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## Orthogonally grown polycarbonate and polyvinyl block copolymers from mechanistically distinct (co)polymerizations†

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Mechanistically distinct polymerization systems can afford unique block copolymers that would not be accessible by mere sequential polymerization. Herein we report a convenient one-pot synthesis of miscellaneous di- and triblock copolymers comprising CO<sub>2</sub>-based and polyvinyl blocks, obtained orthogonally through triethylborane (TEB)-mediated ring opening copolymerization (ROCOP) of CO<sub>2</sub> with epoxides on the one hand and reversible addition fragmentation chain transfer (RAFT) polymerization of vinyl monomers on the other. 4-Cyano-4-[(dodecylsulfanylthiocarbonyl) sulfanyl] pentanoic acid (TTC-COOH), which carries a trithiocarbonate function and a carboxylic acid group, played the dual role of a chain transfer agent for RAFT polymerization and an initiator for the ROCOP of CO<sub>2</sub>/epoxide. Different bases such as tetrabutylammonium hydroxide, N-heterocyclic carbene (NHC), and tributylamine (TBA) were used for the deprotonation of TTC-COOH; in each case the compatibility of the generated carboxylic salts with trithiocarbonate functions was checked when they were utilized to copolymerize CO<sub>2</sub> and epoxides. It was found that the salts produced *in situ* by the deprotonation of TTC-COOH using NHC and TBA did not harm trithiocarbonate functions. The two distinct polymerizations occurred as expected, affording a series of well-defined CO<sub>2</sub>-based AB and ABC block copolymers comprising one or two poly(vinyl) blocks, depending upon the choice of different combinations of epoxides and vinyl monomers. The thermal characterization of these AB and ABC block copolymers revealed either two or three glass transition temperatures indicative of phase-separated materials.

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## Introduction

Over the past decade, several examples of successful syntheses of aliphatic polycarbonates through metal-based catalytic systems,<sup>1–8</sup> and more recently through metal free systems, have been disclosed.<sup>9–15</sup> These chemistries described efficient ring-opening copolymerizations (ROCOP) of CO<sub>2</sub> with epoxides, leveraging the direct utilization of over-emitted CO<sub>2</sub> as a means to reduce carbon footprint and avoid fossil feedstock. However, applications derived from CO<sub>2</sub>-based polymers are still very limited due to their rather poor mechanical and thermal properties. Much effort has thus been dedicated to improve the properties of aliphatic polycarbonates through the incorporation of other types of blocks or segments along with CO<sub>2</sub>-based blocks in di- or triblock copolymers as a potential solution among various other reported strategies.<sup>4,5,16,17</sup> As

summarized by Coates *et al.*<sup>18</sup> CO<sub>2</sub>-based block copolymers could be synthesized following three strategies: (1) sequential monomer addition or using a macroinitiator (macrotransfer agent), (2) resorting to a bifunctional initiator, or (3) kinetic resolution polymerization when one monomer is consumed faster than the other. Based on these strategies, CO<sub>2</sub>-containing block copolymers with different structures and compositions could be generated, as recently reviewed by Zhang and coworkers.<sup>4</sup> Generally the block copolymers described were either all-polycarbonates,<sup>12,19–24</sup> or polycarbonate-*b*-polyesters obtained through the ROCOP of CO<sub>2</sub>/epoxides and ROCOP of anhydrides/epoxides<sup>25–29</sup> or ROP of cyclic esters.<sup>29–37</sup> Due to the compatibility between polyester and polycarbonate blocks, these two blocks hardly phase separate unless the obtained block copolymers exhibit molar masses high enough to comply with the criterion of  $\chi N$  higher than 10.5, as recently demonstrated with the case of polycarbonate thermoplastic elastomers.<sup>20,38</sup> In this context, CO<sub>2</sub>-based block copolymers comprising highly incompatible blocks are desirable, in particular in applications such as nanomaterials where phase separation is required.<sup>39–41</sup> Following the first report by Lee and co-workers describing the synthesis of various CO<sub>2</sub>-based

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block copolymers through the immortal copolymerization of CO<sub>2</sub> with PO,<sup>42</sup> such block copolymers were mainly synthesized by a macroinitiator or macrotransfer agent strategy.<sup>40,41,43–45</sup> Coates *et al.* described the synthesis of polyisoprene-*b*-polystyrene-*b*-poly(propylene carbonate) (PI-*b*-PS-*b*-PPC) triblock copolymers using PI-*b*-PS-OH as the macrotransfer agent which was obtained through anionic polymerization. These triblock terpolymers gave rise to ordered mesoporous templates after the orthogonal degradation of PI and PPC blocks in the self-assembled morphology.<sup>41</sup> Our group on the other hand generated PS-*b*-PCHC and PI-*b*-PCHC diblocks by mere one-pot sequential anionic polymerization of styrene or dienes first and then of CO<sub>2</sub> and CHO in the presence of trialkylaluminum.<sup>44</sup> Wang and Xie reported a one-step synthesis of diblock copolymers including a CO<sub>2</sub>-based polycarbonate block and a polyvinyl block, both grown from a trithiocarbonate compound bearing a carboxylic group, TTC-COOH, that served a bifunctional transfer agent.<sup>43</sup> Because the catalyst used to grow the polycarbonate block was inactive beyond 10 equivalents of TTC-COOH, this synthesis strategy afforded diblock copolymer samples contaminated with homopolymers and of relatively low molar mass. To address this issue, Wu and coworkers resorted to using a bifunctional compound based on a RAFT agent carrying a  $\beta$ -diiminate zinc complex and prepared a series of polyvinyl and polycarbonate block copolymers through the simultaneous ROCOP of CO<sub>2</sub>/epoxides and the RAFT polymerization of vinyl monomers.<sup>46</sup> Recently, Wang and coworkers reported the synthesis of poly(vinyl acetate)-*b*-polycarbonate diblock copolymers mediated by (salen)Co(III)-R, using O<sub>2</sub> to switch from the organometallic mediated radical polymerization (OMRP) of vinyl acetate to the ROCOP of CO<sub>2</sub>/epoxides.<sup>47</sup> In view of the potential application of such copolymers as nanomaterials in the microelectronics field, the contamination by metallic residues in the above CO<sub>2</sub>-based block copolymers was viewed as an issue.

Since the first discovery of ROCOP of CO<sub>2</sub> with epoxides in the presence of triethylborane in 2016,<sup>15</sup> the synthesis of polycarbonates could be achieved through a living anionic approach under metal-free conditions. As an illustration of the advances made, carboxylates were found to be reliable initiators for the ROCOP of CO<sub>2</sub> with epoxides, exhibiting the same performance as the onium halides and onium alkoxides originally used.<sup>13</sup> The wide availability of carboxylic acids and the ease with which they can be deprotonated and can generate carboxylate salts are major advantages for the design and synthesis of CO<sub>2</sub>-based macromolecules with different architectures. For instance, polycarbonate stars could be easily prepared using multifunctional carboxylic acid salts as the initiator.<sup>13</sup> More recently, using a polycarbonate backbone carrying multiple tetrabutylammonium carboxylate salts as the initiator, well-defined all-polycarbonate graft copolymers could be obtained: in such a macromolecular structure all grafts were grown from each of the carboxylate sites of the backbone.<sup>10</sup> In addition, the carboxylate groups serving as ROCOP initiating sites are generally compatible with other functional

groups that are suitable for the initiation of other chain polymerizations. In this investigation, we describe the synthesis of di- and triblock copolymers using TTC-COOH in the dual role of an initiator for the ROCOP of epoxide/CO<sub>2</sub> from its carboxylic acid group and of a transfer agent for the RAFT polymerization of vinyl monomers through its trithiocarbonate function (Scheme 1).<sup>48</sup> The two distinct polymerizations were shown to proceed concomitantly in one pot, allowing the synthesis of AB diblock copolymers from a library of epoxides and vinyl monomers. Lastly, from the generated AB diblock copolymers, a third monomer such as ethylene oxide or cyclohexene oxide/CO<sub>2</sub> could be subsequently copolymerized, leading to the formation of ABC triblock copolymers; a third block could also be grown on the RAFT side through controlled radical polymerization. With TTC-COOH playing the dual role of an initiator for ROCOP of CO<sub>2</sub>/epoxides and of a transfer agent for RAFT polymerization, well-defined miscellaneous triblock copolymers of high molar mass, comprising either two poly(vinyl) blocks and one CO<sub>2</sub>-based block or two CO<sub>2</sub>-based blocks and one poly(vinyl) block exhibiting phase separation, could be generated.

