Polymer Chemistry

PAPER

Cite this: *Polym. Chem.*, 2018, **9**, 1840

Reinvestigation of the mechanism of polymerization of β-butyrolactone from 1,5,7-triazabicyclo[4.4.0]dec-5-ene†

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The questionable mechanism initially proposed to explain how 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) allows us to ring-open β-lactones, such as β-butyrolactone (BL), is reinvestigated here. With the use of a trisubstituted β-lactone, *i.e.* (*R*,*S*)-benzylcarbonyl-3,3-dimethyl-2-oxetanone, and the association of techniques such as ^{1}H/DOSY NMR and MALDI/ESI-MS, we demonstrated that BL is effectively polymerized by the TBD in bulk at 60 °C, minorly from the reported *N*-acyl-α,β-unsaturated TBD species, and majorly from crotonate anions issued from the basic activation of BL. In contrast to what has been reported, the TBD is not covalently linked to the PBL chain but mainly plays the role of a counterion in the $-C(O)O^-$, $TBDH^+$ active site.

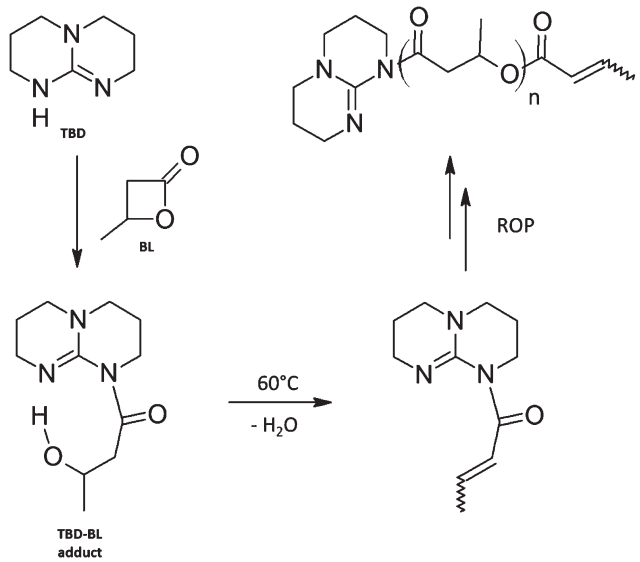
Received 6th February 2018,
Accepted 3rd March 2018

DOI: 10.1039/c8py00206a

rsc.li/polymers

Introduction

Starting in 2012, a series of scientific contributions has been reported on the possibility of initiating the ring-opening polymerization (ROP) of β-lactones, such as β-butyrolactone (BL) and benzyl-β-malolactonate (MLABe), from amidine, guanidine and phosphazene organocatalysts.[1–4] Interestingly, and in contrast to Hedrick *et al.* who demonstrated that the controlled polymerization of BL from the 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) guanidine was not possible in solution at a temperature lower than 50 °C,[5] the authors reported the possibility of controlling the entire process by performing the ROP in bulk at 60 °C. Mainly based on ^{1}H-NMR and Matrix Assisted LASER Desorption/Ionization (MALDI) Time of Flight (ToF) investigations, the proposed mechanism supposedly involves the formation of a TBD-BL adduct which undergoes dehydration to *N*-acyl-α,β-unsaturated species able to initiate the BL ROP process (Scheme 1).[1] As a result, the as-obtained poly (β-butyrolactone) (PBL) chains are expected to be covalently end-capped by both TBD and crotonate moieties.



