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ARTICLE

Control of End Groups in Anionic Polymerizations Using Phosphazene Bases and Protic Precursors As Initiating System (XH-Bu^{t}P$_4$ Approach): Application to the Ring-Opening Polymerization of Cyclopropane-1,1-Dicarboxylates

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ABSTRACT: A synthetic method involving the in situ generation of an anionic initiator X^- obtained by reaction of its conjugate acid precursor XH with Bu^{t}P$_4$ phosphazene base was tested as a possible way to easily and better control the end groups of polymers derived from the anionic ring-opening polymerization of cyclopropane-1,1-dicarboxylates. Several types of precursors were investigated, including thiols, alcohols, a carbazole, and a malonate. In all but one cases, a living polymerization mechanism could be observed, which was exploited to control the nature of the terminal end groups by reaction of the propagating malonate carbanion $R-C(COOPr)_2^-$ with alkylating agents. It was also demonstrated that toluene was a much better solvent than the traditional one used in these reactions (THF) as a larger range of available temperatures was available despite an almost identical solvent influence on the polymerization. Exploitation of this feature provided access to higher degrees of polymerization than previously possible.

Introduction

The past few years have seen a renewed interest in the development of synthetic methodologies capable of controlling the telechelicity of functionalized polymers (i.e., the nature of their end groups) while preserving the structural features achievable by living polymerization techniques, in particular the excellent control over molecular weights.[1−5] The motivations behind this trend are essentially application-driven. First, telechelic polymers constitute the natural access route to reactive high molecular-weight precursors used in polymerization techniques such as macromonomers and macroinitiators.[6,7] In addition, specific end groups such as thiols and azides can be used to covalently attach the polymer to several types of objects and structures (surfaces, particles) − including inorganic ones,[8] or as a way to reversibly interact with other polymers[9−11] or with surfaces.[12,13] Finally, the occurrence of an extra group that can be easily distinguished from the other substituents on the polymer can be exploited to impart further properties to multifunctional macromolecules, in particular, in the oligomeric range.[14,15]

Control over telechelicity is classically obtained by devising efficient initiation and end-capping reactions that can be adapted to living-controlled polymerization processes. A limitation of this approach results from the usual limited scope of proposed techniques, in particular with respect to the use and design of initiators and end-capping agents to be used in ionic polymerizations. One solution is to design methods to generate a family of initiators rather than a specific one in situ, for example, in the case of a nucleophilic initiator for an anionic polymerization, by associating a strong base with a protic precursor (XH) according to general eq 1.

$$\mathrm{base} + \mathrm{X-H} \rightarrow \mathrm{X}^{(-)} + \mathrm{base-H}^{(+)} \qquad (1)$$

Extremely strong, nonionic phosphazene bases developed by Schwesinger[16−18] are theoretically good candidates for the job as they deprotonate very low acidic molecules, thus producing extremely reactive anions associated to highly stable, soft phosphazenium cations (eq 2).

$$\mathrm{XH} + \mathrm{Bu}^t\mathrm{P}_4 \rightarrow \mathrm{X}^{(-)}\mathrm{Bu}^t\mathrm{P}_4\mathrm{H}^{(+)} \qquad (2)$$

The structure of the Bu^{t}P$_4$ base is depicted in Scheme 1.

This technique, which for the sake of convenience will be abbreviated the XH-Bu^{t}P$_4$ approach in this paper, has already proved its usefulness with a limited number of XH precursors and monomers: phosphazene bases in association with aliphatic alcohols are highly efficient for the anionic polymerization of ethylene oxide,[19,20] cyclosiloxanes,[21−23] and cyclic esters[24] and in association with enolate precursors $R_2CHCOOR'$ for the anionic polymerization of (meth)acrylates.[25,26] We recently demonstrated that a successful activation could also be observed using Bu^{t}P$_4$ phosphazene base and thiol precursors (thiophenol or bis(mercaptoethyl)ether) in the anionic ring-opening polymerization of di-*n*-propyl cyclopropane-1,1-dicarboxylate (Scheme 1).[27] Polymers with very narrow polydispersities ($M_w/M_n < 1.08$) could be obtained according to a living process. Moreover, satisfying polymerization rates were obtained under mild conditions ($k_p = 5.8 \times 10^{-4}$ L·mol^{-1}·s^{-1} in THF at 60 °C) compared to the conventional route, which uses alkali metal thiophenolates as initiators.[28−30] Propagation in this reaction occurs via malonate carbanions.[27]

In this paper, we aim at extending the scope of the XH-Bu^{t}P$_4$ initiating system by investigating a large panel of acidic precursors

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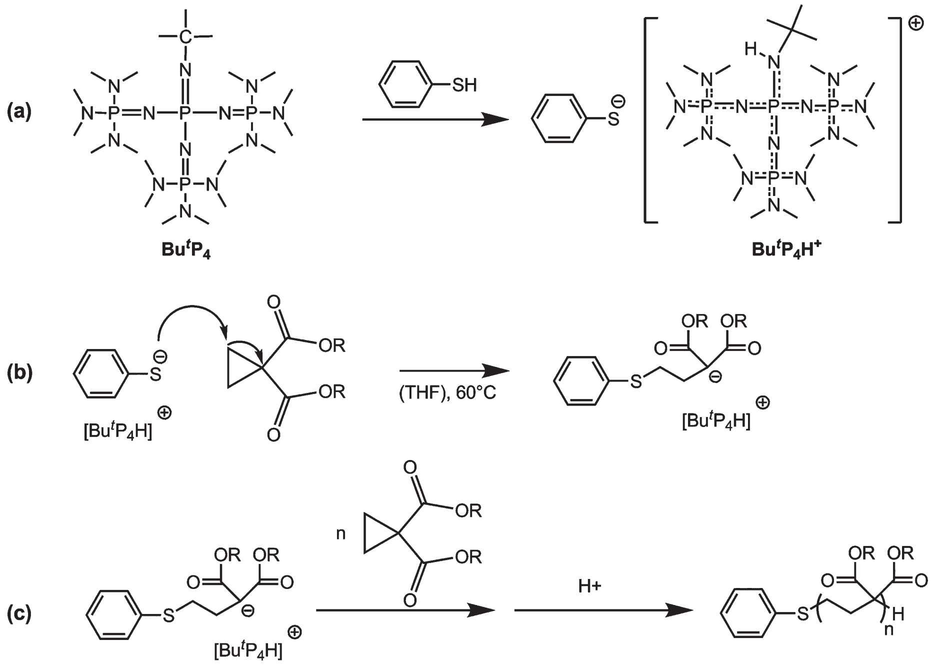
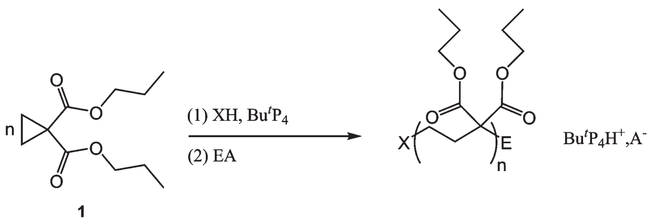
Scheme 1. Postulated Mechanism for the Ring-Opening Polymerization of Dipropyl cyclopropane-1,1-dicarboxylate (1) Using a Protic Precursor to the Anionic Initiator and Phosphazene Base $\mathrm{Bu}^t\mathrm{P}_4$:[a] (a) Activation Step, (b) Initiation Step, (c) Propagation Step and Quenching Reaction