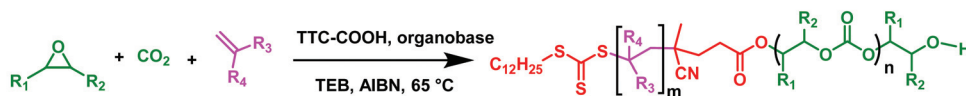
## Results and discussion

### Distinct polymerizations using TTC-COOH in a dual role of an initiator and a chain transfer agent

For our initial attempt at growing a polycarbonate block, we relied on our previous contributions where the use of carboxylate salts as initiators of the ROCOP of CO<sub>2</sub>/epoxides was described;<sup>9,10,13</sup> we thus used 4-cyano-4-[(dodecylsulfanylthiocarbonyl) sulfanyl] pentanoic acid (TTC-COOH) playing a dual role as an initiator for the ROCOP of CO<sub>2</sub>/epoxides and a transfer agent for the RAFT polymerization of vinyl monomers (Scheme 1). The tetrabutylammonium carboxylate salt (TTC-COO<sup>−</sup>, Bu<sub>4</sub>N<sup>+</sup>) obtained after the deprotonation of TTC-COOH using tetrabutylammonium hydroxide was characterized by <sup>1</sup>H NMR to check its structure (Fig. S1A†). TTC-COO<sup>−</sup>, Bu<sub>4</sub>N<sup>+</sup> was subsequently evaluated as the initiator for the copolymerization of CO<sub>2</sub> with propylene oxide (PO). The copolymerization of CO<sub>2</sub> with PO did occur, but the polycarbonates obtained exhibited a bimodal distribution (entry 1, Table 1, Fig. S1C†), indicating the presence of difunctional protic impurities. Drying further TTC-COO<sup>−</sup>, Bu<sub>4</sub>N<sup>+</sup> even worsened the results eventually obtained with a more pronounced bimodal distribution of molar masses (entry 2, Table 1, Fig. S1C†). In fact, freshly prepared yellow TTC-COO<sup>−</sup>, Bu<sub>4</sub>N<sup>+</sup> became dark brown with time upon storage. Its characterization by <sup>1</sup>H NMR (Fig. S1B†) just after generating the carboxylic salts and after 10 days of storage showed the disappearance of the peak at 2.40 ppm assigned to the four methylene protons next to the carboxylic group, suggesting the cleavage of trithiocarbonyl ester. In addition, the integral ratios of other peaks compared to freshly prepared TTC-COO<sup>−</sup>, Bu<sub>4</sub>N<sup>+</sup> have changed, indicating the decomposition of this bifunctional initiator over time. The <sup>13</sup>C

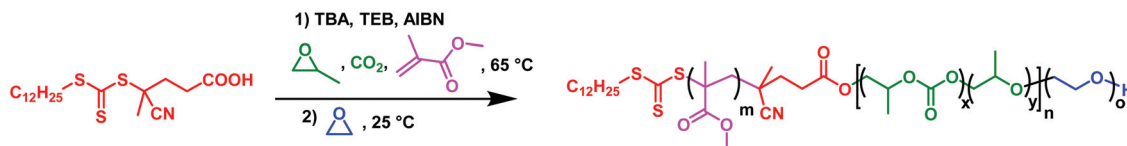
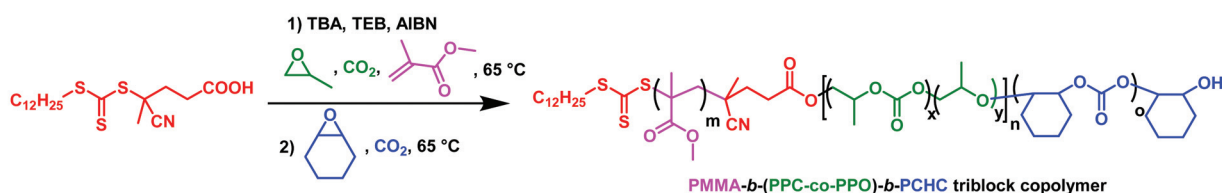


## AB diblock copolymers

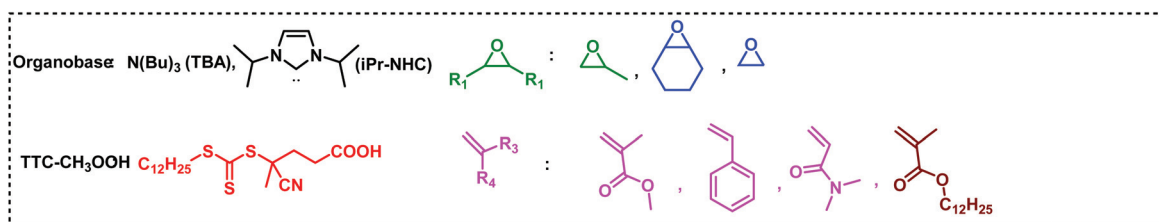
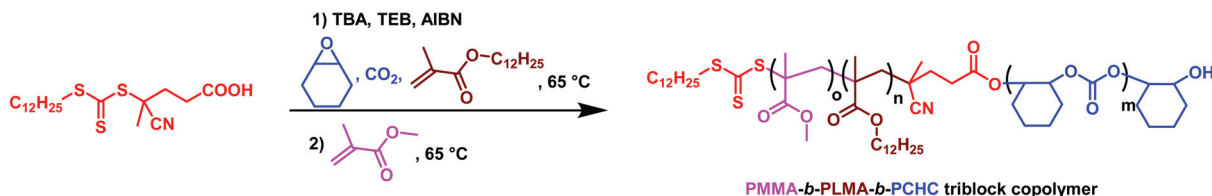


## ABC triblock copolymers

## A) sequential addition of epoxide

B) sequential addition of epoxide/CO<sub>2</sub>

## C) sequential addition of MMA



**Scheme 1** Schematic representation for the one-pot synthesis of AB diblock and ABC triblock copolymers using TTC-COOH in a dual role of an initiator for the ROCOP of epoxide/CO<sub>2</sub> and a transfer agent for the RAFT polymerization of vinyl monomers.

