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Synthesis and polymerization of alkyl halide-functional cyclic carbonates

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ABSTRACT

To increase the diversity in functional aliphatic polycarbonates, a series of novel chloro- and bromo-functional six-membered cyclic carbonate monomers were synthesized. Despite asymmetry in the monomer functionalities, homopolymerization of the monomers afforded semicrystalline polycarbonates with a high tendency to crystallize from the melt and/or on precipitation from a THF solution. Melting points were found in the 90–105 °C or 120–155 °C range for polymers comprising methyl or ethyl moieties, respectively, in the backbone. The monomers were further copolymerized with trimethylene carbonate to form random copolymers. Even among some of these random copolymers elements of semicrystallinity were found as confirmed by melting endotherms in DSC. The results clearly show that the incorporation of alkyl halide functionalities in aliphatic polycarbonates may lead to materials with a high ability to form crystallites, even in random copolymers, likely driven by polar interactions due to the presence of the halide functionalities.

1. Introduction

Aliphatic polycarbonates derived from cyclic carbonates have recently attracted scientific interest for use in biomedical applications [1], largely owing to the biocompatibility and biodegradability of polymers of trimethylene carbonate (TMC), the simplest six-membered cyclic carbonate [2,3]. Much unlike conventional monomers, cyclic carbonates may also undergo volume expansion on polymerization, which has attracted attention for use in applications where net volume contraction is undesirable [4]. Consequently, a wide variety of materials based on polymers of cyclic six-membered carbonates have been synthesized.

Contributing to the synthetic versatility of cyclic carbonates is the diversity in methods available for polymerization; reported polymerization methods include cationic [5,6], anionic [7], enzymatic [8,9], coordination [10] as well as organocatalytic mechanisms [11,12]. With suitable catalyst systems a high level of control over molecular weight and end-group fidelity has been demonstrated as well as complete suppression of decarboxylation associated with the formation of ether groups [11,13].

In an effort to increase the range of applications for these materials by tuning the properties and functionalities of aliphatic polycarbonates, an array of different functional six-membered cyclic carbonate monomers have been synthesized and used for the synthesis of functional materials. These have generally been 2,2-disubstituted trimethylene carbonates, and the structural variety of functional monomers includes e.g. acetal [14,15], alcohol [16], allyl [17], carboxylic acid [18], exomethylene [19], ether [20] and ester [21] functionalities.

In our research on cyclic carbonate monomers, we have turned our attention toward alkyl halide-functional derivatives of TMC as a means of expanding the library of monomers available for ring-opening polymerization. Among cyclic carbonates and cyclic esters, a few examples of halide-functional monomers can be found; Zhang et al. [22] synthesized a 2,2-di(bromomethyl)trimethylene carbonate and Sanders et al. [23] have presented 3-halopropyl ester-functional cyclic carbonates. γ-Bromo [24] as well as α-chloro [25] derivatives of ε-caprolactone are further examples of halide-functional cyclic ester monomers for ring-opening polymerization. Alkyl halide-functional polyesters and polycarbonates from these monomers also constitute reactive substrates for e.g. nucleophilic substitution [22,26,27] and atom transfer radical addition [25] reactions, providing possibilities for post-polymerization functionalization.

In this paper we report on the synthesis of a series of novel alkyl halide-functional cyclic carbonate monomers and the polymerization of these to the corresponding functional aliphatic polycarbonates.

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2. Materials and methods

2.1. Materials

Trimethylene carbonate (Boehringer Ingelheim) and tin(II) 2-ethylhexanoate (Alfa Aesar) were handled and stored in a glove box and used as received. Chloroform-*d* was purchased from Larodan Fine Chemicals and stored over 4 Å molecular sieves and solid K_2CO_3. DMSO-d_6 was purchased from Larodan Fine Chemicals and stored over 3 Å molecular sieves. All other chemicals, including dry dichloromethane (Acros Organics), were obtained from commercial sources and used as received.

2.2. Characterization

^{1}H and ^{13}C NMR spectra were recorded at 25 °C on a JEOL Eclipse+ 400 MHz NMR spectrometer using the residual solvent signal as an internal standard. Quantitative ^{13}C NMR experiments were run using inverse gated decoupling and a relaxation delay of 4 s, assuming equal relaxation times for all carbonyl carbon nuclei. Deconvolution using Lorentzian lineshapes was used to obtain the integrals.

Melting points and glass transition temperatures were determined using differential scanning calorimetry on a TA Instruments DSC Q1000. Melting points for low-molecular-weight compounds were obtained as the onset of the melting endotherm at a heating rate of 0.5 °C/min and the purity (mol%) was estimated using purity analysis in Universal Analysis 2000 version 4.7A (TA Instruments). Any endotherms at higher temperatures were disregarded. Polymer samples were heated to 180 °C at a rate of 10 °C/min and then quenched to −60 °C to erase the thermal history, followed by a heating scan to 180 °C at a rate of 10 °C/min for measurement. Polymer crystallization and melting points are reported as the peak maxima, or the range thereof, of the crystallization exotherm and melting endotherm(s), respectively.

Polymer degradation was measured using thermogravimetric analysis on a TA Instruments TGA Q500. Samples were heated at a rate of 10 °C/min to 500 °C under a nitrogen atmosphere and the decomposition temperature (T_d) was determined as the onset of degradation.

Determination of molecular weights through GPC was performed on a Verotech PL-GPC 50 equipped with a refractive index detector and two PolarGel-M organic GPC columns. Samples were injected using a PL-AS RT autosampler and chloroform was used as the eluent at a flow rate of 1 ml/min. Flow rate fluctuations were corrected by an internal standard and the system was calibrated against narrow polystyrene standards.

Elemental analyses were performed by Analytische Laboratorien, Lindlar, Germany.

