Septiadi, N. S. Kehr and L. De Cola, *Chem. Soc. Rev.*, 2014, **43**, 4144–4166.
13 G. A. Bhat, R. Maqbool and R. Murugavel, *J. Chem. Sci.*, 2018, **130**, 21.
14 A. Winter, G. R. Newkome and U. S. Schubert, *ChemCatChem*, 2011, **3**, 1384–1406.
15 A. Winter and U. S. Schubert, *ChemCatChem*, 2020, **12**, 1–53.
16 J. Limburg, J. S. Vrettos, L. M. Liable-Sands, A. L. Rheingold, R. H. Crabtree and G. W. Brudvig, *Science*, 1999, **283**, 1524–1527.
17 A. O. Adeloye and P. A. Ajibade, *Molecules*, 2014, **19**, 12421–12460.
18 J. J. Leung, J. A. Vigil, J. Warnan, E. E. Moore and E. Reisner, *Angew. Chem.*, 2019, **131**, 7779–7783.
19 N. Liu, Y. Wang, C. Wang, Q. He and W. Bu, *Macromolecules*, 2017, **50**, 2825–2837.
20 Q. He, C. Wang, J. Xiao, Y. Wang, Y. Zhou, N. Zheng, B. Zhang and W. Bu, *J. Mater. Chem. C*, 2018, **6**, 12187–12191.
21 M. Heller and U. S. Schubert, *Macromol. Rapid Commun.*, 2002, **23**, 411–415.
22 S. Bode, R. K. Bose, S. Matthes, M. Ehrhardt, A. Seifert, F. H. Schacher, R. M. Paulus, S. Stumpf, B. Sandmann and J. Vitz, *Polym. Chem.*, 2013, **4**, 4966–4973.
23 K. A. Aamer and G. N. Tew, *Macromolecules*, 2004, **37**, 1990–1993.
24 K. A. Aamer and G. N. Tew, *Macromolecules*, 2007, **40**, 2737–2744.

25 T. M. Folsom, G. A. Bhat, A. Z. Rashad and D. J. Darensbourg, *Macromolecules*, 2019, **52**, 5217–5222.
26 G. A. Bhat, A. Z. Rashad, T. M. Folsom and D. J. Darensbourg, *Organometallics*, 2020, **39**, 1612–1618.
27 S. Bhowmik, B. N. Ghosh, V. Marjomäki and K. Rissanen, *J. Am. Chem. Soc.*, 2014, **136**, 5543–5546.
28 H. Bertrand, D. Monchaud, A. De Cian, R. Guillot, J.-L. Mergny and M.-P. Teulade-Fichou, *Org. Biomol. Chem.*, 2007, **5**, 2555–2559.
29 M. A. n. Martínez, M. P. Carranza, A. Massaguer, L. Santos, J. A. Organero, C. Aliende, R. de Llorens, I. Ng-Choi, L. Feliu and M. Planas, *Inorg. Chem.*, 2017, **56**, 13679–13696.