**Table 1** TEB-assisted copolymerization of propylene oxide and carbon dioxide with carboxylic acid neutralized by different bases<sup>a</sup>

Entry	Initiator	[M] : [I] : [TEB] : [B]	Selectivity <sup>b</sup> (%)	PC <sup>b</sup> (%)	Yield <sup>c</sup> (%)	$M_{n(NMR)}$ <sup>d</sup> kg mol <sup>-1</sup>	$M_{n(GPC)}$ <sup>e</sup> kg mol <sup>-1</sup> / $D$
1 <sup>f</sup>	TTC-COO <sup>-</sup> , Bu <sub>4</sub> N <sup>+</sup>	200 : 1 : 2 : 1	>99	75	78	—	14.7/1.2
2 <sup>f</sup>	TTC-COO <sup>-</sup> , Bu <sub>4</sub> N <sup>+</sup>	200 : 1 : 2 : 1	>99	99	83	—	17.3/1.2
3	TTC-COO <sup>-</sup> , NHCH <sup>+</sup>	20 : 1 : 2 : 0.9	96	99	83	1.8	1.9/1.2
4	SA(Bu <sub>3</sub> NH <sup>+</sup> ) <sub>2</sub>	40 : 1 : 4 : 1	97	95	80	3.1	3.4/1.1
5	SA(Bu <sub>3</sub> NH <sup>+</sup> ) <sub>2</sub>	40 : 1 : 4 : 0.4	98	96	82	3.1	3.3/1.1
6	TTC-COO <sup>-</sup> , Bu <sub>3</sub> NH <sup>+</sup>	40 : 1 : 2 : 0.2	98	96	82	3.5	3.9/1.1

<sup>a</sup> Polymerizations were carried out in a 50 mL Parr reactor under 10 bar CO<sub>2</sub> with stirring at 65 °C. <sup>b</sup> PC (polycarbonate content) and linear vs. cyclic selectivity were determined from the <sup>1</sup>H NMR of the crude product. <sup>c</sup> Calculated by the gravimetric method. <sup>d</sup>  $M_{n(NMR)}$  was calculated based on NMR data:  $M_{n(NMR)} = [102 \times (4I_a/I_c)] + 403$  ( $I_a$  and  $I_c$  are integral values of peaks a and b as shown in Fig. 1A). <sup>e</sup> Determined by GPC with THF as the eluent and calibrated by a polystyrene standard. <sup>f</sup> The initiator was prepared and well dried before using for copolymerization (see Experimental).



NMR study also suggests that the peaks corresponding to carbon of CN at  $\delta = 118$  ppm and to the quaternary carbon next to the CN group at  $\delta = 47$  ppm are completely disappeared, indicating the decomposition of  $\text{TTC-COO}^-$ ,  $\text{Bu}_4\text{N}^+$  (Fig. S2†).

To overcome the issues related to the attack of the trithiocarbonate group by the initiating carboxylate salt, we opted for the deprotonation of  $\text{TTC-COOH}$  by a weaker base such as N-heterocyclic carbenes (NHC). As NHCs can by themselves initiate the ROCOP of PO with  $\text{CO}_2$ ,  $\text{iPr-NHC}$  was used in these experiments in a 0.9 : 1 ratio with respect to  $\text{TTC-COOH}$  just to neutralize enough of  $\text{TTC-COOH}$  and generate carboxylate anions associated with imidazolium cations.<sup>49–51</sup> The formation of anions of weaker nucleophilicity through the choice of a weaker base helped to preserve the integrity of the trithiocarbonate moiety of  $\text{TTC-COOH}$  as confirmed by  $^1\text{H}$  and  $^{13}\text{C}$  NMR characterization (Fig. S3 and S4†). As established in one of our previous reports carboxylate anions associated with imidazolium cations behave similarly to tetrabutylammonium carboxylates with respect to their ability to initiate the ROCOP of epoxides with  $\text{CO}_2$ .<sup>52</sup>

After the deprotonation of  $\text{TTC-COOH}$  by 1,3-diisopropyl-imidazol-2-ylidene ( $\text{iPr-NHC}$ ), the ROCOP of PO with  $\text{CO}_2$  was initiated in a Parr reactor under a  $\text{CO}_2$  pressure of 10 bar in the presence of TEB at 65 °C; at this temperature a high selectivity for linear polycarbonate vs. cyclic carbonate could be achieved during  $\text{CO}_2/\text{PO}$  copolymerization. The polycarbonate obtained after purification was subsequently characterized (entry 3, Table 1). The GPC traces showed a unimodal symmetrical distribution indicating the integrity of the trithiocarbonate moiety during copolymerization (Fig. S5A†). The  $^1\text{H}$  NMR spectrum of the obtained polycarbonate exhibits all the characteristic peaks for the latter polymer and for the trithiocarbonate moiety of  $\text{TTC-COOH}$  (Fig. S5B†). MALDI-TOF analysis results substantiate the incorporation of  $\text{TTC-COOH}$  in the polymer formed, confirming that the polycarbonates produced were initiated by  $\text{TTC-COOH}$  and not by  $\text{iPr-NHC}$  (Fig. S6†). Indeed, all the peaks from the main population satisfy well the following formula:  $m/z = 102.08n + 403.67 + 58.1 + 23$ , where 102.08, 403.67, 58.1 and 23 are, respectively, the molar mass of the propylene carbonate unit,  $\text{TTC-COOH}$ , PO and sodium.

Such results encouraged us to try tributylamine ( $\text{N}(\text{Bu})_3$  or TBA), a weaker base that is cheaper and easier to handle than  $\text{iPr-NHC}$  to deprotonate  $\text{TTC-COOH}$ ; in addition the tributylammonium cation formed after deprotonation possesses a structure similar to that of tetrabutylammonium.  $\text{TTC-COOH}$  neutralization by (TBA) was merely carried out by adding TBA to the solution of  $\text{TTC-COOH}$  in THF. The generated ammonium salt  $\text{TTC-COO}^-$ ,  $\text{Bu}_3\text{NH}^+$  was analyzed by  $^1\text{H}$  and  $^{13}\text{C}$  NMR characterization and all the peaks corresponding to the moieties of TTC and TBA were found, indicating the formation of a stable initiator (Fig. S7 and S8†). Before using  $\text{TTC-COO}^-$ ,  $\text{Bu}_3\text{NH}^+$  as the initiator for the ROCOP of PO with  $\text{CO}_2$ , a control  $\text{CO}_2/\text{epoxide}$  copolymerization was carried out using succinic acid (SA) as the difunctional initiator after