2.3. Synthesis of 3-methyl-3-hydroxymethyloxetane

84.1 g (0.700 mol) of trimethylolethane, 85 ml (0.70 mol) of diethyl carbonate and 400 mg (2.9 mmol) of K_2CO_3 were stirred and heated in a 250 ml round-bottom flask. At 130 °C a clear solution was formed and ethanol started to distil off. The pressure was gradually reduced to distil off all of the ethanol formed in the reaction as well as any residual diethyl carbonate. The temperature was increased to 200 °C and the product was distilled off under reduced pressure. Yield: 44.7 g (63%) as a clear liquid, bp 123–129 °C/100 mbar (litt. bp 80 °C/4 Torr [28]). ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ = 1.18 (s, 3H, $-CH_3$), 3.43 (d, 2H, J = 5.5 Hz, $-CH_2-OH$), 4.15 (d, 2H, J = 5.5 Hz, $-CH_2-O$), 4.35 (d, 2H, J = 5.5 Hz, $-CH_2-O$), 4.84 (t, 1H, J = 5.5 Hz, −OH).

2.4. Synthesis of 3-ethyl-3-hydroxymethyloxetane

93.9 g (0.700 mol) of trimethylolpropane, 85 ml (0.70 mol) of diethyl carbonate and 400 mg (2.9 mmol) of K_2CO_3 were stirred and heated in a 250 ml round-bottom flask. At 110 °C a clear solution was formed and at 130 °C ethanol started to distil off. The pressure was gradually reduced to distil off all of the ethanol formed in the reaction as well as any residual diethyl carbonate. The temperature was increased and at 195 °C the product was distilled off under reduced pressure. Yield: 58.4 g (72%) as a clear liquid, bp 122–127 °C/40 mbar (litt. bp 84 °C/2.8 Torr [28]). ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ = 0.82 (t, 3H, J = 7.4 Hz, $-CH_3$), 1.62 (q, 2H, J = 7.4 Hz, $-CH_2-$), 3.50 (d, 2H, J = 5.4 Hz, $-CH_2-OH$), 4.19 (d, 2H, J = 5.6 Hz, $-CH_2-O$), 4.29 (d, 2H, J = 5.6 Hz, $-CH_2-O$), 4.78 (t, 1H, J = 5.4 Hz, −OH).

2.5. General procedure for the synthesis of 2-(halomethyl)-2-alkyl-1,3-propanediols

A solution of 3-alkyl-3-hydroxymethyloxetane (100 mmol) in 100 ml of THF was stirred and cooled in an ice bath. Aqueous mineral acid (25 ml of conc. HCl or 34 ml of conc. HBr, respectively) was added dropwise. The ice bath was removed and the reaction was allowed to proceed at r.t. overnight. The solution was neutralized with 250 ml of saturated $NaHCO_3$ and was extracted with 3 × 200 ml of diethyl ether. The organic phases were retained, dried with $MgSO_4$ and the solvent was evaporated. The crude products were recrystallized from toluene.

2.5.1. Synthesis of 2-(chloromethyl)-2-methyl-1,3-propanediol

Yield: 11.2 g (81%) as white needles, mp 58.1 °C (99.8% purity). Litt. mp 79–80 °C [29]. ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ = 0.83 (s, 3H, $-CH_3$), 3.27 (m, 4H, $-CH_2-OH$), 3.53 (s, 2H, $-CH_2-Cl$), 4.56 (t, 2H, J = 5.3 Hz, −OH). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 17.6 ($-CH_3$), 41.4 (>C<), 49.0 ($-CH_2-Cl$), 68.0 ($-CH_2-OH$). Anal. calcd for $C_5H_{11}ClO_2$: C, 43.33; H, 8.00; Cl, 25.58. Found: C, 43.37; H, 7.72; Cl, 25.40.

2.5.2. Synthesis of 2-(chloromethyl)-2-ethyl-1,3-propanediol

Yield: 13.6 g (89%) as white flakes, mp 63.7 °C (99.8% purity). Litt. mp 62–63 °C [29]. ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ = 0.81 (t, 3H, J = 7.5 Hz, $-CH_3$), 1.27 (q, 2H, J = 7.5 Hz, $-CH_2-$), 3.26 (d, 4H, J = 5.1 Hz, $-CH_2-OH$), 3.51 (s, 2H, $-CH_2-Cl$), 4.49 (t, 2H, J = 5.1 Hz, −OH). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 7.3 ($-CH_3$), 22.8 ($-CH_2-$), 43.6 (>C<), 46.4 ($-CH_2-Cl$), 66.3 ($-CH_2-OH$). Anal. calcd for $C_6H_{13}ClO_2$: C, 47.22; H, 8.59; Cl, 23.23. Found: C, 47.23; H, 8.36; Cl, 23.48.

2.5.3. Synthesis of 2-(bromomethyl)-2-methyl-1,3-propanediol

Yield: 14.8 g (81%) as white needles, mp 70.7 °C (99.8% purity). Litt. mp 72–73 °C [29]. ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ = 0.86 (s, 3H, $-CH_3$), 3.28 (m, 4H, $-CH_2-OH$), 3.46 (s, 2H, $-CH_2-Br$), 4.58 (t, 2H, J = 5.3 Hz, −OH). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 18.6 ($-CH_3$), 39.4 ($-CH_2-Br$), 40.8 (>C<), 68.4 ($-CH_2-OH$). Anal. calcd for $C_5H_{11}BrO_2$: C, 32.81; H, 6.06; Br, 43.65. Found: C, 32.78; H, 6.03; Br, 41.70.

2.5.4. Synthesis of 2-(bromomethyl)-2-ethyl-1,3-propanediol

Yield: 16.0 g (81%) as white flakes, mp 79.9 °C (99.7% purity). Litt. mp 80–81 °C [29]. ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ = 0.80 (t, 3H, J = 7.5 Hz, $-CH_3$), 1.27 (q, 2H, J = 7.5 Hz, $-CH_2-$), 3.26 (d, 4H, J = 5.1 Hz, $-CH_2-OH$), 3.43 (s, 2H, $-CH_2-Br$), 4.51 (t, 2H, J = 5.1 Hz, −OH). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 7.3 ($-CH_3$), 23.6 ($-CH_2-$), 36.8 ($-CH_2-Br$), 42.9 (>C<), 66.6 ($-CH_2-OH$). Anal.

calcd for $C_6H_{13}BrO_2$: C, 36.57; H, 6.65; Br, 40.55. Found: C, 36.53; H, 6.63; Br, 39.40.