[a] In the provided example, thiophenol is used as the precursor to the initiator and HCl as the quenching agent.

Scheme 2. General Equation for the Polymerization of Di-*n*-propyl cyclopropane-1,1-dicarboxylate (1), Initated by Protic Precursors XH in the Presence of Phosphazene Base $\mathrm{Bu}^t\mathrm{P}_4$ and Terminated by Quenching the Propagating Carbanionic Species with Alkyl Halides EA



X = RS, RO, RR'N, $\mathrm{R}_2\mathrm{CH}$
E = H, allyl, propargyl
A = Cl or Br

(Scheme 2) such as aromatic and aliphatic thiols (S−H precursor), a phenol (O−H precursor), a carbazole (N−H precursor), and a malonate (C−H precursor). A procedure to control the nature of the other end group via the functionalization of the propagating malonate carbanion is investigated as well, using hydrochloric acid (to introduce an hydrogen) or reactive alkylating agents (to introduce alkyl groups). Finally, to determine whether the polymerization reaction could be carried out in a more industrially convenient solvent than THF or DMSO, a study of the polymerization in toluene in the presence of the phosphazene base is described.

Experimental Section

Materials. Phosphazene base $\mathrm{Bu}^t\mathrm{P}_4$ solution (1.0 $\mathrm{mol\cdot L^{-1}}$ solution in hexane, Fluka), thiophenol (≥99%, Aldrich), bis(2-mercaptoethyl) ether (> 95%, Fluka), propargyl bromide (80% in toluene, Aldrich), hydrochloric acid (35%, VWR Prolabo), propan-1-ol (> 99%, Prolabo), and malonyl chloride (99%, Fluka) were used as received. THF and toluene were dried with sodium benzophenone and then distilled. Allyl bromide (99%, Acros) was distilled under argon. Carbazole (≥99%, Aldrich) and phenol (99%, Aldrich) were purified by sublimation. Di-*n*-propyl cyclopropane-1,1-dicarboxylate (**1**) was prepared from di-*n*-propyl malonate as reported previously[30] and distilled under vacuum (74 °C/1.0 mmHg).

Instrumentation. ^{1}H and ^{13}C NMR spectra were recorded in $\mathrm{CDCl_3}$ or $\mathrm{CD_3COCD_3}$ using a Bruker 400 MHz NMR spectrometer. Size exclusion chromatography (SEC) experiments were performed in chloroform (1 $\mathrm{mL\cdot min^{-1}}$) at room temperature using a Spectra Physics P100 pump, and two PLgel Polymer Laboratories linear columns (5 μm Mix-C, separation range 200 to 2×10^6). A Wyatt Technology Optilab Rex interferometric refractometer (690 nm laser) and a Wyatt Technology Minidawn light scattering photometer (three-angle detection, 20 mW semiconductor laser (690 nm)) were used as detectors. Relative molecular weights were obtained using a polystyrene calibration. Absolute molecular weights were determined either by quantitative ^{1}H NMR (see the Results and Discussion for further details) or by SEC-MALLS analysis according to a methodology previously validated for this class of polymers.[31] UV and visible spectra were obtained with a Varian Cay 50Bis instrument. MALDI-ToF (matrix-assisted laser desorption/ionization time-of-flight) spectra were recorded on a Perseptive Biosystems Voyager-DE Pro STR MALDI-TOF mass spectrometer (Applied Biosystems/MDS SCIEX, Foster City, CA, U.S.). This instrument was equipped with a nitrogen laser ($\lambda = 337$ nm). The mass spectrometer was operated in the positive ion reflectron mode with an accelerating potential of +25 kV. Mass spectra were recorded with the laser intensity set just above the ionization threshold to avoid fragmentation and to maximize the resolution. External calibration using polyethylene glycol standards was performed with the same matrix as in the experiment. For all experiments, equal volumes (20 μL) of polymer solution (10^{-3} $\mathrm{mol\cdot L^{-1}}$ in THF) and of matrix solution (dithranol, 10^{-1} $\mathrm{mol\cdot L^{-1}}$ in THF) were mixed. Ten microliters of sodium acetate salt solution (10^{-2} $\mathrm{mol\cdot L^{-1}}$ in methanol) were added to this solution. About 1 μL of the resulting mixture was spotted onto the MALDI sample plate and allowed to air-dry at room temperature just before analysis.