partial neutralization by 0.5 eq. and 0.2 eq. of TBA (entries 4 and 5 Table 1). TBA was purposely used in less amount to avoid independent initiation by TBA. Indeed, recently Zhang and coworkers reported that tertiary amines combined with TEB can effectively initiate the  $\text{CO}_2/\text{PO}$  copolymerization, a mechanism involving the quarternization of the tertiary amine and the formation of zwitterions.<sup>53</sup> Succinic acid was purposely selected to easily distinguish populations of chains initiated by this initiator and putatively by TBA. Interestingly, monomodal and symmetrical GPC traces were found with an expected molar masses and narrow distribution with 0.5 eq. and 0.2 eq. equivalents of TBA (Fig. S9†); the amount of TBA added does not affect the polymerization results. The  $^1\text{H}$  NMR spectrum of the purified sample (entry 4, Table 1) shows the presence of the succinate peak and the absence of any tributyl ammonium peak, indicating that polycarbonate chains were all initiated by succinate salts and not by TBA (Fig. S10†); MALDI TOF analysis confirmed that only initiation by succinate anions occurred and also the absence of any TBA moiety (Fig. S11†). In the presence of carboxylic acid, tertiary amine thus serves to deprotonate succinic acid and generate tributylammonium cations and does not initiate  $\text{CO}_2/\text{PO}$  ROCOP.<sup>53</sup> After noticing the success of the control experiment, we then attempted to copolymerize  $\text{CO}_2/\text{PO}$  using  $\text{TTC-COOH}$  after its deprotonation by TBA (entry 6, Table 1). 0.2 eq. of TBA to the  $\text{TTC-COOH}$  was charged along with other reactants. The characterization by  $^1\text{H}$  NMR of the obtained polycarbonates indicates the integrity of  $\text{TTC-COO}$ , all the characteristic proton peaks of  $\text{TTC-COO}$  moieties 'd, e, f, h, and i' and peaks for polycarbonates 'a, b, and g' being clearly detected as shown in Fig. 1A. The peak 'e' appearing at  $\delta$  2.50 ppm in Fig. 1A can be attributed to the two methylene groups of  $\text{TTC-COO}$  that are located next to the carboxylate group ( $-\text{CH}_2-\text{CH}_2-\text{COO}$ ); the protons of these methylene groups then served to calculate the molar mass of the PPC sample formed. A monomodal and narrowly distributed population of chains revealed by GPC traces (Fig. S12†) and MALDI-TOF (Fig. 1B) results unambiguously confirm the initiation of copolymerization by  $\text{TTC-COO}^-$ ,  $\text{Bu}_3\text{NH}^+$  and the integrity of the trithiocarbonate moiety under the abovementioned polymerization conditions.

After demonstrating that the  $\text{CO}_2/\text{epoxide}$  copolymerization can be carried out using  $\text{TTC-COOH}$  as the initiator after deprotonation by  $\text{iPr-NHC}$  or TBA, we then attempted to polymerize methyl methacrylate (MMA) by RAFT under conditions similar to those described above and in the absence of PO (entry 1, Table 2):  $\text{TTC-COOH}/\text{AIBN}/\text{TEB}/\text{TBA}/\text{CO}_2$  (10 bar) at 65 °C. The polymerization proceeded smoothly and results (expected molar mass and narrow polydispersity) similar to conventional RAFT polymerization were obtained under a  $\text{CO}_2$  atmosphere; the presence of TEB and TBA did not induce any side effect nor did it affect the radical polymerization. Besides  $^1\text{H}$  NMR and GPC characterization (Fig. S13†), the purified polymer was further characterized by MALDI-TOF. As shown in Fig. S14,† PMMA chains were all terminated by the trithiocarbonate group from  $\text{TTC-COOH}$ .





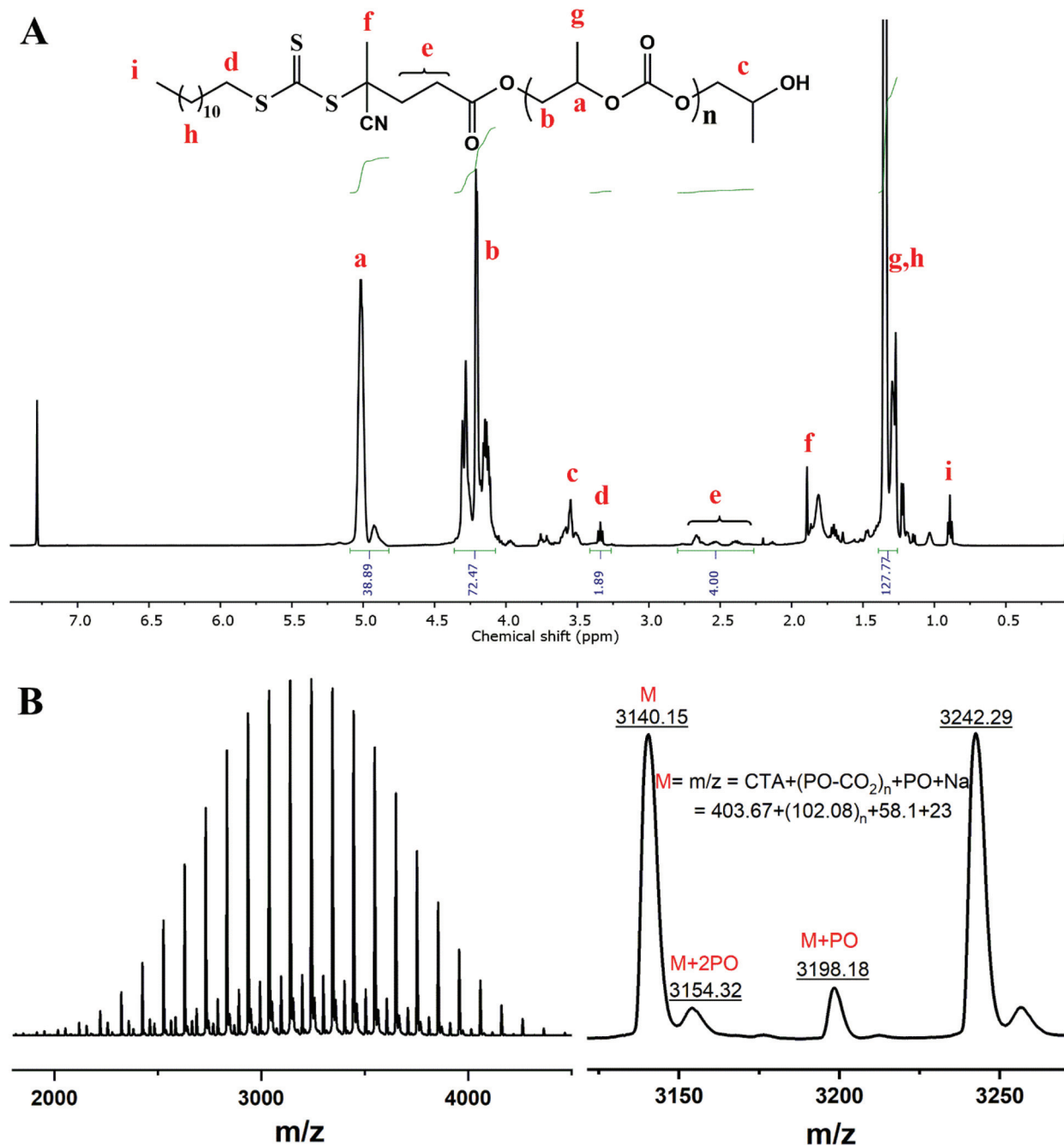


Fig. 1 (A) <sup>1</sup>H NMR spectrum in CDCl<sub>3</sub> and (B) MALDI-TOF mass spectrometry of PPC initiated by *in situ* generated TTC-COO<sup>-</sup>, Bu<sub>3</sub>NH<sup>+</sup> (entry 6, Table 1).