Scheme 1 Possible mechanism for the ROP of BL from TBD as proposed by Guillaume *et al.*[1]

Even though TBD is the strongest nucleophile in the guanidine series,[6] in many guanidine-catalyzed reactions, nucleophilic addition may compete with Brønsted base catalysis.[7] Since the pK_a of BL α-carbonyl protons is lower than that of the conjugated acid of the TBD (<4.5 *vs.* 26 in THF), and because many research groups have already demonstrated the

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†Electronic supplementary information (ESI) available: NMR analyses, ESI-MS and diffusion curves. See DOI: 10.1039/c8py00206a

easy crotonization of BL by α-deprotonation,[8] we thought it is reasonable to consider the proposed mechanism as questionable. The situation stimulated us to examine again the process of BL polymerization by using TBD in bulk at 60 °C and to compare it with the possibility of applying this process to the ROP of an α,α′,β-trisubstituted-β-lactone.

Results and discussion

Like BL, a β-lactone such as MLABe is known to be the subject of easy α-deprotonation during its anionic ROP (AROP).[9] To circumvent this problem, the dimethylated homologue of MLABe, namely the (*R*,*S*)-benzylcarbonyl-3,3-dimethyl-2-oxetanone (dMMLABe, see Fig. 1) has already been successfully used to prepare PdMMLABe by a controlled and living AROP process.[10] Due to its higher ring-strain,[11] dMMLABe is considered as more reactive than MLABe and is an interesting monomer to study. Prior to any investigation with BL, the nucleophilic potential of TBD was first evaluated by initiating the dMMLABe polymerization by mixing 10 equivalents of the oily monomer with TBD at 60 °C. After 2 hours, the ^{1}H-NMR analysis of the homogenous crude mixture reveals less than 1% conversion suggesting that the nucleophilic behaviour of the TBD is not sufficient to trigger the ROP of the protected monomer (Fig. 1-b). To ensure that the "O-acyl" cleavage of such β-lactone is not prevented by the bulky benzyl ester group, a simple polymerization test has been realized by reacting it with the 1,3-bis(2,4,6-trimethylphenyl)imidazole-2-ylidene (IMes) carbene. The reaction has been performed in THF at 21 °C with an initial $[dMMLABe]_0/[IMes]_0$ ratio of 116 ($[dMMLABe]_0$ = 1.45 M).[12] As summarized in Table S1 (see ESI†), few minutes of the reaction allows the production of PdMMLABe polymers corresponding mainly to cyclic chains and demonstration of the "O-acyl" cleavage feasibility of the protected monomer from the adapted IMes nucleophile.

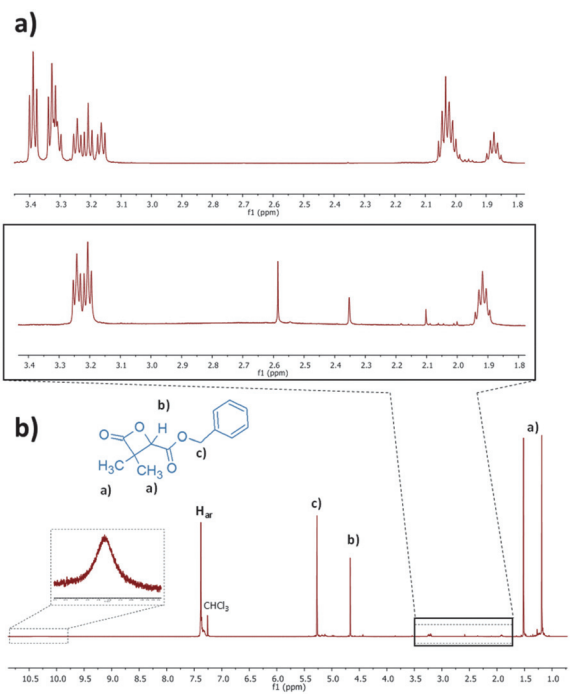
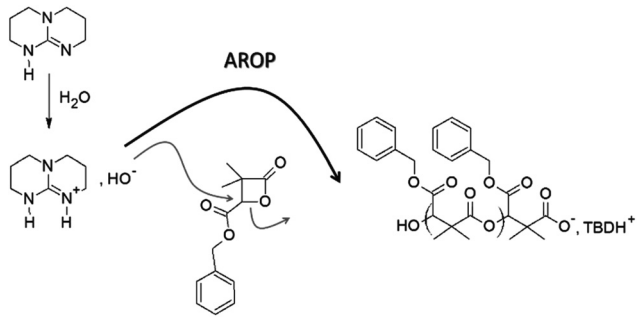


Fig. 1 ^{1}H-NMR spectra of (a) the as-used TBD in $CDCl_3$ and (b) a dMMLABe/TBD (10/1) crude mixture obtained after 2 hours at 60 °C. The full-line square represents the magnification of the spectrum (b) between 1.8 and 3.4 ppm.