2.6. General procedure for the synthesis of 2-(halomethyl)-2-alkyltrimethylene carbonates

To a solution of 2-(halomethyl)-2-alkyl-1,3-propanediol (30.0 mmol) in 160 ml of dry DCM was added 6.3 g (39 mmol) of solid 1,1′-carbonyldiimidazole (CDI) over the course of 1 h. Residual solid CDI stuck to the inside of the glassware was washed into the reaction with a small amount of dry DCM. The reaction mixture was immediately washed with 160 ml of 1 M HCl and 160 ml of saturated $NaHCO_3$. The organic phase was retained, dried with $MgSO_4$ and the solvent was evaporated. The resulting solids were recrystallized from either diethyl ether or a mixture of THF/diethyl ether.

2.6.1. Synthesis of 2-(chloromethyl)-2-methyltrimethylene carbonate (CMTC)

Yield: 2.75 g (66%) as colorless crystals (from THF/diethyl ether), mp 86.1 °C (99.9% purity). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): $\delta = 1.17$ (s, 3H, $-CH_3$), 3.59 (s, 2H, $-CH_2-Cl$), 4.18 (BB′ of AA′BB′, 2H, $-CH_2-O$), 4.34 (AA′ of AA′BB′, 2H, $-CH_2-O$). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): $\delta = 17.7$ ($-CH_3$), 33.6 (>C<), 46.8 ($-CH_2-Cl$), 73.8 ($-CH_2-O$), 147.6 (O–C(=O)–O). Anal. calcd for $C_6H_9ClO_3$: C, 43.78; H, 5.51; Cl, 21.54. Found: C, 43.69; H, 5.52; Cl, 21.97.

2.6.2. Synthesis of 2-(chloromethyl)-2-ethyltrimethylene carbonate (CETC)

Yield 3.97 g (74%) as colorless flakes (from diethyl ether), mp 50.3 °C (99.9% purity). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): $\delta = 0.95$ (t, 3H, $J = 7.7$ Hz, $-CH_3$), 1.60 (q, 2H, $J = 7.7$ Hz, $-CH_2-$), 3.62 (s, 2H, $-CH_2-Cl$), 4.21 (BB′ of AA′BB′, 2H, $-CH_2-O$), 4.33 (AA′ of AA′BB′, 2H, $-CH_2-O$). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): $\delta = 7.1$ ($-CH_3$), 23.4 ($-CH_2-$), 36.1 (>C<), 43.8 ($-CH_2-Cl$), 72.8 ($-CH_2-O$), 147.9 (O–C(=O)–O). Anal. calcd for $C_7H_{11}ClO_3$: C, 47.07; H, 6.21; Cl, 19.85. Found: C, 47.00; H, 6.21; Cl, 20.04.

2.6.3. Synthesis of 2-(bromomethyl)-2-methyltrimethylene carbonate (BMTC)

Yield 3.75 g (60%) as colorless crystals (from THF/diethyl ether), mp 93.8 °C (99.9% purity). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): $\delta = 1.20$ (s, 3H, $-CH_3$), 3.46 (s, 2H, $-CH_2-Br$), 4.21 (BB′ of AA′BB′, 2H, $-CH_2-O$), 4.34 (AA′ of AA′BB′, 2H, $-CH_2-O$). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): $\delta = 18.7$ ($-CH_3$), 32.9 (>C<), 35.6 ($-CH_2-Br$), 74.4 ($-CH_2-O$), 147.5 (O–C(=O)–O). Anal. calcd for $C_6H_9BrO_3$: C, 34.47; H, 4.34; Br, 38.22. Found: C, 34.43; H, 4.54; Br, 37.45.

2.6.4. Synthesis of 2-(bromomethyl)-2-ethyltrimethylene carbonate (BETC)

Yield 4.16 g (62%) as colorless flakes (from diethyl ether), mp 55.4 °C (>99.9% purity). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): $\delta = 0.92$ (t, 3H, $J = 7.7$ Hz, $-CH_3$), 1.59 (q, 2H, $J = 7.7$ Hz, $-CH_2-$), 3.46 (s, 2H, $-CH_2-Br$), 4.23 (BB′ of AA′BB′, 2H, $-CH_2-O$), 4.32 (AA′ of AA′BB′, 2H, $-CH_2-O$). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): $\delta = 7.0$ ($-CH_3$), 24.1 ($-CH_2-$), 32.8 ($-CH_2-Br$), 35.2 (>C<), 73.3 ($-CH_2-O$), 147.9 (O–C(=O)–O). Anal. calcd for $C_7H_{11}BrO_3$: C, 37.69; H, 4.97; Br, 35.82. Found: C, 37.61; H, 5.09; Br, 35.60.

2.7. General procedure for the polymerization of 2-(halomethyl)-2-alkyltrimethylene carbonates

In a glove box, 2-(halomethyl)-2-alkyltrimethylene carbonate (1 g) and $Sn(Oct)_2$ catalyst (5–11% relative to initiator) were combined in an oven-dried 50 ml round-bottom flask. The flask was sealed with a septum and transferred out. Using a syringe, benzyl alcohol was added as an initiator and the flask was heated under magnetic stirring at 110 °C for polymerization. CMTC and BMTC polymers were purified by dissolving in THF and precipitating in cold methanol, followed by drying *in vacuo* at 40 °C.

2.8. General procedure for the copolymerization of 2-(halomethyl)-2-alkyltrimethylene carbonates with trimethylene carbonate

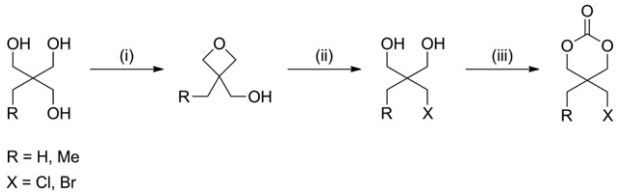
In a glove box, 2-(halomethyl)-2-alkyltrimethylene carbonate and trimethylene carbonate were combined (a total of 1 g), in a 1:1 molar ratio, with $Sn(Oct)_2$ catalyst (5–9% relative to initiator) in an oven-dried 50 ml round-bottom flask. The flask was sealed with a septum and transferred out. Using a syringe, benzyl alcohol was added as an initiator and the flask was heated under magnetic stirring at 110 °C for polymerization. The resulting polymers were purified by dissolving in THF and precipitating in cold methanol, followed by drying *in vacuo* at 40 °C.