### One pot orthogonal CO<sub>2</sub>/epoxide ROCOP and RAFT polymerization of vinyl monomers

**AB diblock copolymers.** After successfully demonstrating that CO<sub>2</sub>/PO ROCOP and MMA RAFT polymerizations can be separately carried out from TTC-COOH serving as an initiator or a chain transfer agent, we turned our attention towards their simultaneous polymerizations. Our initial interest was to prepare block copolymers made of PPC and PMMA. Block

copolymers made of PPC and PMMA are of special interest as PPC is degradable and PMMA is recyclable. PPC blocks can be easily depolymerized into five membered cyclic propylene carbonate in the presence of a base or at higher temperature. On the other hand PMMA is the only vinyl based polymer prepared by a radical mechanism that can be degraded back to the MMA monomer upon heating the polymer above 400 °C.<sup>54,55</sup> All monomers, MMA, PO along with the bifunctional initiator TTC-COOH, TEB, TBA and AIBN were charged



**Table 2** Related data of CO<sub>2</sub>-based diblock copolymers prepared in one-pot through a bifunctional approach<sup>a</sup>

Entry	Polymer designation	Base (B)	Feeding ratio Ep/VM/B/I	Conv. <sup>b</sup> %		PC <sup>b</sup> (%)	$M_{n(\text{NMR})}$ <sup>c</sup> [kg mol <sup>-1</sup> ]	$M_{n(\text{GPC})}$ <sup>d</sup> [kg mol <sup>-1</sup> ]/ $\bar{D}$
				Ep	VM			
1	PMMA <sub>38</sub>	TBA	0/50/0.2/1	—	76	—	3.8	5.7/1.1
2	PPC <sub>105</sub> - <i>b</i> -PMMA <sub>28</sub>	TBA	100/50/0.2/1	99	60	97	13.4	11.3/1.04
3	PPC <sub>100</sub> - <i>b</i> -PMMA <sub>82</sub>	TBA	100/100/0.2/1	99	82	98	18.5	16.5/1.04
4	PPC <sub>78</sub> - <i>b</i> -PMMA <sub>150</sub>	TBA	100/200/0.2/1	78	75	98	22.5	18.2/1.06
5	PCHC <sub>46</sub> - <i>b</i> -PMMA <sub>98</sub>	TBA	50/100/0.2/1	90	99	99	16.1	13.9/1.08
6 <sup>e</sup>	PPC <sub>69</sub> - <i>b</i> -PS <sub>19</sub>	TBA	100/50/0.2/1	69	38	97	9.2	7.8/1.08
7	PPC <sub>42</sub> - <i>b</i> -PDMA <sub>32</sub>	TBA	50/40/0.2/1	84	64	97	8.2	7.2/1.06
8	PEC <sub>89</sub> - <i>b</i> -PMMA <sub>29</sub>	TBA	100/50/0.2/1	89	60	68	9.9	11.1/1.2
9	PPC <sub>66</sub> - <i>b</i> -PMMA <sub>72</sub>	NHC	100/100/0.9/1	66	72	98	14.0	11.6/1.07
10	PPC <sub>127</sub> - <i>b</i> -PMMA <sub>80</sub>	NHC	200/100/0.9/1	51	78	98	21.2	15.2/1.1

<sup>a</sup> Polymerizations were carried out in a 50 mL Parr reactor under 10 bar CO<sub>2</sub> with stirring at 65 °C. <sup>b</sup> Determined from the <sup>1</sup>H NMR of the crude product. <sup>c</sup>  $M_{n(\text{NMR})}$  was calculated based on NMR data. <sup>d</sup> Determined by GPC with THF as the eluent and calibrated by a polystyrene standard.

<sup>e</sup> Polymerization was carried out in a 50 mL Parr reactor under 10 bar CO<sub>2</sub> with stirring at 70 °C. Ep: epoxide, VM: vinyl monomer, B: Base, I: TTC-COOH, PC: polycarbonate, TBA: tributylamine, NHC: 1,3-diisopropylimidazol-2-ylidene, PPC: poly(propylene carbonate), PCHC: poly(cyclohexene carbonate), PEC: poly(ethylene carbonate), PMMA: poly(methyl methacrylate), PS: polystyrene, PDMA: poly(*N,N*-dimethyl acrylamide).

into a Parr reactor filled with 10 bar of CO<sub>2</sub> and brought to 65 °C for 12 h. To avoid the cleavage of the thiocarbonylthio group at the polymer chain ends that may occur in the presence of O<sub>2</sub>, the polymerization was stopped and quenched under an inert atmosphere.<sup>56</sup> The GPC traces exhibited a monomodal and narrow distribution with molar mass 11.3 kg mol<sup>-1</sup> and a polydispersity index of 1.04 (entry 2, Table 2, Fig. S24†). As shown by the <sup>1</sup>H NMR characterization of the copolymer formed (Fig. 2), the characteristic peaks due to two blocks of PPC and PMMA were clearly detected. In addition, the peak 'f' appearing at  $\delta$  2.50 ppm corresponds to two methylene groups next to the carboxylic group (–CH<sub>2</sub>–CH<sub>2</sub>–COOH) and peak 'e' at  $\delta$  3.32 ppm corresponds to methylene protons next to the sulfur atom (C<sub>11</sub>H<sub>23</sub>–CH<sub>2</sub>–S–) of TTC-COOH, indicating the incorporation of the TTC-COO moiety within the copolymer formed. The following diffusion-ordered spectroscopy (DOSY, Fig. 2B) analysis of this copolymer sample shows a single diffusion coefficient, further confirming the formation of a block copolymer containing PPC and PMMA. With the peak f at  $\delta$  2.50 ppm serving as the reference, the composition and degree of polymerization of each block could be calculated; for instance, entry 2 in Table 2 corresponds to PPC<sub>105</sub>-*b*-PMMA<sub>28</sub>. Varying the feeding ratio of PO to MMA, PPC-*b*-PMMA block copolymers with different compositions and molar masses could be easily obtained. In all cases, the block polymers obtained exhibited the expected molar masses and narrow distributions, and high carbonate contents in the PPC block (entries 2–4, Table 2). In addition to PO and MMA as the monomer combination, some other epoxides and vinyl monomers could also be (co)polymerized orthogonally. As shown in entries 5–8 of Table 2, after the copolymerization of CO<sub>2</sub>/epoxides such as cyclohexene oxide (CHO) and ethylene oxide (EO) was carried out simultaneously with the RAFT polymerization of MMA, styrene and *N,N*-dimethyl acrylate (DMA) were also polymerized by RAFT, leading to well-defined PCHC-*b*-PMMA, PEC-*b*-PMMA, PPC-*b*-PSt and PPC-*b*-PDMA diblock copolymers (Fig. S15–S22†).

Access to diblock copolymers with different block combinations of hard, soft, hydrophilic and hydrophobic natures was thus possible through the choice of various epoxides and vinyl monomers. The criteria to consider when choosing epoxide and vinyl monomers for orthogonal polymerization were the polymerization temperature and compatibility between monomers with respect to their reaction mechanisms: too high a polymerization temperature for epoxide/CO<sub>2</sub> may for instance increase the formation of cyclics. In a control experiment, we showed that iPr-NHC functions like TBA in these one-pot polymerizations, allowing the successful synthesis of diblock copolymers (entries 9 and 10, Table 2, Fig. S21 and S22†).

