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Dual Versatility of Triazolium-Based Cyclic Carbonate Inimer: From Homopolymerization to On-Demand Thermally Activated Initiating Site

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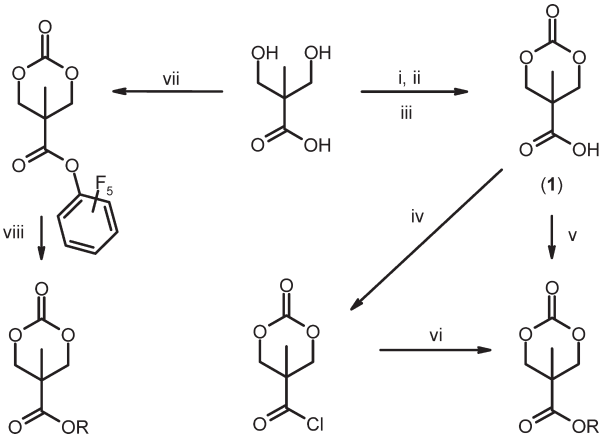
Supporting Information

Over the past decades, associations of complementary polymerization techniques have attracted considerable attention since they allow the preparation of materials generated from monomers that polymerize either by different mechanisms or from disparate catalysts. To date, block,[1] brushlike,[2] grafted,[3] star-shaped,[4] miktoarm,[5] and cross-linked copolymers[6] have been prepared by various strategies employing dual initiators or chain-ends/dangling groups transformations. Subsequently, inimers and functional monomers bearing an active initiator as a pendent group have also been developed.[7] In 2008, Hedrick et al. demonstrated the feasibility to produce a six-membered cyclic carbonate ring bearing different esters as easily obtained from the 2,2-bis(methylol)propionic acid (Scheme 1, steps i to vi).[8] Since ring-opening polymerization (ROP) mediated by metal-free organocatalytic systems has recently emerged as a tremendous research area,[9] and because the ROP of cyclic carbonates provides narrowly dispersed polymers of predictable molecular weights and end-group fidelity,[10] some of us demonstrated that cyclic carbonate ring bearing a reversible addition−fragmentation chain transfer (RAFT) function might be easily prepared and polymerized in the absence of metal residue.[11] Whatever the origin of the side group present on the cyclic carbonate ring, the approach developed by Hedrick requires the esterification of a six-membered cyclic carbonate ring bearing free carboxylic acid group, **1**, with a suitable ROH alcohol (Scheme 1, steps i to vi).

In order to shortcut the preparation of functionalized cyclic carbonates, an improved two-step route featuring a cyclic carbonate functionalized by a pentafluorophenyl ester group has then been developed by the same group (Scheme 1, steps vii to viii).[12] The elevated cost of production of such versatile ester intermediate prompted us to investigate the direct protection of **1** by an equimolar amount of 1,3,4-triphenyl-4,5-dihydro-1*H*-1,2,4-triazol-5-ylidene since such triazolium carbene is known to react quantitatively with free carboxylic acid functions at room temperature.[13] Since carboxylic acid/triazolium adduct is an efficient initiating system for the ROP of [*R*,*S*]-*β*-butyrolactone (BL) at high temperature,[13c] the preparation of such triazolium ester cyclic carbonate, **2**, is of interest since the triazolium function might act as either thermally removable protecting group of **1** or "catalyst" for the ROP of BL at elevated temperature.

We reasoned that if the triazolium ester cyclic carbonate **2** is stable at rt and if the catalytic system designed for its (co)polymerization is compatible with free triazolium carbene and carboxylic acid at elevated temperature, then a one-pot process might be expected for the preparation of model copolymers composed by a polycarbonate backbone grafted by polyester chains.

Scheme 1. Synthesis of 1-Type Monomers Adapted from Ref 8[a]



[a] Conditions: (i) BnBr, DMF, KOH, 100 °C, 15 h; (ii) triphosgene, pyridine, CH_2Cl_2, −78 → 0 °C; (iii) H_2, Pd/C, EtOAc, rt, 24 h; (iv) $(COCl)_2$, THF, rt, 1 h; (v) ROH, DCC, THF, rt, 16 h; (vi) ROH, NEt_3, rt, 3 h; (vii) $(C_6F_5O)_2CO$, CsF, 20 h; (viii) ROH, Nu.