3. Results and discussion

3.1. Monomer synthesis

To broaden the diversity of aliphatic polycarbonates, we have synthesized a series of alkyl halide-functional cyclic carbonate monomers. In a three-step synthesis, as outlined in Scheme 1, chloro- and bromo-functional six-membered cyclic carbonates were synthesized using a common synthetic pathway. Starting from trimethylolethane and trimethylolpropane, respectively, hydroxy-functional oxetanes were synthesized through transesterification with diethyl carbonate and decarboxylation under basic conditions. This transesterification reaction can be used to synthesize the corresponding hydroxyl-functional six-membered carbonate as well as the oxetane. The cyclic carbonate, however, is prone to decarboxylation, a fact that is well-known from literature [28,30], and only the pure 3-hydroxymethyloxetanes were obtained under the reaction conditions used. The oxetanes were subsequently ring-opened using concentrated aqueous solutions of HCl and HBr according to a procedure similar to that described by Rosen et al. [31], yielding halide-functional 1,3-propanediols suitable for the synthesis of the cyclic six-membered carbonates.

For the synthesis of cyclic carbonate monomers from 1,3-propanediols several methods have been described [1]. Transacylation is suitable for large-scale preparation of cyclic carbonates, employing e.g. a dialkyl carbonate [32] or urea [33] as the carbonyl source and producing alcohols and ammonia, respectively, as by-products under rather harsh conditions. An alternative that is more suitable on a laboratory scale is to use a phosgene derivative as the carbonyl source. Standard methods for the synthesis of cyclic carbonate monomers employ triphosgene [34] as well as ethyl chloroformate [13] for the formation of the six-membered ring. As these reagents are highly reactive, the reactions are typically conducted at temperatures below ambient.



Scheme 1. Synthesis of 2-(halomethyl)-2-alkyltrimethylene carbonates starting from trimethylolethane (R = H) and trimethylolpropane (R = Me), respectively. Reaction conditions: (i) Diethyl carbonate, K_2CO_3, Δ; (ii) HX, THF, 0 °C/r.t.; (iii) CDI, DCM, r.t.

Table 1
Polymerization and molecular weight data for alkyl halide-functional homopolycarbonates.

Polymer	[M]/[I][a]	t (h)	Yield[b] (%)	$M_{n,\ theory}$[c] (kg/mol)	$M_{n,\ NMR}$[d] (kg/mol)	$M_{n,\ GPC}$[e] (kg/mol)	PDI[e]
$PCMTC_{40}$	40	4	81	6.7	7.5	16.5	1.46
$PCMTC_{100}$	100	16	88	16.6	21.3	38.5	1.69
$PCETC_{40}$	40	4	97[b]	7.2	8.6	16.0	1.46
$PCETC_{100}$	100	16	97[b]	18.0	20.0	20.9	1.81
$PBMTC_{40}$	40	4	75	8.5	9.9	14.3	1.42
$PBMTC_{100}$	100	16	89	21.0	27.7	51.9	1.63
$PBETC_{40}$	40	4	97[b]	9.0	9.1	8.5	1.41
$PBETC_{100}$	100	16	96[b]	22.4	23.7	31.9	1.62

[a] Targeted DP.
[b] For largely insoluble polymers, the conversion as determined by ^{1}H NMR is reported instead of the isolated yield.
[c] Targeted molecular weight.
[d] Determined by ^{1}H NMR end-group analysis.
[e] Determined by GPC.

To facilitate the use of mild reaction conditions and avoid the use of highly toxic phosgene derivatives, 1,1′-carbonyldiimidazole (CDI) was used as the ring-closing reagent at room temperature. Experimental data suggest that the reactivity of the second imidazolide group of CDI is significantly lower than the first; whereas the diimidazolide readily reacts with alcohols at room temperature, reactions with secondary and tertiary alcohols yield nothing but the respective alkyl carbamates [35]. In the synthesis of cyclic carbonates, the second reaction step would be intramolecular, and the lower reactivity of the second imidazolide group could thus expected to be less of an issue than for the synthesis of acyclic carbonates. Indeed, upon gradual addition of a slight excess of solid CDI to solutions of the 1,3-propanediols in dry DCM, the cyclic carbonates were obtained in what appeared to be an instant reaction. The formation of the cyclic carbonates was indicated by the appearance of the AA′BB′ multiplet pattern in ^{1}H NMR typical of 2,2-disubstituted trimethylene carbonates, resulting from a weak w-coupling between equatorial protons in the 1- and 3-positions. No formation of any major by-products other than imidazole was observed, and the imidazole formed could easily be removed through acidic work-up following the reaction. Simple recrystallizations afforded the pure monomers.

3.2. Homopolymerization of alkyl halide-functional cyclic carbonates

The alkyl halide-functional monomers CMTC, CETC, BMTC and BETC were all successfully polymerized at 110 °C in bulk using $Sn(Oct)_2$ as a catalyst and benzyl alcohol as a protic initiator to control the molecular- weight. Low-molecular-weight (targeted DP = 40) as well as high-molecular weight (targeted DP = 100) polymers were synthesized from each monomer, denoted by a subscript 40 and 100, respectively. Polymerization and molecular weight data for each polymer are summarized in Table 1.

All homopolymers were obtained as opaque solids, indicating semicrystallinity. The crystallinity of PCETC and PBETC was found to render the polymers virtually insoluble in common organic solvents such as DCM, chloroform, THF and DMF. Although small samples were possible to dissolve in chloroform to allow for NMR and GPC analyses, the solubilities were too low to permit purification by precipitation, and these polymers were instead analyzed further as the crude materials. The methyl-functional PCMTC and PBMTC, however, were freely soluble in chloroform as well as THF, and could thus be easily manipulated.