Scheme 2 AROP of dMMLABe from "basic" activation of water from TBD.

To gain more insight into the residual polymerization product obtained when dMMLABe is reacted with TBD, Electrospray Ionization Mass spectrometry (ESI-MS) was then employed and the presence of oligo-dMMLABe end-capped by a water molecule was confirmed. Since a nucleophilic attack from the TBD is not possible, these oligomers have probably been obtained from residual water initiating an AROP process in which TBD acts as the active species counter-anion (Scheme 2).

Very interestingly, we serendipitously observed that the proton signals of the TBD molecule changed when comparing the ^{1}H-NMR spectra of the dMMLABe/TBD mixture before and after the reaction (Fig. 1-a and zoom of Fig. 1-b, respectively). This is in accord with Scheme 2 in which TBD goes from its basic state (TBD) to its conjugated acidic one ($TBDH^+$). As highlighted, a drastic change in the splitting of the TBD protonic signals is observed between 1.8 and 3.4 ppm. Noteworthy here is that the peculiar ^{1}H-NMR spectrum of the as-used TBD (recorded in $CDCl_3$) might be caused from its ability to promote H/D exchange with the solvent.[13]

Observing these TBD signals after the reaction suggested to us that we are in the presence of a protonated TBD which is, in contrast to the as-used one, a symmetrical entity. Such a hypothesis was validated by the ^{1}H-NMR analysis (in $CDCl_3$) of a TBD/benzoic acid salt which presents the same TBD signature, *i.e.* three well-resolved protonic signals between 1.8 and 3.4 ppm, due to the symmetry of the $TBDH^+$ cation (Fig. 2).

Ironically since TBD is nucleophilically inactive against the highly reactive dMMLABe, we decided to reinvestigate its ability to properly lead the BL polymerization as previously published. Two polymerization reactions were then performed between BL and TBD in bulk at 60 °C. Polymerization degrees ($DP = [BL]_0/[TBD]_0$) of 10 and 50 were targeted by mimicking

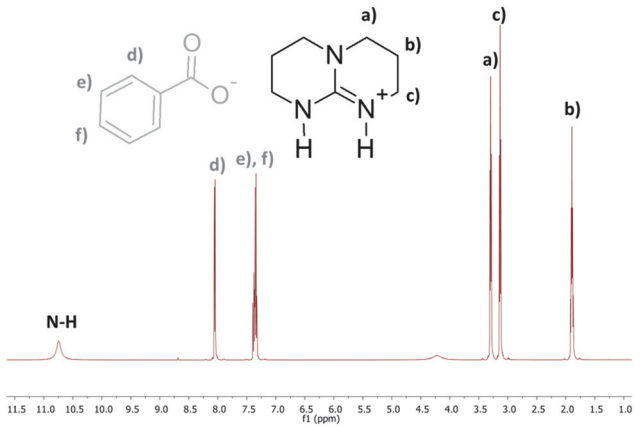


Fig. 2 ^{1}H-NMR spectrum of the TBD/benzoic acid salt in $CDCl_3$.