To date, a large variety of selected functionalized cyclic carbonate monomers have been polymerized by using a catalytic system composed by an equimolar mixture of 1-(3,5-bis(trifluoromethyl)phenyl)-3-cyclohexyl-2-thiourea (TU) and 1,8-diazabicyclo-[5.4.0]undec-7-ene (DBU).[8,11,12] Despite its very high ROP activity, DBU (and by correlation 1,5,7-triazabicyclo[4.4.0]dec-5-ene, TBD) causes at high temperature some degradation when exposed to polylactide (PLA) chains and more especially if that base is in the presence of carboxylic acid residues.[14] Fearing an even faster degradation on PBL chains by transesterification, the TU/DBU association has been ruled out. Alternatively, some of us demonstrated that the association of fluorinated tertiary

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alcohols and (−)-sparteine provides narrowly dispersed polycarbonates of predictable molecular weights.[15] Even if such system is less active, its compatibility regarding free triazolium carbene and carboxylic acid group is expected without any damage on PBL chains.[16] However, to broaden the scope of the tertiary alcohol catalysts family, the fluorinated tertiary alcohol species was replaced by a simple phenol derivative also known to activate carbonyl compounds (such as carbonate) by hydrogen bonding.[17]

In a first attempt, *p*-chlorophenol (CP) was surveyed as organocatalyst for the ROP of commercially available trimethylene carbonate (TMC). Polymerizations were conducted using an alcohol initiator, such as benzyl alcohol (BnOH), with (−)-sparteine (S) as a cocatalyst base. The ROP of TMC was evaluated both in CH_2Cl_2 ($[TMC]_0 \sim 2$ M at 23 and 50 °C) and in bulk (90 °C) for a [TMC]/[BnOH]/[S]/[CP] ratio of 100:1:5:5, and relative conversions were determined by using SEC analysis (Table 1; a typical ^{1}H NMR spectrum is shown in Figure 1 and confirms the expected structure and end-group fidelity).

Clearly, higher temperature in bulk state provides high TMC conversions and predictable molecular weights with reasonable narrow dispersities ($Đ_M = M_w/M_n$). A comparison between the measured molecular weights (M_nSEC) of PTMC samples and determined conversions shows a linear fit consistent with a controlled process (Figure 1, inset). While SEC chromatograms show Gaussian distribution of molecular weights for each sample and since the plot of M_nSEC versus conversions reveals that polymer chains grow regularly (for temperatures comprised between 23 and 90 °C), the competition of recently revealed active chain end (ACE) propagating mechanism is of well minor importance to the expected activated monomer mechanism (AM) (Scheme 2).[18]

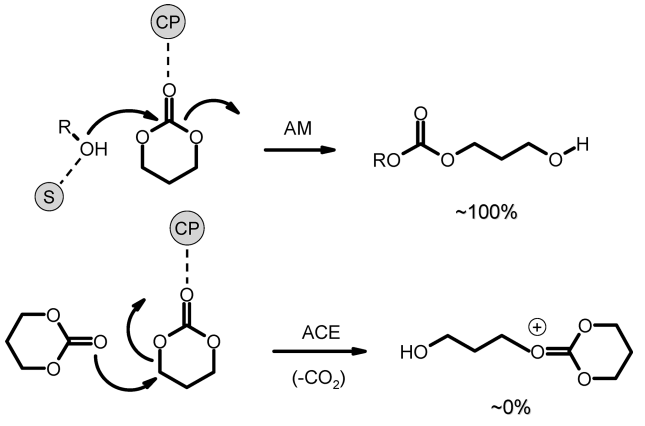
In the frame of this research, the CP/S catalytic complex has then been used for the copolymerization of TMC and functionalized cyclic carbonate **2**. The molecule **2** is obtained as aforementioned by the nucleophilic reaction between cyclic carbonate **1** and triazolium carbene in THF at room temperature (rt) (Scheme 3). Evolution of the reaction is followed by FT-IR analysis. After 3 h of reaction, the nucleophilic addition of the triazolium carbene to the carboxylic acid group is proved quantitative since the recrystallized and dried product does not show the wide initial ν(C═O) vibration band characterizing the −COOH group of **1** (∼1700 cm^{-1}). Moreover, the as-obtained adduct keeps safe the ν(−OC(O)O−) band of the carbonate