Polymerization of 1. Filling the polymerization tube with the reagents prior to its closure was carried out in a glovebox. Monomer **1** (2.15 g, 10.05 mmol) was introduced under argon into a polymerization tube fitted with a Rotaflo. THF or toluene

Table 1. Summary of the Experimental Conditions Used for the Polymerization of 1 and of the Observed Results[a]

							$M_{n,exp}$ ($\times 10^{-3}$)[g]				
no.	XH	end-capping agent[b]	XH: Bu^tP_4:**1**	time (h)	conversion (%)	$M_{n,th}$ ($\times 10^{-3}$)	SEC-PS[c]	SEC-MALLS[d]	^{1}H NMR[e]	^{1}H NMR[f]	M_w/M_n SEC-PS
1	thiophenol	**2**	1:1:50	50	97	10.4	9.0	10.1	11.7	11.8	1.08
2	thiophenol	**3**	1:1:25	17	99	5.3	4.2	5.6	5.8	6.0	1.07
3	thiophenol	**4**	1:1:15	15	100	3.2	2.9	5.0	3.9	4.0	1.07
4	bis(2-mercaptoethyl) ether	**2**	1:1:25	64	99	10.6	8.6	12.0	10.7	11.9	1.06
5	phenol	**2**	1:1:50	44	100	10.7	8.5		10.7	11.2	1.07
6	carbazole	**2**	1:1:25	24	99	5.5	4.0	6.0	6.1	5.3	1.06
7	di-*n*-propyl malonate	**2**	1:1:25	156	100	5.3	4.8	7.7	7.1		1.09

[a] In THF at 60 °C. [b] End-capping agents: **2** = hydrochloric acid, **3** = propargyl bromide, **4** = allyl bromide. [c] Relative measurement (SEC columns calibrated with polystyrene standards). [d] Absolute measurement (detection with a multiangle laser light-scattering detector). [e] Calculated on the basis of signals provided by the initiator fragment. [f] Calculated on the basis of signals provided by the end-capping agent fragment. [g] Linear correlation parameters between relative (SEC-PS) and absolute (SEC-MALLS) number-average molecular weight measurements: M_n(SEC-MALLS) = 1.33M_n(SEC-PS); $R^2 = 0.92$.

(2.2 mL), the initiator precursor (see Table 1 for the exact amounts), and the phosphazene base (1.0 mol·L^{-1} solution in hexane, 1.0 equiv with respect to the initiator precursor) were successively added at room temperature. After careful closure of the reaction tube, the mixture was stirred at a set temperature for the required period of time (see Table 1). The reaction was quenched with a large excess of the appropriate electrophilic agent (see Table 1) according to the following conditions: (a) HCl, suitable volume of a 12 mol·L^{-1} HCl aqueous solution (corresponding to 20 equiv with respect to the initiator precursor); (b) allyl bromide (entry 3 in Table 1), 3.24 g (26.8 mmol, 40 equiv); (c) propargyl bromide (80 wt % solution in toluene) (entry 2 in Table 1), 50.0 μL (0.46 mmol, 1.1 equiv). The polymer was recovered by dissolution of the final mixture in chloroform and precipitation in methanol. The white powder obtained after filtration was dried under vacuum at 50 °C for 48 h.

^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) = 0.90 (t, 6H, $-CH_2CH_2C\underline{H}_3$), 1.62 (sextuplet, 4H, $CH_2C\underline{H}_2CH_3$), 1.71 (s, 4H, $-C\underline{H}_2C\underline{H}_2C(CO_2R)_2$), 4.05 ($-C\underline{H}_2CH_2CH_3$). ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) = 10.3 ($-CH_2CH_2\underline{C}H_3$), 21.8 ($-CH_2\underline{C}H_2CH_3$), 26.9 ($-\underline{C}H_2\underline{C}H_2C(CO_2R)_2$), 56.8 ($(CH_2)_2\underline{C}(CO_2R)_2$), 66.8 ($-\underline{C}H_2CH_2CH_3$), 170.7 ($C(\underline{C}O_2R)_2$).

Results and Discussion

Polymerizations of electrophilic cyclopropanes such as **1** are typically initiated by soft nucleophiles such as cyanide or thiolate anions.[28] Several reports have already established that thiophenolates PhSM (with M = Li, Na, K, or tetraalkylammonium (R_4N)) are particularly convenient as initiators in the polymerization of **1**, yielding full conversion of the ring-opened adduct, with higher initiation rate constants than those observed for the propagation step and without side reactions.[29,30,32] In a recent report, we established that the Bu^tP_4/PhSH couple generated an excellent initiator in situ, requiring lower reaction temperatures for the initiation step than those typically needed with alkali metal thiophenolates ($k_p = 5.8 \times 10^{-4}$ L·mol^{-1}·s^{-1} in THF at 60 °C for the Bu^tP_4/PhSH initiator vs $k_p = 2.0 \times 10^{-4}$ L·mol^{-1}·s^{-1} in DMSO at 130 °C for a sodium thiophenolate initiator (Figure S1 in the Supporting Information)).[27] As a result, the thiophenolate anions, and more specifically the Bu^tP_4/PhSH couple, will be used in this study as a benchmark to evaluate the efficiencies of other Bu^tP_4/XH couples, as well as the possibility of controlling the nature of the other end group via an end-capping reaction.

Initially, all polymerization experiments were performed in THF at 60 °C, using 1 equiv of the phosphazene base with respect to the initiator precursor XH. Targeted degrees of polymerization, as calculated from the $[M]_0/[XH]_0$ ratio (i.e., assuming quantitative initiation), were deliberately set at rather low values (15−50) so that chain ends could be easily characterized by ^{1}H NMR and MALDI-ToF mass spectrometry. The progress of the