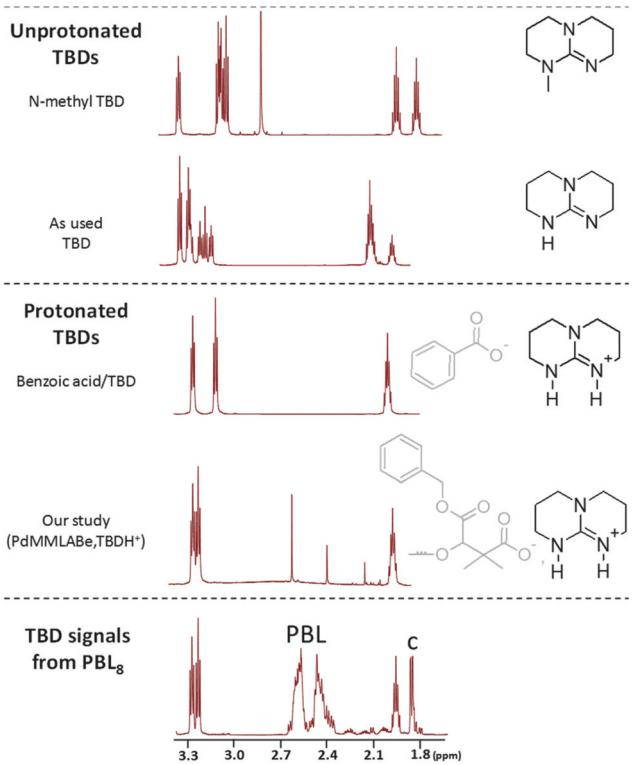


Fig. 3 ^{1}H-NMR spectra (between 1.6 and 3.4 ppm, $CDCl_3$, 21 °C) comparing unprotonated TBDs (including the as-used TBD and *N*-methyl-TBD, MTBD), protonated TBDs (including a benzoic acid/TBD adduct and the TBD protonic signals observed in Fig. 2) and the TBD signals extracted from the PBL_8 proton spectrum. PBL and c are assigned to PBL methylene protons and crotonate methyl group, respectively (see text).

the experimental conditions reported by Guillaume *et al.*,[1] *i.e.* by limiting the polymerization reactions to 0.5 and 2 hours, respectively. Regarding the degree of conversion recorded for both polymerizations, PBL samples were called PBL_8 (DP = 8, M_nSEC = 550, $Đ_M$ = 1.8) and PBL_{48} (DP = 48, M_nSEC = 3700, $Đ_M$ = 1.8), respectively. ^{1}H-NMR analyses of both crude media reveal the effective production of PBL structures in the presence of crotonate, TBD and residual monomer protonic signals. Interestingly, in both spectra (recorded in $CDCl_3$), the guanidine protonic signals are appearing perfectly defined with no decoupling effect suggesting a symmetrical $TBDH^+$ structure. Such signature discredits either unsymmetrical TBD-BL or *N*-acyl-α,β-unsaturated adducts and suggests more a protonated TBD cationizing the carboxylate end-group PBL chains. This has been attested by comparing a series of symmetrical and unsymmetrical TBD-based structures (Fig. 3). Clearly, ^{1}H-NMR analyses (in $CDCl_3$) confirmed a "splitting effect" of unsymmetrical structures (*e.g.* the as-used TBD and the *N*-methyl TBD) while no splitting effect is observed whatever the protonated symmetrical TBD moieties studied.

To confirm that the suspected *N*-acyl-α,β-unsaturated species drawn by Guillaume *et al.* is not formed – or at least produced in a very low amount – by dehydration of the TBD-BL adduct during the ROP process (see Scheme 1), we focused our attention on the eventual presence of water in the PBL_8 crude sample. Since for such a low molar mass polymer (M_nSEC = 550 g mol^{-1}), the dehydration process should lead to ~10 mol% of water, we anticipated that a H_2O signal should appear in the ^{1}H-NMR analysis (at least qualitatively). Each step was then realized in the total absence of moisture including the preparation of the NMR sample in a glovebox by using dried $CDCl_3$. As suspected, no water protonic signal was observed in the spectroscopy analysis (Fig. S1-a, ESI†), while the intentional addition of 10 mol% of H_2O in the NMR tube is accompanied by the appearance of a broad signal between 2.82 and 3.2 ppm (Fig. S1-b, ESI†). These results reinforce the hypothesis that the crotonate moieties observed in the NMR spectra do not correspond to the ω-end group of PBL chains from a dehydration process, but, in contrast, could represent the α-chain end of a PBL macromolecule as being issued from an α-deprotonation of a BL monomer from the basic TBD.