The structure of the polymers was confirmed by ^{1}H NMR. As can be seen in Fig. 1, the spectra displayed well-defined peaks that were easily assigned. For the bromo-functional polymers PBMTC and PBETC, a broad doublet from the methylene protons geminal to the ω-end-group hydroxyl could be identified at ~3.5 ppm and the size of its integral corresponded well to the integral of the signal from the methylene protons of the α-end benzyl group at ~5.2 ppm. In the spectra corresponding to the chloro-functional polymers,

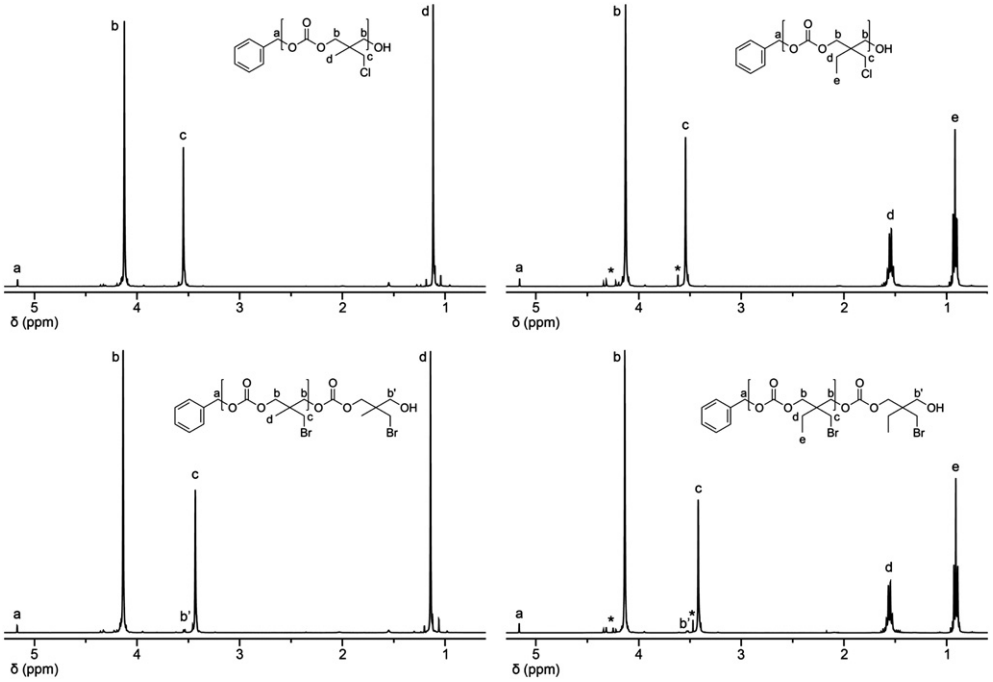


Fig. 1. ^{1}H NMR spectra of chloro-functional homopolycarbonates $PCMTC_{40}$ (top left) and $PCETC_{40}$ (top right) as well as bromo-functional homopolycarbonates $PBMTC_{40}$ (bottom left) and $PBETC_{40}$ (bottom right) in $CDCl_3$. The aromatic region comprising the phenyl group of the benzyl alcohol initiator and the residual solvent signal has been omitted. * indicates monomer residues.

Table 2
Thermal analysis data for alkyl halide-functional homopolycarbonates.

Polymer	T_g (°C)	T_c (°C)	T_m (°C)	T_d (°C)
$PCMTC_{40}$	14.7	57.5	90.4	240.7
$PCMTC_{100}$	n/o[a]	74.7[b]	105.3	249.3
$PCETC_{40}$	9.5	53.1	131.7–150.1	239.6
$PCETC_{100}$	12.5	56.5	131.1–151.6	255.7
$PBMTC_{40}$	17.9	n/o[a]	96.2[c]	240.0
$PBMTC_{100}$	22.6	n/o[a]	100.1[c]	263.7
$PBETC_{40}$	14.7	83.7	120.5–150.6	230.2
$PBETC_{100}$	17.5	89.5	124.8–153.3	265.6

[a] Not observed.
[b] Measured during quench.
[c] Measured during the 1st heating scan.

however, this ω-end-group peak was obscured by the peak from the protons of the repeating unit chloromethyl group.

3.3. Thermal properties and crystallinity

The thermal properties of the alkyl halide-functional homopolycarbonates, as measured by DSC and TGA, are summarized in Table 2. All polymers were found to be semicrystalline, but with widely differing crystallization behavior. As the polymerization temperature was below the melting temperature of the ethyl-functional PBETC and PCETC, these polymers crystallized during polymerization, whereas PCMTC crystallized immediately upon cooling after polymerization. PBMTC did not crystallize on cooling of the melt following polymerization, but crystallized when precipitated from THF into cold methanol. These differences in the ease and rate of crystallization were also apparent in DSC measurements, where neither $PBMTC_{40}$ nor $PBMTC_{100}$ was able to recrystallize after the first heating scan above the melting temperature. High-molecular-weight PCMTC, on the other hand, showed crystallization even during rapid cooling. In fact, for $PCMTC_{100}$ the crystallization was so rapid that the sample reached full crystallization during the cooling quench, as indicated by the absence of a crystallization exotherm during the second heating cycle. The high level of crystallinity of this material also hindered the detection of the glass transition during the second heating cycle.

When a lower cooling rate (5 °C/min) was used, PCETC as well as PCMTC crystallized during cooling, indicating higher crystallization rates for the chloro-functional polymers as compared to the bromo-functional polymers. None of the polymers showed crystallization during the first heating cycle. The glass transition temperatures were in the same range for all polymers with slight differences depending on the respective functionality (Fig. 2). Bromo-functional polymers were found to have a T_g higher than for the corresponding chloro-functional polymers, and methyl-functional polymers were found to have a higher T_g than the corresponding ethyl-functional polymers. The lower glass transition temperatures observed for the ethyl-functional polymers can likely be attributed to increased mobility introduced by the ethyl moiety. The observed melting points were also consistently higher for the ethyl-functional polymers as compared to the methyl-functional polymers.