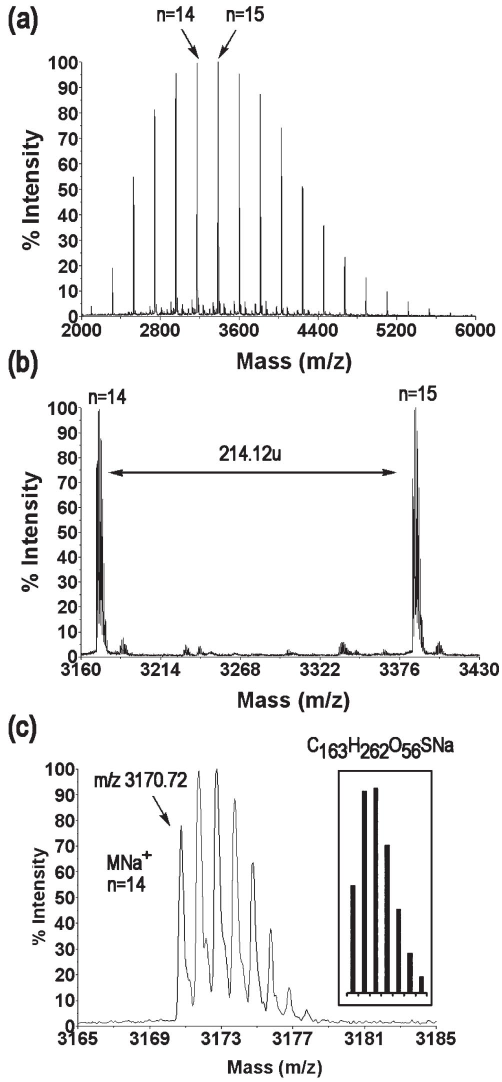


Figure 1. MALDI-ToF mass spectrum of a poly(**1**) sample obtained using the thiophenol/Bu^tP_4 combination as initiating system and terminating with allyl bromide (entry 3 in Table 1, PhSH:Bu^tP_4:**1** = 1:1:25, THF, 60 °C, 15 h, quantitative conversion, M_n(NMR or MALLS) = (3.9−5.0) × 10^3, M_w/M_n(SEC) = 1.07): (a) full mass spectrum; (b) expended view within the *m*/*z* 3160−3376 mass range; (c) isotopic distribution of the Na$^+$-adduct containing 14 repeat units and simulation of the isotopic distribution (inset).

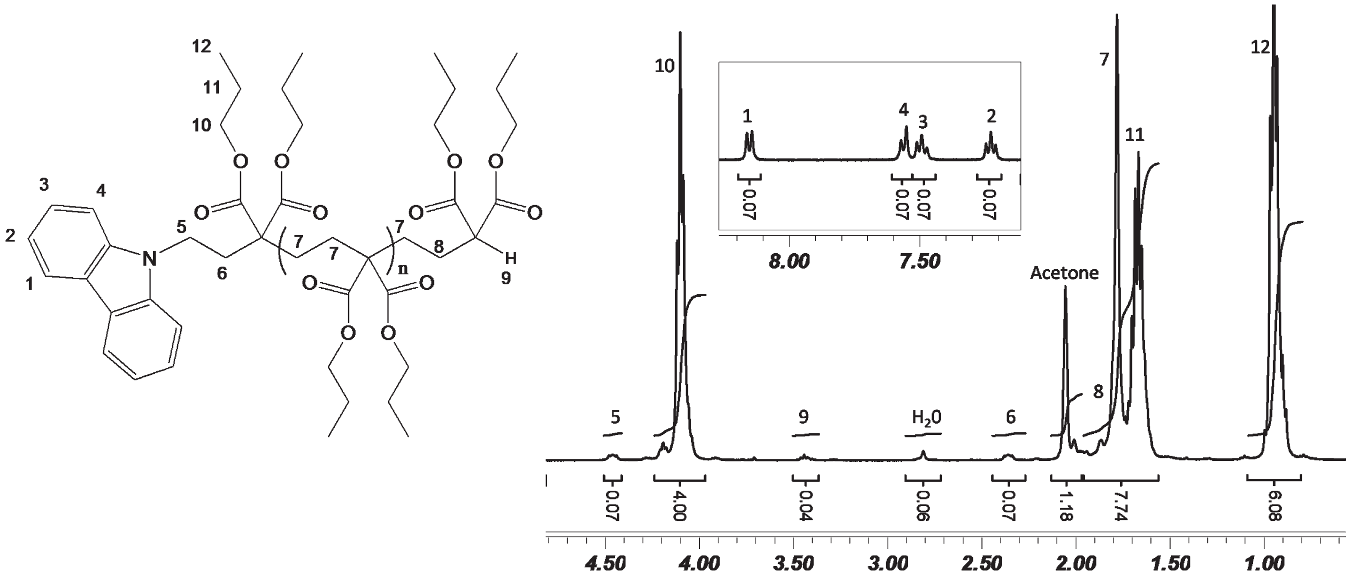


Figure 2. ^{1}H NMR spectrum in CD_3COCD_3 at room temperature of a poly(**1**) sample obtained by initiating with carbazole/$\mathrm{Bu}^t\mathrm{P}_4$ and terminating with HCl (entry 6 in Table 1, carbazole:$\mathrm{Bu}^t\mathrm{P}_4$:**1** = 1:1:25, THF, 60 °C, 24 h, quantitative conversion, M_n(NMR or MALLS) = (5.3−6.1) × 10^3, M_w/M_n(SEC) = 1.06).

polymerization was monitored by removing samples regularly from the polymerization reactor, quenching the carbanions with hydrochloric acid, and comparing the signals corresponding to the $COOC\underline{H}_2$ protons on the monomer and polymer, respectively. All polymers were fully characterized by ^{1}H and ^{13}C NMR and by IR spectroscopy; a few selected ones (those obtained using the thiophenol/$\mathrm{Bu}^t\mathrm{P}_4$ combination as the initiating system; Table 1, entries 2 and 3) were also characterized by MALDI-ToF mass spectrometry (Figures 1 and 2 and Figure S29 in the Supporting Information). Reactions were ultimately quenched by adding either hydrochloric acid or a carbon-based electrophile (i.e., allyl bromide or propargyl bromide; see following section). Relative molecular weights were determined by SEC using polystyrene standards (abbreviated as SEC-PS in the text). Absolute molecular weights were determined by SEC-MALLS and by ^{1}H NMR (end-group analysis) using characteristic protons of the initiator and the CH_2 located on the α-position of the propyl ester function in each repeat unit. A comparison between the two values provides access to the initiation efficiency. In practice, however, an excellent agreement between M_n measured by SEC-PS (relative measurement) and SEC-MALLS (absolute measurement) was observed. Although this agreement is entirely fortuitous, it helped in comforting the reliability of the molecular weight determination and ultimately of the comparison made with end-group measurements to evaluate the efficiencies of the initiation and end-capping reactions.

Experimental conditions and obtained results are summarized in Table 1. Full conversions could be obtained after 1−7 days although the reaction times have not been fully optimized. In the first approximation, the polymerization rate was observed to depend primarily, as expected, on the XH:$\mathrm{Bu}^t\mathrm{P}_4$:**1** ratio.