In particular we checked the compatibility of the RAFT polymerization of DMA in the presence of TEB that may be prone to interact with the amide function of DMA, which may in turn disrupt the ROCOP of CO<sub>2</sub> with PO. Actually, both ROCOP and RAFT polymerization proceeded as expected without interference resulting in high linear/cyclic polycarbonate selectivity and a high carbonate content of the PPC block, affording a well-defined amphiphilic diblock copolymer (Fig. S19†). Amide groups of DMA were thus found not to affect the activity of Lewis acid TEB during terpolymerization. A 0.1 wt% aqueous solution of PPC<sub>42</sub>-*b*-PDMA<sub>32</sub> was prepared and the self-assembly of this diblock copolymer was characterized by DLS measurements. Micelles of an average size of 59 nm were formed (Fig. S23†). Such block copolymers prepared from metal free reaction conditions may serve as promising candidates for drug delivery applications.<sup>57</sup>

**ABC triblock copolymers.** Based on the success of AB diblock copolymer synthesis, the synthesis of ABC triblock copolymers was also attempted with a focus on the synthesis of copolymer samples of high molar mass. Due to the versatility of the TEB/onium initiating system,<sup>9,38</sup> as shown in Scheme 1, more than one block could be grown by the ROCOP of CO<sub>2</sub>/epoxide or by the ROP of a cyclic monomer. A similar observation can be made about the RAFT trithiocarbonate



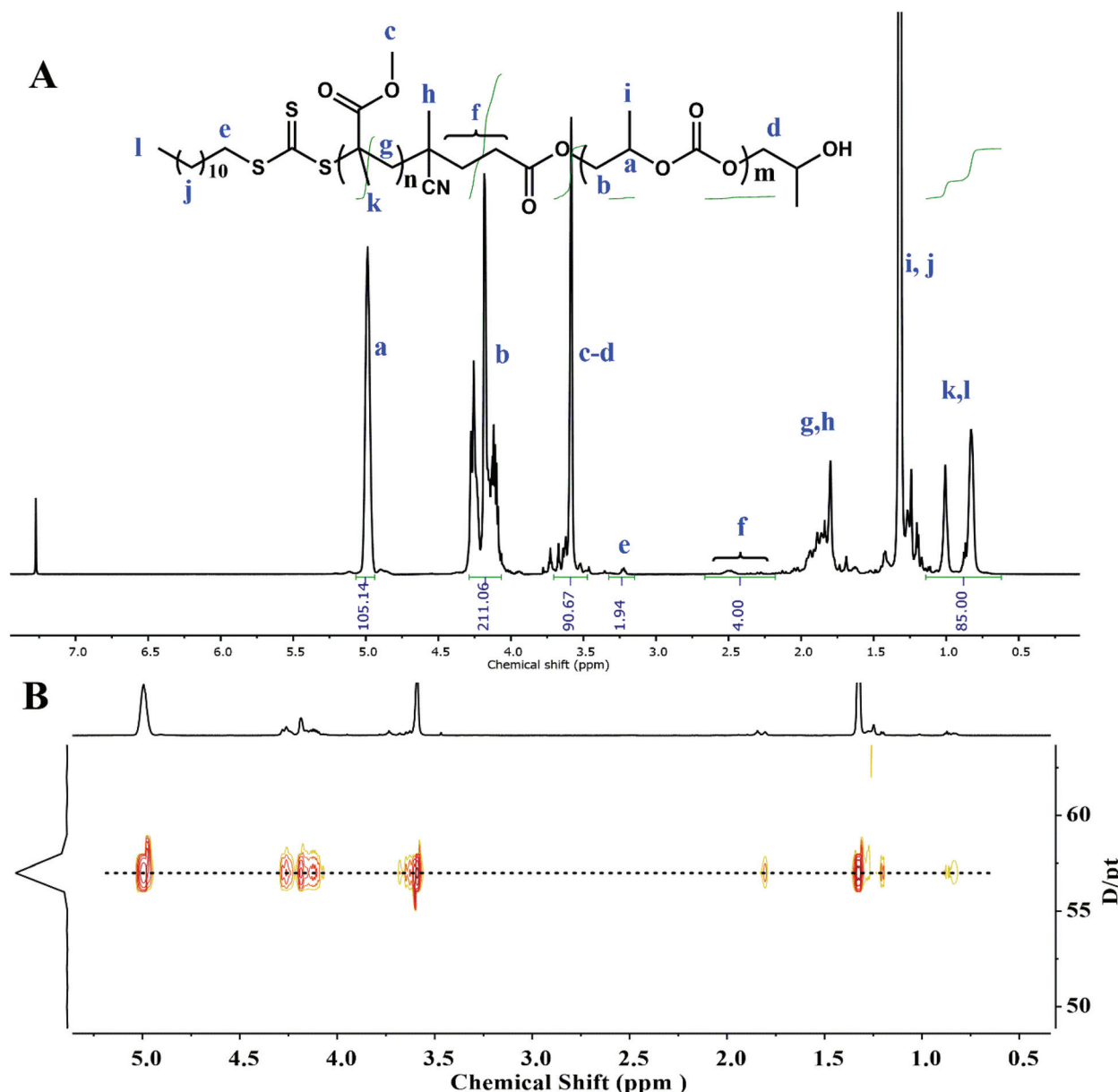


Fig. 2  $^1\text{H}$  NMR spectrum (A) and (B) DOSY NMR spectra of the PPC-*b*-PMMA diblock copolymer in  $\text{CDCl}_3$  (entry 2 in Table 2).

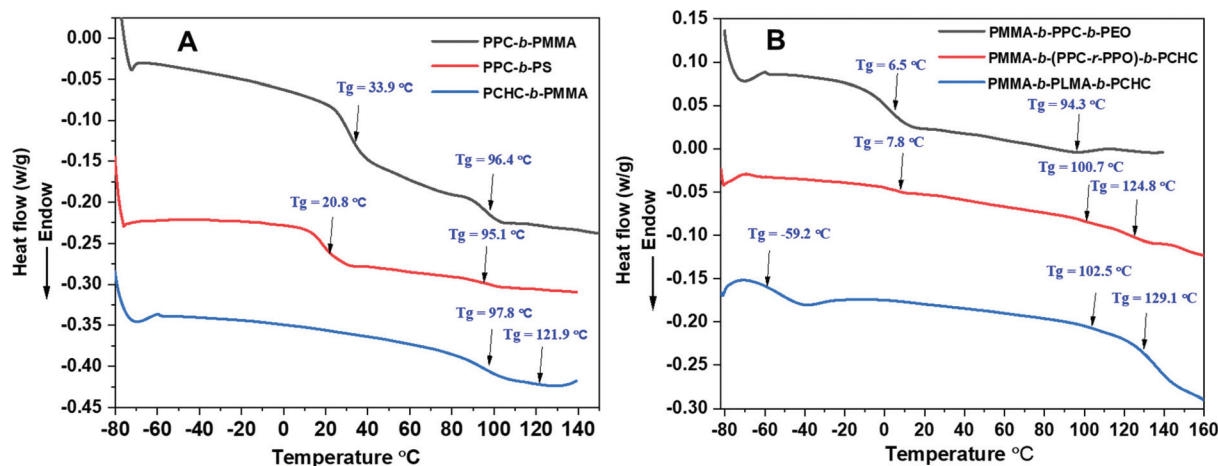
chain transfer agent which also allows the controlled growth of more than one poly(vinyl) block. We have decided to first grow three blocks made of one poly(vinyl) block obtained through the RAFT polymerization of MMA, and two blocks obtained by the ROCOP of  $\text{CO}_2/\text{PO}$  and the ROP of EO. After obtaining the  $\text{PPC}_{105}\text{-}b\text{-PMMA}_{28}$  diblock copolymer (entry 2, Table 2), EO was sequentially charged in the same reactor after the release of  $\text{CO}_2$  and full conversion of PO: the growth of the PEO block afforded an amphiphilic  $\text{PMMA-}b\text{-PPC-}b\text{-PEO}$  triblock copolymer (entry 1, Table 3). A complete shift in the GPC overlay was observed after EO polymerization (Fig. S24 $^\dagger$ ).  $^1\text{H}$  NMR characterization showed the presence of new peaks at  $\delta$  3.65 ppm corresponding to the methylene protons of ethylene oxide units (Fig. S25 $^\dagger$ ). On the other hand, after the simultaneous