Table 1. Molecular Characteristic Features of PTMC Obtained at Different Temperatures and Using a CP/S Catalytic Complex

entry	temp (°C)	polym time (h)	conv (%)[a]	M_nSEC (g/mol)[a]	$Đ_M$[a]
1	23	1.5	3	500	1.02
2		19	13	1300	1.14
3	50	22	31	3400	1.09
4	90	2	70	6800	1.24
5		4	86	8350	1.33

[a] As determined by SEC in THF/NEt_3 at 35 °C using PS standards.

Scheme 2. Illustration of ACE and AM Mechanisms for the ROP of TMC Catalyzed by CP/S Catalytic Complex



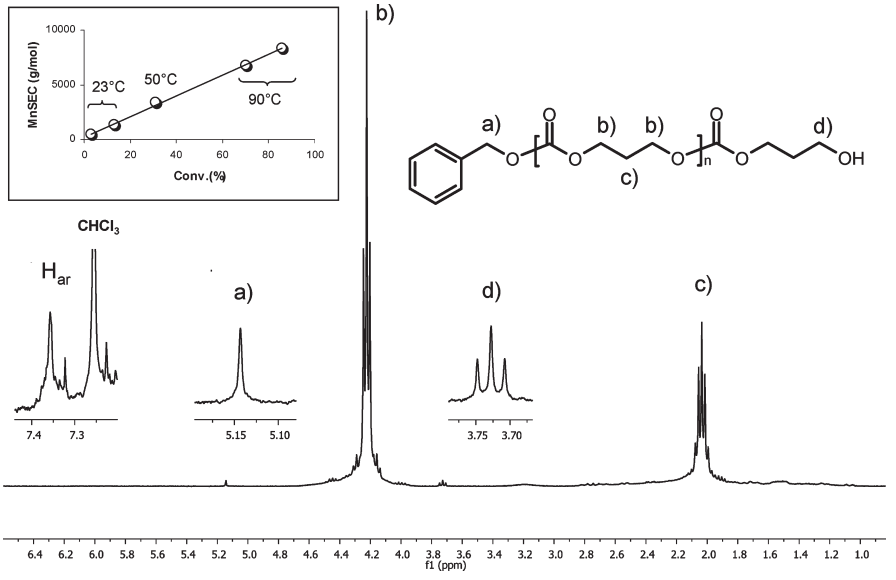


Figure 1. ^{1}H NMR spectrum of representative PTMC obtained by a CP/S catalytic complex (entry 5, Table 1). Inset: evolution of M_nSEC to conversions determined at different temperatures.

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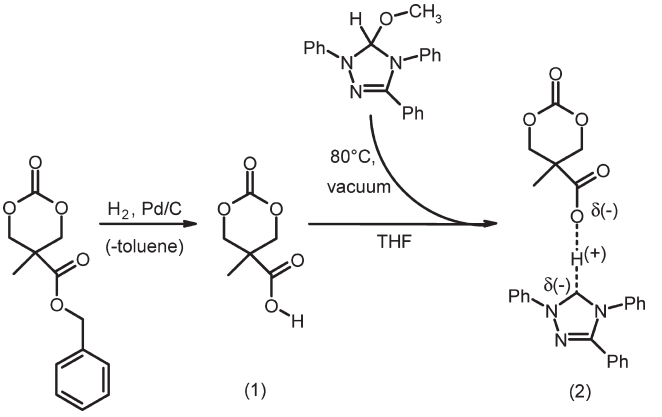
function at 1750 cm^{-1}, attesting for the selectivity of the nucleophilic addition to the prejudice of the nucleophilic substitution of the cyclic carbonate from the carbene unit. Additionally, a new band shows up between 1650 and 1550 cm^{-1}, confirming the presence of the triazolium aromatic groups (Figure S1 in Supporting Information). In the ^1H NMR spectrum, the nonequivalence of both methylene carbonate protons attests for the cyclic structure of the monomer **2**, confirming that free triazolium carbene does not cause any damage on cyclic carbonate monomer in THF in presence of carboxylic acid functions (at least at rt). It is also worth noting that the theoretical ratio of the proton integration ($[CH_3]/[CH_2]/[H_{ar}]$ = 3:4:15) fits well with the experimental one, i.e., 3:4.2:15.1, attesting then for the completeness of the reaction (Figure S2).