Control of the End-Capping Step (Thiophenol/$\mathrm{Bu}^t\mathrm{P}_4$ Initiating System). Almost all polymerizations of cyclopropane-1,1-dicarboxylates reported in the literature thus far have been terminated using hydrochloric acid. As malonate carbanions are well-known to react with various electrophilic species such as alkyl halides, there are clearly opportunities available to introduce functionalized chain ends by this approach. Given this perspective, two terminating agents that could be further functionalized via their double or triple bonds, i.e., allyl and propargyl bromides, were investigated (Table 1, entries 2 and 3) on polymerizations performed in THF at 60 °C, with thiophenol/$\mathrm{Bu}^t\mathrm{P}_4$ as the initiating system.

When the polymerization was quenched with hydrochloric acid (20 mol equiv) as usual (Table 1, entry 1), the acid−base reaction was instantaneous and introduced quantitatively a hydrogen atom as the end group. The presence of the resulting $-CH(COOR)_2$ end group can be attested by ^{1}H NMR (weak but discernible triplet signal at 3.44 ppm). A degree of polymerization calculated by comparing the intensity of this signal to that for the CH_2 located on the α-position of the propyl ester available in each repeat unit is in good agreement with the one based on the aromatic protons of the thiophenol subunit (CH ortho/meta, 7.35 ppm; CH para, 7.22 ppm) as well as with another one obtained by size exclusion chromatography. This result provides unambiguous evidence that both initiation and termination are quantitative. None of the side reactions that could be realistically envisioned on the basis of the known organic reactivity of involved intermediates could be detected by NMR; a particular attention was paid to some possible decarbalkoxylation of malonate esters (Krapcho reaction),[33] backbiting of the malonate carbanion on the ester of the neighboring unit (Dieckmann condensation) as well as the formation of a thioester by addition−elimination of the thiophenolate on an ester carbonyl (see Scheme S1 in the Supporting Information).

When allyl bromide was used (40 mol equiv, 8 h at room temperature, entry 3 in Table 1), the protons of the introduced allyl end group could be easily detected on the ^{1}H NMR spectrum (4.96−5.04 ppm (CH_2), 5.46−5.57 ppm (vinyl protons)). A number-average molecular weight M_n of 4.0 × 10^3 was calculated from the signal of this end group and compares favorably with the one based on the integration of the initiator moieties (M_n = 3.9 × 10^3) as well as with the theoretical M_n (3.2 × 10^3; see Table 1), confirming that the termination reaction with allyl bromide is quantitative. A MALDI-ToF spectrum of the polymer (Figure 1) displays a major peak distribution corresponding to the expected polymer cationized by a sodium ion and end-terminated by a phenylthio group on one end and by an allyl group on the other end. As expected, the molecular weight difference between two successive peaks of the main distribution is strictly equal to the molecular weight of one repeat unit (214.12 mass units). Figure 1b shows this mass difference between two monoisotopic ions, *m*/*z* 3170.72 and 3384.84, corresponding to the Na^+-cationized oligomers containing 14 and 15 repeat units, respectively. The anticipated atomic composition was confirmed by a simulation of the isotopic distribution of the Na^+-cationized oligomer containing 14 repeat units ($C_{163}H_{262}O_{56}SNa$, monoisotopic ion at *m*/*z* 3170.7; see Figure 1c). Five very minor distributions with the same isotopic distribution and unit repetition as the main one could also be observed on the spectrum. One of them corresponds to a cationization by potassium ions; the others could not be identified but do not correspond to any of the structure that could be envisioned on the basis of probable pathways and reactivities (see Scheme S1 in the Supporting Information).

Finally, when propargyl bromide was used as an end-capping agent (1.1 mol equiv, 2 h at room temperature, entry 2 in Table 1), the molecular structure of the purified polymer could also be fully confirmed by ^{1}H NMR. The propargyl end group is clearly visible, with signals at 2.49 ppm (acetylene C$-$H) and 2.83 ppm ($-C\underline{H}_2-C$, $^4J_{H-H2} = 0.6$ Hz). Integration of these signals with respect to the CH_2-O protons of the propyl groups provided a M_n value equal to 6.0×10^3, in excellent agreement with the one determined by ^{1}H NMR using the initiator protons ($M_n = 5.8 \times 10^3$) as well as with the theoretical and SEC-PS M_n values (Table 1, entry 2). As a result of these spectroscopic experiments, it can be concluded that the quenching reaction with propargyl bromide is quantitative under these conditions, within NMR experimental errors. A MALDI-ToF spectrum (see Supporting Information, Figure S29) confirmed a quantitative initiation by phosphazenium thiophenolate and an almost quantitative termination by propargyl bromide, with a distribution of much lower intensity (accounting for less than 5% of the intensities observed for the main distribution) being observed that could be assigned to a polymer end-terminated by a proton.

The obtained set of results suggests that the anionic ring-opening polymerization of **1** initiated by Bu^{t}P$_4$/XH systems leads easily to heterotelechelic oligomers if the terminating agent is a reactive alkyl halide. Functionalizable polymers are obtained with allyl or propargyl end groups that could undergo possible postmodifications, for instance, by thiol$-$ene addition or "click chemistry", respectively.

Polymerizations Initiated by Other Types of XH Precursors. Several protic precursors XH were investigated in this study, including S$-$H, O$-$H, N$-$H, and C$-$H acidic compounds, to cover a large variety of structures and a wide range of reactivities for the in situ generated initiators $X^{(-)}$. The selection was also based on the fact that attack of nucleophiles on cyclopropane-1,1-dicarboxylates is a well-known organic reaction whose details have been extensively investigated.[34] As a cyclopropanedicarboxylate monomer displays two sites for nucleophilic attack, i.e., the CH_2 on the cyclopropane ring (inducing a ring-opening by nucleophilic substitution on the carbon) and the carbonyl groups (inducing a nucleophilic addition), two types of adducts can be expected in the initiation step, depending on the regioselectivity of the attacking species. As a rule of thumb, hard bases such as Grignard reagents and alcoholates attack the ester functions preferentially and must be avoided as prospective initiators.[35,36] Soft bases such as organocuprates, thiolates or azides open the cyclopropyl ring, and are theoretically good candidates as initiators.[36−39]