ROCOP of  $\text{PO}/\text{CO}_2$  under low pressure ( $\sim 1$  bar) of  $\text{CO}_2$  and the RAFT polymerization of MMA producing the poly(ether-carbonate)-*b*-PMMA diblock copolymer, an alternating polycarbonate block was grown through the ROCOP of  $\text{CHO}/\text{CO}_2$  under 10 bar of  $\text{CO}_2$ : in the latter case  $\text{PMMA-}b\text{-P(PO-}r\text{-PPC)-}b\text{-PCHC}$  triblock copolymers comprising two hard blocks at the end and a soft central poly(ether-carbonate) block were obtained (entry 2, Table 3) (Fig. S26 $^\dagger$ ). Similarly the versatility of our polymerization system was utilized to grow two poly(vinyl) blocks by RAFT polymerization and one block by ROCOP. A  $\text{PCHC-}b\text{-PLMA}$  diblock copolymer was prepared in one-pot by the simultaneous ROCOP of  $\text{CHO}$  with  $\text{CO}_2$  and the RAFT polymerization of (lauryl methacrylate) (LMA) at  $65^\circ\text{C}$  and 10 bar  $\text{CO}_2$  pressure. After releasing  $\text{CO}_2$  RAFT polymerization

**Table 3** One-pot preparation of triblock copolymers through the sequential addition of epoxide or vinyl monomers using TTC-COOH for the ROCOP of epoxide with CO<sub>2</sub> and the RAFT polymerization of vinyl monomers<sup>a</sup>

Polymer designation	Base (B)	Conv. <sup>b</sup> %		PC % PC <sub>1</sub> /PC <sub>2</sub>	<i>M</i> <sub>n(NMR)</sub> <sup>c</sup> (kg mol <sup>-1</sup> )	<i>M</i> <sub>n(GPC)</sub> <sup>d</sup> (kg mol <sup>-1</sup> )/ <i>D</i>
		Ep <sub>1</sub> /Ep <sub>2</sub>	VM			
PMMA <sub>28</sub> -PPC <sub>105</sub> -PEO <sub>58</sub>	TBA	99/98	—	99/0	16.0	13.8/1.04
PMMA <sub>208</sub> -(PPO <sub>404</sub> - <i>r</i> -PPC <sub>77</sub> )-PCHC <sub>180</sub> <sup>e</sup>	TBA	90/99	99	16/99	77.5	57.1/1.1
PMMA <sub>140</sub> -PLMA <sub>310</sub> -PCHC <sub>60</sub>	TBA	99	99	100	101.6	52.4/1.1

<sup>a</sup> Polymerizations were first carried out in a 50 mL Parr reactor under initially 10 bar CO<sub>2</sub> with stirring at 65 °C, then the second monomer was sequentially added and polymerized after the release of CO<sub>2</sub>. <sup>b</sup> Determined from the <sup>1</sup>H NMR of the crude product. For entry 1, Ep<sub>1</sub> = PO and Ep<sub>2</sub> = EO; for entry 2, Ep<sub>1</sub> = PO and Ep<sub>2</sub> = CHO. <sup>c</sup> *M*<sub>n(NMR)</sub> was calculated based on NMR data. <sup>d</sup> Determined by GPC with THF as the eluent and calibrated by a polystyrene standard. <sup>e</sup> PO/CO<sub>2</sub>/MMA polymerization was initially carried out at 1 bar of CO<sub>2</sub> in a 50 mL Parr reactor, then CO<sub>2</sub> was raised to 10 bar after the addition of CHO.



**Fig. 3** DSC graph showing different *T*<sub>g</sub>s for diblock copolymers (A) PPC-*b*-PMMA (entry 3, Table 2), PPC-*b*-PS (entry 6, Table 2), PCHC-*b*-PMMA (entry 5, Table 2); and triblock copolymers (B) PMMA-*b*-PPC-*b*-PEO (entry 1, Table 3), PMMA-*b*-(PPC-*r*-PPO)-*b*-PCHC (entry 2, Table 3), PMMA-*b*-PLMA-*b*-PCHC (entry 3, Table 3).

was carried on upon the addition of MMA; in the latter case a triblock copolymer PMMA-*b*-PLMA-*b*-PCHC (entry 3, Table 3) was obtained (Fig. S27 and S28†). All these three triblock copolymers exhibited unimodal and narrow distributions of molar masses, with peaks characteristic of each block in the <sup>1</sup>H NMR spectra, confirming the triblock nature of the generated copolymers.

**Thermal analysis.** The block copolymers prepared were characterized by thermal analysis using differential scanning calorimetry (DSC). Due to the distinct nature of the composed blocks, two different *T*<sub>g</sub>s corresponding to the polycarbonate block and the vinyl polymer block were detected. As shown in Fig. 3A, PPC-*b*-PMMA (entry 3, Table 2) diblock copolymers show two distinct *T*<sub>g</sub> values around 33.9 °C and 96.4 °C corresponding to the PPC block and the PMMA block; the two other diblock copolymer samples PPC-*b*-PS and PCHC-*b*-PMMA also exhibit two *T*<sub>g</sub>s appearing at 20.8 °C, 95.1 °C and 97.8 °C, 121.9 °C, respectively. In the case of triblock PMMA-*b*-PPC-PEO due to the compatibility between PEO and PPC blocks only two *T*<sub>g</sub>s were observed at 6.5 °C for the PEO-*b*-PPC block and

94.3 °C for the PMMA block. The PMMA-*b*-(PPC-*r*-PPO)-*b*-PCHC (entry 2, Table 3) ABC triblock copolymer with three distinct blocks made up of PMMA and PCHC as hard blocks and poly(propylene ether carbonate) as a middle soft block with 16% carbonate content exhibits three different *T*<sub>g</sub>s corresponding to the three distinct blocks. Here a low carbonate content is the key factor to obtain phase separation between poly(propylene ether carbonate) and the PCHC block. Similarly ABC triblock PMMA-*b*-PLMA-*b*-PCHC (entry 3, Table 3) also exhibits three different *T*<sub>g</sub>s corresponding to three different blocks (Fig. 3B).

## Conclusion

We have demonstrated a convenient process for the one-pot synthesis of di and triblock copolymers obtained through the orthogonal ROCOP of CO<sub>2</sub>/epoxides and the RAFT polymerization of vinyl monomers. Using *in situ* produced TTC-COO<sup>-</sup>, Bu<sub>3</sub>NH<sup>+</sup> salts obtained by the deprotonation of TTC-COOH





with TBA these two distinct (co)polymerizations could be carried out without interference to produce miscellaneous pure diblock AB and triblock ABC copolymers exhibiting a well-defined structure and phase separation. In a subsequent investigation the mechanical behavior of these phase separated triblock copolymers will be disclosed and discussed. Considering the versatility of RAFT polymerization for vinyl monomers and the TEB/onium initiating system for the ROCOP of epoxides with CO<sub>2</sub> and more generally for oxygenated monomers, the described process can be used to produce block copolymers with a wide range of block compositions and structures. In addition, the produced polymers are metal-free and therefore could be resourceful in bio-medical, microelectronic and lithographic areas.