Although it is interesting to note that these asymmetrically functionalized polymers are all semicrystalline, it is by no means the first time such a behavior has been observed. In fact, semicrystallinity has been observed for several polymers of 2,2-difunctional trimethylene carbonates, including poly(2-ethyl-2-hydroxymethyltrimethylene carbonate) [36], poly(2-cyano-2-methyltrimethylene carbonate) [37] as well as the ester-functional poly(2-acetoxymethyl-2-ethyltrimethylene carbonate) and poly(2-methoxycarbonyl-2-methyltrimethylene carbonate) [16]. With the exception of poly(2-cyano-2-methyltrimethylene carbonate), however, all of these asymmetrically difunctional polymers only displayed melting endotherms on the first heating in DSC [16], whereas the majority of the alkyl halide-functional polycarbonates easily crystallize from the melt. Similar to what was proposed for poly(2-cyano-2-methyltrimethylene carbonate) [37], it is believed that the crystallization behavior of these alkyl halide-functional polymers can be largely attributed to polar interactions due to the presence of the halide functionalities.

3.4. Copolymerization of alkyl halide-functional cyclic carbonates with TMC

A common procedure to tune the properties of functional polymers is to synthesize copolymers that include several functional monomers. To show the synthetic versatility of the alkyl halide-functional monomers, a series of copolymers with TMC were synthesized in bulk using a similar procedure to the synthesis of the halide-functional homopolymers. Low-molecular-weight (targeted DP = 40) and high-molecular-weight (targeted DP = 100) copolymers were synthesized, denoted by a subscript 40 and 100, respectively. The polymerizations are summarized in Table 3.

The repeating unit sequence distribution of the copolymers was characterized using ^{13}C NMR, utilizing the fact that the peak corresponding to the carbonyl carbon of the carbonate groups appeared at distinctly different shifts depending on the dyad connected by the respective carbonate group. As can be seen in Fig. 3, the peak corresponding to the TMC–TMC (TT) and TMC–halocarbonate (TH) dyads consistently appeared downfield relative to the peak corresponding to the halocarbonate–halocarbonate (HH) dyad. This allowed for the quantitative determination of the dyad distribution and the determination of the respective number-

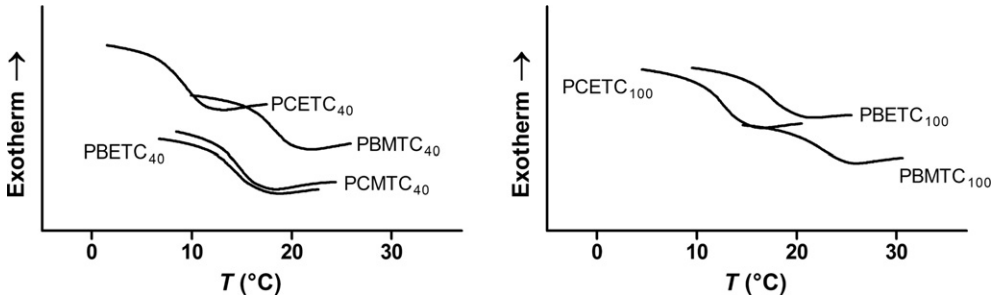


Fig. 2. DSC glass transition traces for low-molecular-weight (left) and high-molecular-weight polymers (right) of alkyl halide-functional cyclic carbonates. Data are normalized to sample mass. No glass transition could be detected for $PCMTC_{100}$ due to excessive crystallinity.

Table 3
Polymerization and molecular weight data for copolymers of alkyl halide-functional cyclic carbonates and TMC.

Polymer	[M]/[I][a]	f_{TMC}[b]	F_{TMC}[c]	t (h)	Yield (%)	$M_{n,\ theory}$[d] (kg/mol)	$M_{n,\ NMR}$[e] (kg/mol)	$M_{n,\ GPC}$[f] (kg/mol)	PDI[f]
Poly(CMTC-*co*-TMC)$_{40}$	40	0.50	0.47	4	87	5.4	6.2	16.3	1.52
Poly(CMTC-*co*-TMC)$_{100}$	100	0.50	0.46	16	81	13.4	15.8	39.7	1.64
Poly(CETC-*co*-TMC)$_{40}$	40	0.50	0.49	4	70	5.7	7.5	21.5	1.51
Poly(CETC-*co*-TMC)$_{100}$	100	0.50	0.44	16	73	14.1	17.7	44.8	1.64
Poly(BMTC-*co*-TMC)$_{40}$	40	0.50	0.48	4	69	6.3	7.9	21.4	1.53
Poly(BMTC-*co*-TMC)$_{100}$	100	0.50	0.45	16	83	15.7	20.5	45.3	1.71
Poly(BETC-*co*-TMC)$_{40}$	40	0.50	0.47	4	81	6.6	7.0	18.4	1.54
Poly(BETC-*co*-TMC)$_{100}$	100	0.50	0.43	16	84	16.4	16.7	38.0	1.67

[a] Targeted DP.
[b] Molar fraction of TMC in feed.
[c] Molar fraction of TMC in the isolated polymer.
[d] Targeted molecular weight.
[e] Determined by ^{1}H NMR end-group analysis.
[f] Determined by GPC.