The first experiment summarized in Table 1 (entry 4) involved an aliphatic bifunctional initiator of the SH-type, i.e., bis(2-mercaptoethyl) ether $O(CH_2CH_2SH)_2$. Full conversion was obtained with a high initiator efficiency and a low polydispersity for the polymer. All spectroscopic evidence suggests the absence of side reactions. If the polymerization occurs through a living process as expected on the basis of previous experiments with aromatic thiols,[27] the use of bis(2-mercaptoethyl) ether as a bifunctional initiator and of HCl as an end-capping agent induces the presence of a $-CH_2-CH_2-S-CH_2-CH_2-O-CH_2-CH_2-S-CH_2-CH_2-$ unit at the statistical midpoint of the polymer chain and $-CH_2-C(R)_2H$ units (where R stands for an *n*-propyl ester group) at both ends. A ^{1}H NMR study confirmed this assumption, with distinct signals for the $-C\underline{H}_2-CH_2-S-CH_2-CH_2-O$, $-CH_2-C\underline{H}_2-S-CH_2-CH_2-O$, $-CH_2-CH_2-S-C\underline{H}_2-CH_2-O$, $-CH_2-C(R)_2\underline{H}$, and $-CH_2-CH_2-S-CH_2-C\underline{H}_2-O$ protons at 2.14, 2.40, 2.68, 3.29, and 3.57 ppm, respectively. Integration of these subunits and of $COO-CH_2$ protons of the esters present on each monomer unit confirms that the initiation is quantitative and that the propagation proceeds bidirectionally from the initiator.

Attempts to use an aliphatic alcohol as an OH-type initiator remained unsuccessful. For example, using a monofunctional OH-terminated polyethylene glycol (PEG$-$OH) as a macromolecular precursor did not induce a polymerization of the cyclopropane.[40] This observation is compatible with known reactivities of aliphatic alcoholates and the expectation that transesterification (i.e., attack on the ester carbonyl rather than on the cyclopropyl methylene) would occur preferentially. A precursor to a phenolate, i.e., a softer alcoholate, was tested as an alternative (Table 1, entry 5) and provided excellent results in contrast to its aliphatic homologue. As a phenolate (pK_a = 18.0 in DMSO[41]) is more basic and a harder nucleophile than a thiophenolate (pK_a = 10.3 in DMSO[41]), a clean reaction was not necessarily expected in regard of the poor behavior exhibited by the PEG$-$OH. However, no side reaction was noticed and the molecular structure of the obtained oligomers was as expected. In particular, phenyl chain ends were clearly visible by ^{1}H NMR (ppm, CH ortho 6.90, CH meta 7.27, CH para 6.92) (see Supporting Information, Figure S18).

Carbazole was used as an acidic precursor of the NH-type. Here again, effective initiation was observed during the polymerization (entry 6 in Table 1). Functionalized chain ends are perfectly identifiable in the ^{1}H NMR spectrum (Figure 2), with no side reactions observed. Using the terminal carbazyl signals to determine the oligomer molecular weight (assuming that each carbazyl phosphazenium generates one macromolecule), good agreement could be observed with SEC-PS analysis, confirming that the initiation is quantitative. To the best of our knowledge, no other examples of an anionic polymerization initiated by an amine after deprotonation by a phosphazene base has previously been reported. As a result, the formation of carbazyl phosphazenium species was independently checked by UV$-$visible spectroscopy by adding Bu^{t}P$_4$ to a THF solution of carbazole (2.87×10^{-4} mol$\cdot$L^{-1}) at a 1.4 [Bu^{t}P$_4$]/[carbazole] molar ratio (see Supporting Information, Figure S32). An instantaneous bathochromic shift of the peaks was observed, with values of the maxima located at 399 and 422 nm, i.e., very close to those observed for THF solutions of carbazyl potassium complexed by the [222] cryptand at 398.5 and 420 nm,[42] and of carbazylcesium complexed by a spheroidal macrotricyclic ligand of larger size than the [222] cryptand as synthesized by Lehn et al.[43,44]

Finally, using di-*n*-propyl malonate $CH_2(COOCH_2CH_2CH_3)_2$ as a precursor of the CH-type (entry 7 in Table 1) proved successful as well. Analyses of the polymers performed

Table 2. Polymerization of 1 in Toluene at Three Temperatures (Initiating System Thiophenol/$\mathrm{Bu}^t\mathrm{P}_4$, Quenching Agent HCl)

						$M_{n,exp}$ ($\times 10^{-3}$)			M_w/M_n	
entry	PhSH:$\mathrm{Bu}^t\mathrm{P}_4$:**1**	T (°C)	time (h)	conversion (%)	$M_{n,th}$ ($\times 10^{-3}$)	SEC-PS	SEC-MALLS	^{1}H NMR	SEC-PS	SEC-MALLS
1	1:1:50	30	172	48	5.1	3.8		4.4	1.10	
2	1:1:50	60	89	100	10.7	6.8	8.7	9.8	1.07	1.08
4	1:1:50	100	4.5	100	10.7	7.6	9.6	10.7	1.08	1.09
5	1:1:50	100	7	100	10.7	8.6	11.6	11.1	1.07	1.18
6	1:1:200	100	32	99	42.4	33.0	42.0	43.0	1.14	1.10

by NMR, IR, and MALDI-ToF confirmed the expected structure and provided no evidence for side reactions, including a possible Dieckman condensation (backbiting reaction of the malonate carbanion on the a neighboring ester group; see Scheme S1 in the Supporting Information) that had been observed previously when sodium malonate had been used as an initiator for the ring-opening polymerization of another cyclopropanedicarboxylate although under more drastic conditions than the ones used presently.[45] The ^{1}H NMR spectrum exhibits a signal at 3.28 ppm corresponding to both terminal protons ($-\mathrm{C\underline{H}(COOPr)_2}$), an assignment confirmed by a HSQC experiment (see Supporting Information, Figure S28) that indicated a correlation between the $\mathrm{CH_2{-}C\underline{H}(COOPr)_2}$ triplet and a signal at 52 ppm on the ^{13}C NMR spectrum compatible with the $\mathrm{CH_2{-}\underline{C}H(COOPr)_2}$ terminal carbons. The good agreement observed between M_n values derived from end-group measurements (integration of the terminal protons with respect to the $\mathrm{CH_2}$ protons of the repeat units) and from SEC experiments implies that the initiation with di-*n*-propyl malonate/$\mathrm{Bu}^t\mathrm{P}_4$ is quantitative as well. Given the fact the initiator has two acidic protons on the methylene unit, a possible proton transfer reaction between protonated and carbanionic polymer chain ends (i.e., $\mathrm{RCH(COOR)_2}$ and $\mathrm{RC(COOR)_2}^{(-)}$) may occur during the polymerization (see Scheme S2 in the Supporting Information). A very low polydispersity index of 1.09 suggests, however, that the equilibrium between protonated and active species, if occurring, is rather fast compared to the propagation. Under this mechanistic scheme, each chain end has the same probability to be deprotonated and the polymer chain grows equally from both chain ends. An alternate explanation would involve a very slow proton transfer compared to the propagation. As we consider an acid−base reaction whose rates are known to be fast compared to nucleophilic substitutions, this hypothesis is less likely to be operative.