## Experimental section

### Materials and characterization

All chemicals were purchased from Aldrich chemicals and used as received unless otherwise mentioned. PO, CHO, MMA, styrene, DMA, tributyl amine (TBA) were stirred over CaH<sub>2</sub> and distilled under reduced pressure. TTC-COOH was freeze-dried in dioxane. iPr-NHC was prepared from 1,3-diisopropyl imidazolium chloride following a reported procedure.<sup>58</sup> A 1 M solution of iPr-NHC was prepared in THF and stored under argon in a freezer. Tetrahydrofuran (THF) was dried over sodium metal and distilled under reduced pressure. CO<sub>2</sub> (99.995%), purchased from Abdullah Hashim Industrial & Gas Co., was further purified by passing through a CO<sub>2</sub> purifier (VICI Co., US). All <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker AVANCE III-400 Hz, 500 Hz and 600 Hz instrument. GPC traces were recorded by VISCOTEK VE2001 equipped with Styragel HR2 THF and Styragel HR4 THF using THF (1 mL min<sup>-1</sup>) as the eluent. Narrow Mw polystyrene standards were used to calibrate the instrument. MALDI-TOF MS experiments were carried out by using *trans*-2-[3-(4-*t*-butyl-phenyl)-2-methyl-2-propenylidene] malononitrile (DCTB) as the matrix in THF at a loading of 1:5 with sodium trifluoroacetate as an ionizing agent. DSC measurements were performed with a Mettler Toledo DSC1/TC250 under nitrogen. The samples were first heated from 25 °C to 120 °C to erase the thermal history, then cooled to -80 °C, and heated again to 140 °C at a heating rate of 5 °C min<sup>-1</sup> for block copolymers. Dynamic Light Scattering (DLS) measurements were carried out by preparing 0.1 wt% aqueous solution on a Malvern Zetasizer Nano ZS instrument with a 30 mW He-Ne laser light source with emission wavelength 632.8 nm at a scattering angle of 90°.

### Initiator synthesis: synthesis of TTC-COO<sup>-</sup>, Bu<sub>4</sub>N<sup>+</sup>

In a 100 mL round bottom flask equipped with a magnetic stirring bar, 4-cyano-4-[(dodecyl sulfanyl thiocarbonyl) sulfanyl] pentanoic acid (TTC-COOH) (2.02 g, 5.0 mmol) was dissolved in 5 mL of THF. A 55 wt% aqueous solution of tetrabutyl ammonium hydroxide (2.45 mL, 5 mmol) was added and stirred for 1 h. The organic volatiles were removed using a

rotary evaporator. The reaction mixture was further diluted with distilled water. The aqueous solution was lyophilized to obtain dried tetrabutylammonium salt TTC-COO<sup>-</sup>, Bu<sub>4</sub>N<sup>+</sup>.

### Synthesis of the AB diblock copolymer

A typical experimental procedure for one-pot polymerization, represented by entry 2 in Table 2 as an example is described below. A well dried 50 mL Parr reactor in an oven at 120 °C with a magnetic stir bar and a small glass vial inside was immediately transferred into a glovebox under an argon atmosphere. The reactor was cooled to 25 °C and then TTC-COOH (0.1 g, 0.25 mmol) dissolved in 1.5 mL of THF, and TBA (0.012 mL, 0.049 mmol) and TEB (0.49 mL, 1 M solution in THF, 0.49 mmol) were sequentially charged and well mixed. AIBN (0.08 g, 0.049 mmol) and MMA (1.32 mL, 12.4 mmol) were added into the reactor, while propylene oxide (1.74 mL, 24.8 mmol) was added into a glass vial inside the reactor. The reactor was quickly sealed and taken out from the glovebox. After charging CO<sub>2</sub> to a pressure of 10 bar, the reactor was vigorously shaken and polymerization was carried out at 65 °C for 14 h with stirring. The reactor was cooled, the unreacted CO<sub>2</sub> was slowly released, and the polymer solution was quenched inside the glovebox with 1 M HCl solution in THF. The crude product was diluted with THF and purified by precipitation in methanol. The product was collected and dried in a vacuum at 40 °C.

### Synthesis of triblock copolymers

#### Synthesis of ABC triblock copolymer PMMA-*b*-PPC-*b*-PEO.

Following the above reaction procedure for preparing the PPC-*b*-PMMA diblock copolymer (0.125 mmol), EO was charged (0.372 mL, 7.4 mmol) after the release of CO<sub>2</sub> and the reactor was sealed and stirred at 25 °C for 1 h. The polymer solution was quenched inside the glovebox with 1 M HCl solution in THF and purified by precipitation in methanol and dried under vacuum at 40 °C for 48 h.

#### Synthesis of PMMA-*b*-(PPC-*r*-PPO)-*b*-PCHC, ABC tri-block copolymer. Step 1: one pot synthesis of PMMA-*b*-(PPC-*r*-PPO)

The first step for the synthesis of the diblock copolymer is carried out upon modifying the above procedure of synthesis of the AB diblock copolymer. To a well dried reactor, TTC-COOH (0.05 g, 0.124 mmol), TBA (0.012 mL, 0.025 mmol), TEB (0.248 mL, 1 M solution in THF), MMA (0.372 mL, 3.72 mmol), AIBN (3.8 mg, 0.024 mmol) and 2 mL of THF were charged under argon. The reactor was sealed and charged with CO<sub>2</sub> to ensure the reaction occurred under a CO<sub>2</sub> atmosphere and then PO (4.3 mL, 62 mmol) was injected through a syringe and the reactor was connected to a CO<sub>2</sub> line with 1.0 bar continuous pressure. The reaction mixture was stirred at 65 °C for 24 h to ensure the complete consumption of PO.

#### Step-2: synthesis of PMMA-(PPC-*r*-PPO)-*b*-PCHC by sequential addition

Cyclohexene oxide (0.375 mL, 3.72 mmol) was injected into the reactor and CO<sub>2</sub> was re-filled to 10 bar. The reaction was carried at 65 °C for another 14 h, then the reactor was cooled



and excess CO<sub>2</sub> was released. The polymerization was quenched inside the glovebox with 1 M HCl solution in THF, and the mixture was diluted with THF and precipitated in methanol. The precipitation procedure was repeated three times. The obtained polymer was dried in a vacuum at 40 °C.

#### Synthesis of ABC triblock copolymer PMMA-*b*-PLMA-*b*-PCHC. Step 1: one pot synthesis of PCHC-*b*-PLMA

The first step of diblock copolymer synthesis was carried out upon modifying the above procedure of synthesis of the AB diblock copolymer. The procedure followed for entry 2 in Table 3 is described as an example: to a well dried reactor, TTC-COOH (0.05 g, 0.124 mmol), TBA (0.012 mL, 0.025 mmol), TEB (0.248 mL, 1 M solution in THF), CHO (0.75 mL, 7.44), LMA (10.9 mL, 37.2 mmol), AIBN (3.8 mg, 0.024 mmol) and 2 mL of THF were charged under argon. The reactor was sealed and charged with 10 bar CO<sub>2</sub>. The reaction mixture was stirred at 65 °C for 24 h to ensure the complete consumption of monomers, the unreacted CO<sub>2</sub> was released and the reactor was moved to a glovebox.

#### Step-2: synthesis of PMMA-*b*-PLMA-*b*-PCHC by sequential addition

MMA (1.5 mL, 15.0 mmol) was then charged to the reactor and the reaction was carried at 65 °C for another 24 h, then the reactor was cooled and the polymerization was quenched with 1 M HCl solution in THF, the mixture was diluted with THF and precipitated in methanol. The precipitation procedure was repeated three times. The obtained polymer was dried in a vacuum at 40 °C.

## Conflicts of interest

The authors declare no competing financial interest.

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