The cyclic carbonate carbene adduct **2** has then been evaluated with respect to thermal stability. As already performed on other carbene adducts,[19] a modulated differential scanning calorimetry (M-DSC) analysis of **2** has been carried out under nitrogen. Similarly to the 5-methoxy-1,3,4-triphenyl-4,5-dihydro-1*H*-1,2,4-triazol-5-ylidene obtained by covalent association between methanol and free triazolium carbene, the cyclic carbonate **2** presents its first endothermic transition at ca. 103 °C. Such a temperature corresponds to the point for which both carbonate **1** and triazolium carbene are totally dissociated (Figure 2). In correlation with the nature of the bond linking the two partners within the adduct, i.e., hydrogen bond, the variation of enthalpy recorded for such adduct thermal dissociation is of about 67 J/g, significantly lower than the one recorded for the covalent methanol adduct (~215 J/g) and in agreement with theory.[20]

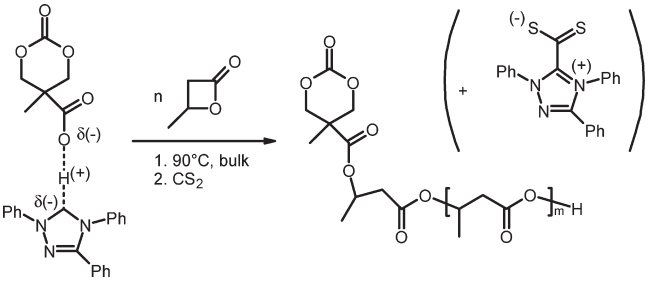
Finally, and prior to any copolymerization with TMC, the reactivity of the carboxylic-type carbene group of the carbonate adduct **2** has been assessed in anionic ROP of BL monomer (Scheme 4).

Practically, the anionic polymerization of BL has been carried out in bulk at 90 °C for an initial monomer-to-initiator molar ratio ($[BL]_0/[\mathbf{2}]_0$) of 70. After 40 min reaction time (conversion ~ 0.62; DP_{th} = 44), the ^1H NMR analysis of the precipitated product attests for the effective polymerization of BL (Figure S3). While a negligible signal of backbiting crotonization is observed in the resolution limit of the ^1H NMR spectroscopy (at around 5.75 ppm), the presence of the cyclic carbonate end-group is clearly visible between 4.1 and 4.6 ppm. By comparing the intensities of methylene butyrate repeating units (~2.4 ppm) and methylene carbonate end-group protons (~4.1−4.6 ppm), an experimental DP of 49 is estimated. Such DP_{exp} is in good accordance with the theoretical DP of 44. The control over the polymerization has finally been attested for by a narrow $Đ_M$ of 1.21 as determined by SEC. This combined set of data demonstrates end-group fidelity, predictable molecular weights (particularly for targeted DPs lower than 40), and the selectivity of the carbene catalyst for the lactone polymerization. It is worth