Polymerizations in Toluene. All experiments reported so far, including those presented in our preliminary report,[27] were carried out with THF as the solvent. Although THF exhibits many suitable physicochemical characteristics (e.g., polarity, melting and boiling points, ability to solvate metallic species) that makes it one of the solvents of choice for anionic polymerizations, it also presents features, mostly cost, that severely restrict its use in industrial applications where solvents such as toluene are preferred. Phosphazenium ions, contrary to small metallic cations, can delocalize their charge in a large volume and on many atoms and, as such, are inherently more lipophilic and prone to be used in less polar solvents. Although this possibility has not been routinely exploited in previously reported polymerization experiments, we wondered whether conditions could be identified to obtain in toluene the excellent polymerization performances demonstrated in THF. To test this hypothesis, experiments (Table 2, entries 1−5) were carried out in toluene, under conditions otherwise identical to the standard one used in THF (PhSH/$\mathrm{Bu}^t\mathrm{P}_4$ as the initiating system with PhSH:$\mathrm{Bu}^t\mathrm{P}_4$:**1** = 1:1:50) and at three temperatures (30, 60, and 100 °C).

Except for experiment 1 (30 °C) that was deliberately stopped for practical considerations (due to a very slow polymerization rate), full conversions were obtained after rather convenient reaction times (in particular, less than 4.5 h at 100 °C). Experiments 2 and 3, performed at the same temperature (60 °C), as well as experiments 4 and 5 (at 100 °C) exhibited an excellent reproducibility. Analysis of the polymers by ^{1}H NMR did not indicate any side reactions occurring. An excellent agreement between M_n measured by SEC-PS and by ^{1}H NMR was obtained, consistent with previous observations in THF. Moreover, experimental M_n values were practically equal to the theoretical ones. It can thus be concluded that the initiation is quantitative and that each initiator molecule generates one macromolecule.

Whatever the temperature, the polymer remained soluble during the entire polymerization, facilitating prospective postpolymerization reactions (e.g., end-capping, initiation of a second polymerization to generate a blocky architecture, ...) and making kinetic investigations up to high conversion possible. Nevertheless, at 30 °C the polymerization medium was quite viscous, contrary to what had been observed in THF under the same conditions. This behavior may be attributed to the presence of aggregates or to the fact that toluene is a rather poor solvent for poly(**1**) compared to THF.

Kinetic data could be fitted according to a first-order equation. In all cases, the reaction was first order with respect to the monomer over the entire conversion range, and the degree of polymerization increased linearly with conversion over the same conversion range. These results are illustrated in Figure 3, which corresponds to experimental data obtained at 100 °C, but the conclusion applies equally well to the three sets of temperature (see Supporting Information, Figures S30−S31). The above kinetic results, coupled to the very narrow molecular weight distributions observed for the obtained polymers, provide the traditional unambiguous experimental evidence that support a living polymerization mechanism under the investigated polymerization conditions.

Propagation rate constants k_p were extracted from the slope of the regression lines and are reported in Table 3 along with a data point previously measured for the same system in THF.[27] As a result, the value of $5.7 \times 10^{-4}\ \mathrm{L \cdot mol^{-1} \cdot s^{-1}}$ calculated for the experiments at 60 °C can be directly compared to the $5.8 \times 10^{-4}\ \mathrm{L \cdot mol^{-1} \cdot s^{-1}}$ value obtained in THF at the same temperature and for identical monomer and initiator initial concentrations ($[\mathrm{M}]_0 = 2.3\ \mathrm{mol \cdot L^{-1}}$ and $[\mathrm{I}]_0 = 0.046\ \mathrm{mol \cdot L^{-1}}$). These practically identical values obtained whatever the solvent used are surprising as THF is a more polar and therefore more dissociative solvent than toluene (ε(THF) = 7.39 and ε (toluene) = 2.408 at 25 °C,[46] ε(THF) = 6.49 and ε (toluene) = 2.31 at 60 °C[46]). As the amount of free ions in THF at 60 °C must be rather low at the concentration in living ends used in the reported experiments, the main ionic species involved should be ion pairs in both solvents.[47]

Before any analysis is attempted about the solvent influence on the polymerization rate, one has to remember first