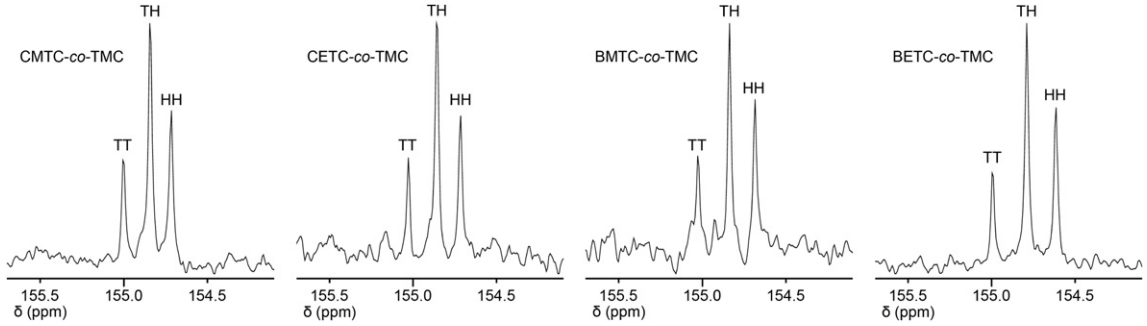


Fig. 3. ^{13}C NMR carbonyl region of high-molecular-weight copolymers of alkyl halide-functional cyclic carbonates and TMC. Signals labeled TT, TH and HH correspond to TMC–TMC, TMC–halocarbonate and halocarbonate–halocarbonate dyads, respectively.

average sequence lengths $\bar{n}_x$ of the different repeating units according to the following equations [38]:

$$\bar{n}_{TMC} = \frac{N_{TT} + \frac{1}{2}N_{TH}}{\frac{1}{2}N_{TH}} \quad (1)$$

$$\bar{n}_{H} = \frac{N_{HH} + \frac{1}{2}N_{TH}}{\frac{1}{2}N_{TH}} \quad (2)$$

where N_i is the relative frequency of the respective dyad, given by the dyad distribution. The thus obtained sequence lengths, as well as the sequence lengths predicted by Bernoullian statistics [38], can be found in Table 4.

Table 4
Number-average sequence lengths of the respective repeating units for copolymers of alkyl halide-functional cyclic carbonates and TMC.

Polymer	$\bar{n}_{TMC}$ [exptl[a] (calcd[b])]	$\bar{n}_{H}$ [exptl[a] (calcd[b])]
Poly(CMTC-*co*-TMC)$_{40}$	1.94 (1.90)	2.24 (2.12)
Poly(CMTC-*co*-TMC)$_{100}$	1.79 (1.86)	2.21 (2.16)
Poly(CETC-*co*-TMC)$_{40}$	2.12 (1.95)	2.06 (2.06)
Poly(CETC-*co*-TMC)$_{100}$	1.79 (1.79)	2.27 (2.27)
Poly(BMTC-*co*-TMC)$_{40}$	1.68 (1.93)	2.11 (2.07)
Poly(BMTC-*co*-TMC)$_{100}$	2.03 (1.81)	2.51 (2.23)
Poly(BETC-*co*-TMC)$_{40}$	1.84 (1.89)	2.07 (2.13)
Poly(BETC-*co*-TMC)$_{100}$	1.75 (1.76)	2.42 (2.31)

[a] Determined using quantitative ^{13}C NMR.
[b] Predicted from the observed molar fraction of TMC in the isolated polymer using Bernoullian statistics.

The experimentally determined number-average repeating unit sequence lengths are generally in good agreement with those predicted by the Bernoullian model. This indicates that the copolymers are largely statistical in composition, and that the reactivities in the ring-opening polymerization are similar for TMC and the alkyl halide-functional cyclic carbonate monomers.

As would be expected for such statistical 1:1 copolymers, the copolymers were typically obtained as largely transparent, rubbery materials, with the notable exception of poly(CETC-*co*-TMC)$_{100}$, which on inspection was found to be an opaque, soft and surprisingly tough material. DSC confirmed semicrystallinity, with a bimodal melting endotherm detected at 65.6–88.0 °C (Fig. 4) during the first heating cycle, significantly lower than for the CETC homopolymers (see Table 2). A closer investigation also confirmed semicrystallinity for the low-molecular-weight CETC–TMC copolymer (T_m = 61.1 °C) as well as the BETC–TMC copolymers

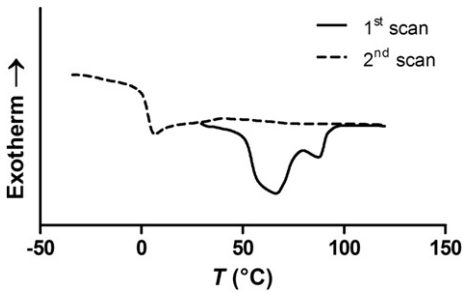


Fig. 4. DSC traces displaying the melting endotherm (1st scan) as well as the glass transition (2nd scan) for poly(CETC-*co*-TMC)$_{100}$.

(T_m = 51.6–67.2 °C and T_m = 64.2 °C for the low- and high-molecular-weight polymers, respectively). Crystallization was absent during cooling as well as heating, and no melting endotherm was detected during the second heating cycle for either of the materials. It should also be noted that homopolymerization of the CETC and BETC monomers afforded the highest-melting homopolycarbonates, suggesting a high ability for these repeating units to form crystallites.

It is remarkable that despite the random structure of the polymer, the CETC and BETC repeating units are able to impart semicrystallinity to the materials, giving particularly the high-molecular-weight CETC–TMC copolymer drastically different properties from the other copolymers. Again, the same crystallization phenomenon has been described for copolymers of 2-cyano-2-methyltrimethylene carbonate and 2,2-dimethyltrimethylene carbonate [37], further supporting the view that polar interactions due to the halide functionalities are the main driving force for the crystallization of these alkyl halide-functional polycarbonates.

4. Conclusion

Pathways for the synthesis of alkyl halide-functional six-membered cyclic carbonates were developed and utilized to synthesize a series of novel chloro- and bromo-functional cyclic carbonate monomers – CMTC, CETC, BMTC and BETC. The monomers were successfully polymerized in bulk using $Sn(Oct)_2$ as a catalyst to form the high- and low-molecular-weight homopolycarbonates as well as 1:1 random copolymers with TMC. Homopolymerization consistently afforded semicrystalline polymers, with a tendency to crystallize that ranged from PBMTC, crystallizing only following precipitation from a THF solution, to PCMTC, which as a high-molecular-weight material crystallized from the melt even during rapid cooling to a high enough extent to completely obscure the glass transition in DSC measurements. PCETC and PBETC were also found to crystallize easily, although for these polymers it was possible to obtain amorphous materials by rapid cooling of the respective melts. Thermal analysis further revealed similar glass transition temperatures for all homopolycarbonates, whereas the melting points were found to be dependent on primarily the alkyl rather than the halomethyl functionality of the repeating unit.