Scheme 3. Synthesis of Triazolium Ester Cyclic Carbonate 2



Scheme 4. Polymerization of BL from Cyclic Carbonate 2



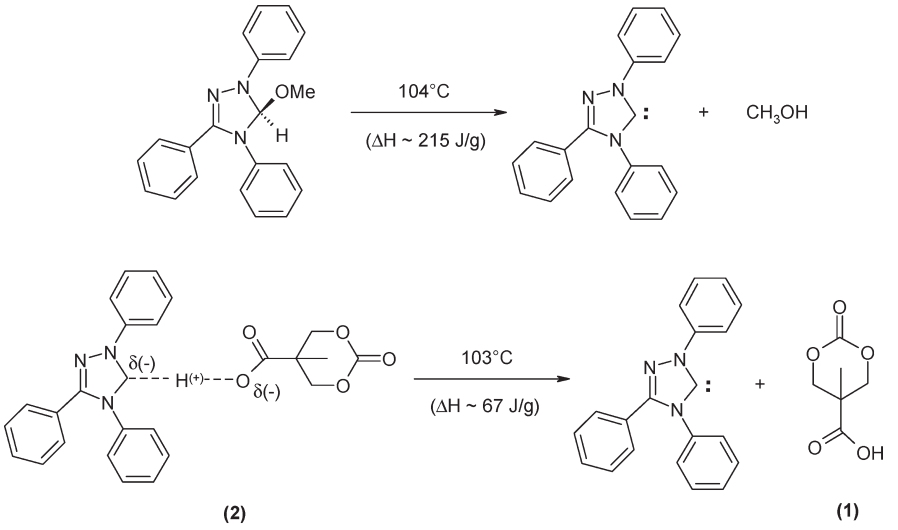


Figure 2. Temperatures and enthalpies of carbene adducts destructurations.

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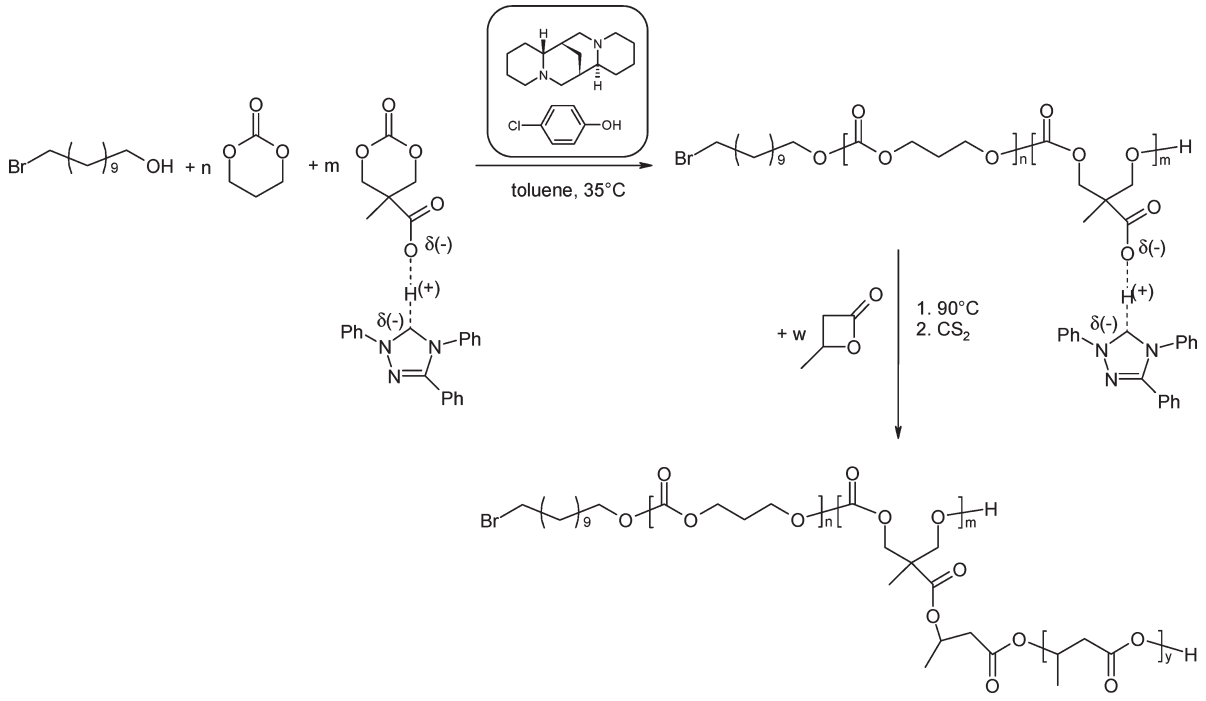
Scheme 5. One-Pot Two-Step Procedure for the Preparation of Poly(carbonate)-*graft*-Poly(butyrolactone) (PC-*g*-PBL) Copolymers