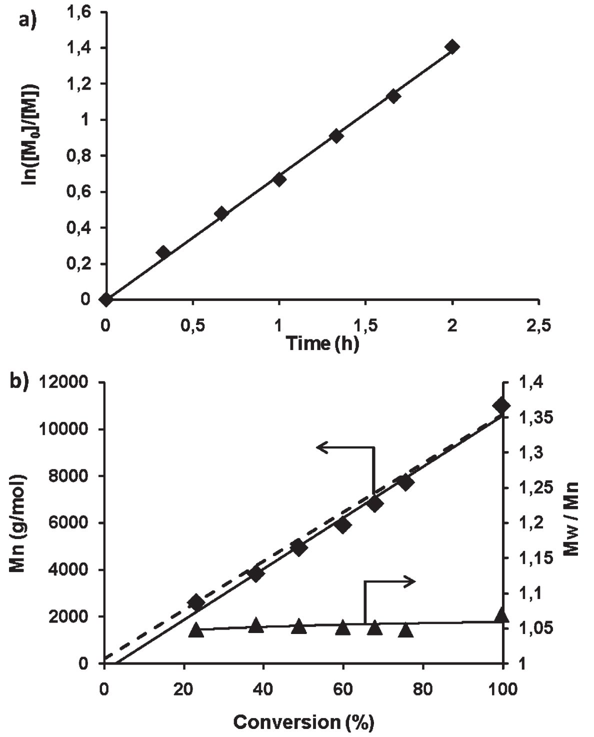


Figure 3. Anionic ring-opening polymerization of **1** at 100 °C in toluene ($[\mathrm{I}]_0$ = 0.046 mol·L^{-1}, $[\mathrm{M}]_0$ = 2.3 mol·L^{-1}, PhSH:$\mathrm{Bu}^t\mathrm{P}_4$:**1** = 1:1:50): (a) first-order kinetic plot (slope = 0.6856 h^{-1}, R^2 = 0.99); (b) relationships observed between absolute number-average molecular weight (squares; theoretical values indicated by the dashed line) or polydispersity index (triangles) and monomer conversion. The number-average molecular weights were measured by SEC-PS (polystyrene calibration) and corrected by applying a multiplication factor of 1.33 to yield absolute M_n numbers (see note *g* in Table 1).

Table 3. Influence of the Solvent and Temperature on the Propagation Rate Constant k_p during the Ring-Opening Polymerization of 1 Using Thiophenol/$\mathrm{Bu}^t\mathrm{P}_4$ as the Initiating System

solvent	*T* (°C)	k_p (L·mol^{-1}·s^{-1})
THF	60	5.8×10^{-4}
toluene	30	3.1×10^{-5}
toluene	60	5.7×10^{-4}
toluene	100	7.1×10^{-3}

that the monomer itself is more polar than both solvents and accounts for a significant volume fraction (about 50%) of the initial reaction mixture. For instance, a dipole moment of 2.4 D has been measured at 25 °C for diethyl cyclopropane-1,1-dicarboxylate,[48] and dielectric constants in the range of 7.8 to 8.4 have been observed at or close to 25 °C for structurally close diethyl malonate $CH_2(COOEt)_2$.[49−51] These data support the idea that the presence of the monomer (and progressively polymer as the polymerization proceeds) in large amounts attenuates significantly the change in dielectric constant when one "solvent" is substituted for the other. Without knowing which ionic species are present, possibly in equilibrium, in the reaction mixture and their involvement (or not) in the polymerization, it is difficult to speculate further.

As already mentioned, the reaction was rather slow at 30 °C (k_p = 3.08×10^{-5} L·mol^{-1}·s^{-1}). Practically, after 1 week, the conversion rate had not reached 50% yet. At 100 °C, however, the much higher reactivity observed (k_p = 7.1×10^{-3} L·mol^{-1}·s^{-1}) lowered significantly the reaction times required for reaching complete conversion of the monomer, down to a few hours. From the three values at 30, 60, and 100 °C, an activation energy of 72.9 kJ·mol^{-1} could be estimated (pre-exponential factor $A = 1.25 \times 10^8$).

In addition to the industrial issue already mentioned, one of the main advantages of using toluene rather than THF ended up being the accessibility to higher temperatures than possible with THF (while maintaining similar reactivities at identical temperatures). The higher polymerizabilities thus obtained allowed us to use higher monomer/initiator molar ratios while maintaining still reasonable reaction times. This attribute ultimately opened access to higher molecular weights than usual for this polymer. For instance, polymers with an x_n of about 187 could be obtained at 100 °C after 32 h (Table 2, entry 6). Theoretically, even higher molecular weights could be achieved by increasing further the $[\text{monomer}]_0$/$[\text{initiator}]_0$ ratio, at the expense of waiting for longer times (several weeks for degrees of polymerization in the thousands range). Experimental molecular weights determined by SEC-PS and ^{1}H NMR were in good agreement with the theoretical ones, and the polydispersity index was low (1.10). This indicated that the structural characteristics of a living polymerization are maintained at 100 °C. Finally, one must note that it would not be practically feasible to access these high degrees of polymerization neither in THF (due to a lower k_p at temperatures below the boiling point) nor with the traditional initiating system based on alkali metal thiophenolates (due to lower reactivities of these species during the propagation step).

Conclusions

$\mathrm{Bu}^t\mathrm{P}_4$ phosphazene base associated with several acidic S−H, O−H, N−H, and C−H molecules, including thiol, phenol, amine, or malonate precursors, was found to be a very efficient initiating system for the metal-free anionic ring-opening polymerization of di-*n*-propyl cyclopropane-1,1-dicarboxylate. These observations agree with the few $\mathrm{Bu}^t\mathrm{P}_4$ phosphazene-induced anionic polymerizations reported in the literature, where faster polymerizations than those performed with traditional alkali organometallics had been observed as well. Heterotelechelic polymers with narrow molecular weight distributions and a control over the nature of both end groups could be prepared according to this approach. The nature of one end group is controlled by selecting the required acidic precursor, while the living character of the anionic polymerization can be exploited to control the nature of the other end group via the reaction of the propagating malonate carbanion with alkylating agents. The efficiency of a broad array of acidic XH precursors as co-initiators in the investigated process suggests that this approach could be extended to other type of acidic precursors, including polyfunctional or reactive ones, as long as the included reactive groups are compatible with the reaction conditions required in an anionic polymerization or are suitably protected.

It was also found that toluene is an excellent substitute to THF as the solvent of choice for these polymerizations, displaying an almost identical influence on the polymerization rate while allowing for the use of higher temperatures (100 °C) without loss of the required living character. By exploiting the above parameters, higher degrees of polymerizations become accessible, opening an access route to polymers of satisfying degrees of polymerization which will be used to investigate in more details the physicochemical properties of this class of unusual semirigid, highly substituted polymers.[52,53]

The fact that several types of anionic species associated with the large phosphazenium counterion give living polymers open interesting perspectives for the synthesis of novel architectures such as block, random or graft copolymers, hyperbranched, or dendritic structures, ...

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Supporting Information Available: Time-conversion data plot, NMR spectra (^{1}H, ^{13}C, COSY, and HSQC) for all polymers reported in Table 1, MALDI-ToF results for the polymer reported in Table 1 (entry 2), ring-opening polymerization plots, UV spectra, and side reaction and transfer reaction schemes (see text). This material is available free of charge via the Internet at http://pubs.acs.org.

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