Indisputably, such a hypothesis leads to the assumption that a crotonic acid/TBD salt acts as potential initiator in the BL polymerization. To confirm that an $\cdots C(O)O^-$, $TBDH^+$ propagating end-group is sufficiently active towards the BL ROP, a single turnover reaction was performed between a preformed benzoic acid/TBD salt and the BL monomer in bulk ($[salt]_0/[BL]_0$ = 1/1.5). The activity of the salt was primarily confirmed at r.t. After 12 hours, the ^{1}H-NMR analysis of the crude medium revealed that 77% of the monomer were converted with no trace of crotonate species suggesting that the $\cdots C(O)O^-$, $TBDH^+$ is active for the BL ROP even at low temperature (Fig. S2-a, ESI†). More interestingly, increasing the temperature to 60 °C, for an extra hour, allows the complete consumption of the monomer but also induces the appearance of new crotonate signals (Fig. S2-b, ESI†). Such an observation tends to indicate that the control polymerization of BL in bulk at 60 °C is not possible due to the poisoning deprotonation of the monomer from the free TBD during the propagation and that high DPs could not be obtained under such conditions.

To explain such deprotonation during the ROP process at 60 °C, we speculated that free TBD is in equilibrium with its

corresponding salt or that the chemical bond formed between the protonated TBD and the carboxylate end-group is slowly disrupted by increasing the temperature. Under both conditions, this allows the basic TBD to eliminate the BL acidic methylene protons by deprotonation, explaining the appearance of crotonate moieties at 60 °C in the model experiment. To confirm it, a crotonic acid/TBD salt ($[\text{crotonic acid}]_0/[\text{TBD}]_0$ = 1/1) has been prepared and analysed by ^{1}H-NMR spectroscopy at different temperatures (from 25 to 70 °C) in CD_3CN. Both acid and deuterated solvent have been chosen to mimic the BL polymerization process in terms of possible initiators and polarities. Interestingly, even at 25 °C, only 64 mol% of salt are produced and its relative content diminishes linearly with the temperature, dropping down to 53 mol% at 70 °C (Fig. S3, ESI†). This clearly indicates that free TBD is always present during the BL polymerization course and explains why the crotonate content, observed during the BL ROP from a benzoic acid/TBD mixture, increases at higher temperature.

The ability of the TBD to deprotonate BL monomers during the ROP course has also been proven by a kinetic study where the amount of crotonate functions has been recorded (Fig. 4-a). According to the Guillaume's mechanism, the $[\text{TBD}]_t/[\text{crotonate}]_t$ ratio should be equal to 1 and, for a targeted DP of 50, such $[\text{crotonate}]_t$ is estimated to 2 mol% all along the ROP process. Fig. 4-a demonstrates that it is actually not the case and that the crotonate content, during the BL ROP, increases during the polymerization to ultimately reach,