Copolymerization of the alkyl halide-functional monomers with TMC afforded random copolycarbonates. Quite unexpectedly, copolymers of CETC and TMC, as well as BETC and TMC, were found to be semicrystalline, with a higher extent of crystallinity for the high-molecular-weight CETC–TMC copolymer, giving a completely different material as compared to the other copolymers.

The results show that the incorporation of halide functionalities in the polymer chains leads to efficient formation of semicrystalline polycarbonates, particularly considering the asymmetry of the functional polymer backbone. The crystallization is likely driven by polar interactions due to the halide functionalities along the polymer chains.

The high ability of the alkyl halide-functional repeating units to crystallize enables the potential use of materials synthesized using these cyclic carbonate monomers for applications such as fibers and biodegradable thermoplastic elastomers. Further functionalization of the polymer backbones using nucleophilic substitution or atom transfer radical addition is also a possible route toward new functional materials starting from these monomers. It is our hope that the addition of this series of functional cyclic carbonate monomers to the set of cyclic ester monomers available to polymer chemistry will aid in the design of functional polymers and thus provide opportunities for the synthesis of new and unique functional polymer materials.

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Appendix. Supplementary material

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.polymer.2011.10.027.

References

[1] Rokicki G. Prog Polym Sci 2000;25(2):259–342.
[2] Zhu KJ, Hendren RW, Jensen K, Pitt CG. Macromolecules 1991;24(8):1736–40.
[3] Zhang Z, Kuijer R, Bulstra SK, Grijpma DW, Feijen J. Biomaterials 2006;27(9):1741–8.
[4] Takata T, Sanda F, Ariga T, Nemoto H, Endo T. Macromol Rapid Commun 1997;18(6):461–9.
[5] Kricheldorf HR, Dunsing R, Serra i Albet A. Makromol Chem 1987;188(10):2453–66.
[6] Kricheldorf HR, Jenssen J. J Macromol Sci Chem 1989;A26(4):631–44.
[7] Keul H, Bacher R, Hocker H. Makromol Chem 1986;187(11):2579–89.
[8] Bisht KS, Svirkin YY, Henderson LA, Gross RA, Kaplan DL, Swift G. Macromolecules 1997;30(25):7735–42.
[9] Matsumura S, Tsukada K, Toshima K. Macromolecules 1997;30(10):3122–4.
[10] Kricheldorf HR, Jenssen J, Kreiser-Saunders I. Makromol Chem 1991;192(10):2391–9.
[11] Nederberg F, Lohmeijer BGG, Leibfarth F, Pratt RC, Choi J, Dove AP, et al. Biomacromolecules 2007;8(1):153–60.
[12] Mindemark J, Hilborn J, Bowden T. Macromolecules 2007;40(10):3515–7.
[13] Ariga T, Takata T, Endo T. J Polym Sci Part A Polym Chem 1993;31(2):581–4.
[14] Chen XH, McCarthy SP, Gross RA. J Appl Polym Sci 1998;67(3):547–57.
[15] Vandenberg EJ, Tian D. Macromolecules 1999;32(11):3613–9.
[16] Weilandt KD, Keul H, Hocker H. Macromol Chem Phys 1996;197(11):3851–68.
[17] Mullen BD, Tang CN, Storey RF. J Polym Sci Part A Polym Chem 2003;41(13):1978–91.
[18] Al-Azemi TF, Bisht KS. J Polym Sci Part A Polym Chem 2002;40(9):1267–74.
[19] Takata T, Igarashi M, Endo T. J Polym Sci Part A Polym Chem 1991;29(5):781–4.
[20] Al-Azemi TF, Bisht KS. Macromolecules 1999;32(20):6536–40.
[21] Liu ZL, Zhou Y, Zhuo RX. J Polym Sci Part A Polym Chem 2003;41(24):4001–6.
[22] Zhang QJ, Zhu WP, Shen ZQ. Chin Chem Lett 2010;21(10):1255–8.
[23] Sanders DP, Fukushima K, Coady DJ, Nelson A, Fujiwara M, Yasumoto M, et al. J Am Chem Soc 2010;132(42):14724–6.
[24] Detrembleur C, Mazza M, Halleux O, Lecomte P, Mecerreyes D, Hedrick JL, et al. Macromolecules 2000;33(1):14–8.
[25] Lenoir S, Riva R, Lou X, Detrembleur C, Jerome R, Lecomte P. Macromolecules 2004;37(11):4055–61.
[26] Nederberg F, Zhang Y, Tan JPK, Xu KJ, Wang HY, Yang C, et al. Nat Chem 2011;3(5):409–14.
[27] Riva R, Schmeits S, Jerome C, Jerome R, Lecomte P. Macromolecules 2007;40(4):796–803.
[28] Pattison DB. J Am Chem Soc 1957;79(13):3455–6.
[29] Reiff H, Dieterich D, Braden R, Ziemann H. Liebigs Ann 1973;1973(3):365–74.
[30] Jansen J, Dias AA, Dorschu M, Coussens B. Macromolecules 2003;36(11):3861–73.
[31] Rosen BM, Lligadas G, Hahn C, Percec V. J Polym Sci Part A Polym Chem 2009;47(15):3931–9.
[32] Carothers WH, Van Natta FJ. J Am Chem Soc 1930;52:314–26.
[33] Bhanage BM, Fujita S, Ikushima Y, Arai M. Green Chem 2003;5(4):429–32.
[34] Burk RM, Roof MB. Tetrahedron Lett 1993;34(3):395–8.
[35] Rannard SP, Davis NJ. Org Lett 1999;1(6):933–6.
[36] Kuhling S, Keul H, Hocker H, Buysch HJ, Schon N. Makromol Chem 1991;192(5):1193–205.
[37] Kalbe M, Keul H, Hocker H. Macromol Chem Phys 1995;196(10):3305–21.
[38] Randall JC. Polymer sequence determination: carbon-13 NMR method. New York: Academic Press; 1977.