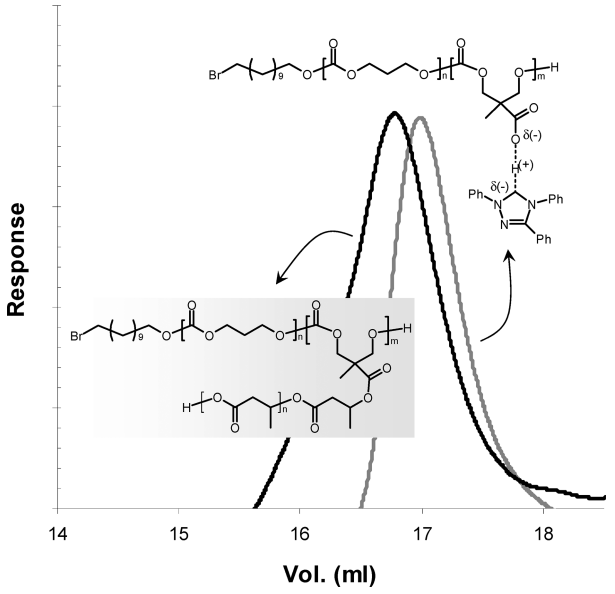


Figure 3. Representative size exclusion chromatography traces of P(TMC-*co*-**2**) (in gray) and PC-*g*-PBL**1** (in black).

noting that polymerizations targeting higher conversions (DPs ranging from 50 to 100) tended to show broadening in the $Đ_M$ (data not shown here). Moreover, for these DPs, an important amount of crotonate was observed, consistent with typical proton abstraction reactions leading to a second mode of polymerization. The loss of control and end-group fidelity at the high targeted DPs is fully consistent with that observed by Duda, Coates, and also some of us.[21]

The ability of the cyclic carbonate **2** to copolymerize with TMC from a CP/S catalytic complex has then been investigated using 11-bromo-1-undecanol (11-BU) as alcohol initiator (Scheme 5). Because of possible reaction between free carbene and chlorinated solvents,[19a] the copolymerization has been performed in toluene at 35 °C for a total monomer concentration of 2 M ($[11\text{-BU}]_0/[TMC]_0/[\mathbf{2}]_0$ = 1:45:5). In order to slightly improve the kinetics recorded and presented in Table 1, a 10-fold excess of CP/S complex has been used regarding the alcohol initiator content ($[11\text{-BU}]_0/[CP]_0/[S]_0$ = 1:10:10). As attested by SEC analysis, 44.25 h is sufficient to completely consume both comonomers and generate a controlled P(TMC-*co*-**2**) copolymer (M_nSEC = 4100 g mol^{-1}; $Đ_M$ = 1.19; Figure 3). The as-obtained P(TMC-*co*-**2**) has then been used to initiate the ROP of BL monomer from the dangling triazolium functions present on the polycarbonate backbone (Scheme 5). At this stage, two thermally on-demand polymerizations were performed at 90 °C: (i) the first copolymerization was realized by using an initial $[BL]_0/[11\text{-BU}]_0$ of 60 ($[BL]_0 \sim 2$M) and (ii) the second one after evaporation of the toluene ($[BL]_0/[11\text{-BU}]_0$ = 150). ^{1}H NMR analysis attests for the effective ROP of BL by the appearance of characteristic signals of butyrate repeating units observed at 2.5 and 5.2 ppm (Figure 4). Molecular parameters of both poly(carbonate)-*graft*-poly([R,S]-butyrolactone) (PC-*g*-PBL) copolymers are gathered in Table 2.

While 1 h is required to lead to 20% conversion in BL when the copolymerization is performed in solution (PC-*g*-PBL **1**), polymerization conducted in bulk conditions increases the propagation kinetics and conversions up to 99% are obtained within 45 min (PC-*g*-PBL **2**). Whatever the experimental conditions, a relatively good accordance between experimental and calculated DPs is observed (by taking into account the inherent experimental error of the ^{1}H NMR spectroscopy). Moreover, SEC

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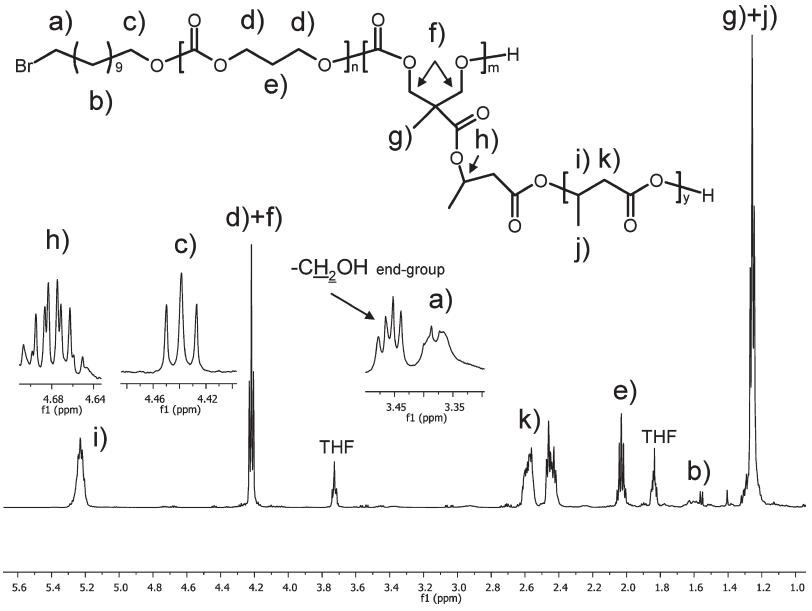

Figure 4. ^{1}H NMR spectrum of PC-*g*-PBL **2** (Table 2) in $CDCl_3$.

Table 2. Molecular Characteristic Features of PC-*g*-PBL Obtained after BL ROP from P(TMC-*co*-2)

sample[a]	polym time (min)	conv (%)[b]	$DP_{th}PBL$	$DP_{exp}PBL$[c]	M_nSEC copo (g/mol)[d]	$Đ_M$[d]
PC-*g*-PBL **1**	60	20	12	17	6200	1.32
PC-*g*-PBL **2**	45	99	150	160	8600	1.26

[a] Sample 1 refers to the copolymer obtained after polymerization of BL in presence of toluene; sample 2 was obtained after polymerization in bulk. [b] As determined by gravimetry. [c] As determined by ^{1}H NMR in $CDCl_3$. [d] As determined in THF/NEt_3 at 35 °C by using PS calibration.

analyses attest for the controlled behavior of both copolymerizations by $Đ_M$ varying from 1.26 to 1.32 (Figure 3). Since PC-*g*-PBL **1** and **2** are mainly different by the length of PBL chain (5 side chains per backbone and DP of side chain is 3 for **1** and 32 for **2**), the small variation of experimental molecular weight determined by SEC is probably due to the variation of hydrodynamic volumes between those two copolymers different in terms of topology. As expected, no degradation of the polycarbonate backbone has been observed neither during the thermal activation of the triazolium adduct nor after the BL polymerization. More importantly, if 45 min is required to polymerize BL from dangling triazolium functions of P(TMC-*co*-**2**) for a DP of 32 and in the presence of CP and S, it might be concluded that very limited interactions between free carbene and CP take place during the polymerization of BL. Indeed, 40 min is necessary to generate a PBL of a DP 44 from BL ROP initiated from **2** without CP and S (all other experimental conditions identical).

In conclusion, a new triazolium-based cyclic carbonate monomer has been prepared by nucleophilic addition of the 1,3,4-triphenyl-4,5-dihydro-1*H*-1,2,4-triazol-5-ylidene *N*-heterocyclic carbene to a six-membered cyclic carbonate ring bearing a free carboxylic acid group. That new inimer may act as an active initiator for the ROP of BL and is also easily polymerized by an organocatalytic complex based on (−)-sparteine and *p*-chlorophenol. The complementarity of triazolium and sparteine/*p*-chlorophenol active species allowed the generation of controlled poly(carbonate)-*graft*-poly(butyrolactone) copolymers.

■ ASSOCIATED CONTENT

Supporting Information. Figures S1−S3 and experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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