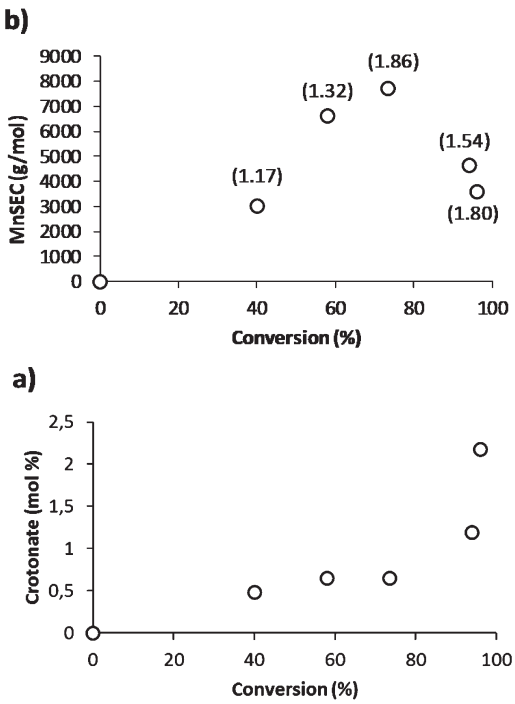


Fig. 4 Crotonate molar content (a) and molar masses (b) evolution recorded during a BL ROP from TBD at 60 °C ($[\text{BL}]_0/[\text{TBD}]_0$ = 50). Dispersity values are given in parentheses.

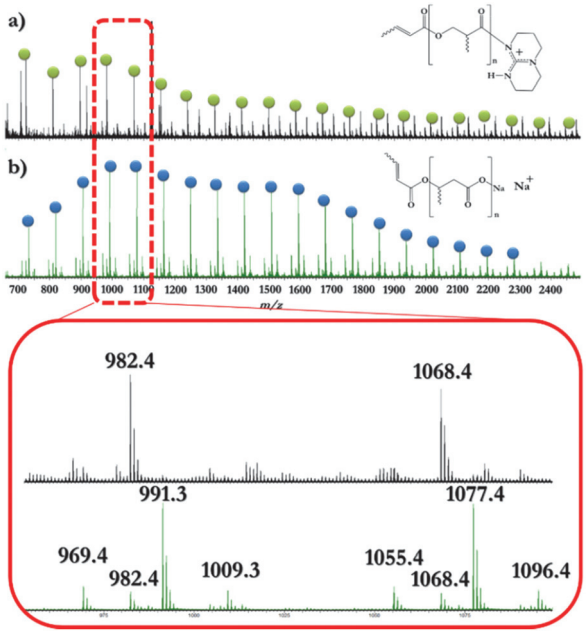


Fig. 5 MALDI analyses of PBL_8 without the cationizing agent (a) and in the presence of sodium (b). The bottom part represents the magnification of both spectra between 960 and 1100 *m/z*.

after 2 hours, 2.2 mol%. Such an increase in the crotonate content is also accompanied by a clear modification of the TBD protonic signals during the ROP course (Fig. S4, ESI†). If the generation of a possible TBD-BL adduct or *N*-acyl-α,β-unsaturated species is not excluded, it seems clear that most of the TBD used is transformed in $TBDH^+$. The continuous production of potential ROP initiators discredits a controlled process as also demonstrated by an associated "up and down" molar mass evolution (Fig. 4-b).

PBL_8 and PBL_{48} samples were then analysed by spectrometry methods including MALDI & ESI-MS, concomitantly to DOSY NMR spectroscopy. Fig. 5 presents two MALDI analyses performed on PBL_8 as recorded by two sets of experimental conditions. First, the MALDI analysis was performed in the absence of a cationizing agent (Fig. 5-a). Although polymer distribution has been observed, the intensity of the signal is extremely low, suggesting a weak ionization efficiency and the necessity to add a cationization agent. Interestingly, under these specific experimental conditions, dehydrated PBL chains naturally cationized by a protonated TBD are observed in accordance with Guillaume's results.[1] To gain a better insight and improve the signal-to-noise ratio, the sample was then analysed by adding sodium (Fig. 5-b). Interestingly, a completely different MALDI fingerprint was observed unveiling four populations which have been clearly assigned by using adequate isotopic models (Fig. 6).

Under these specific experimental conditions, the population (b) assigned to dehydrated PBL chains cationized by a protonated TBD is in clear minority. The most intense population (c) represents the distribution corresponding to

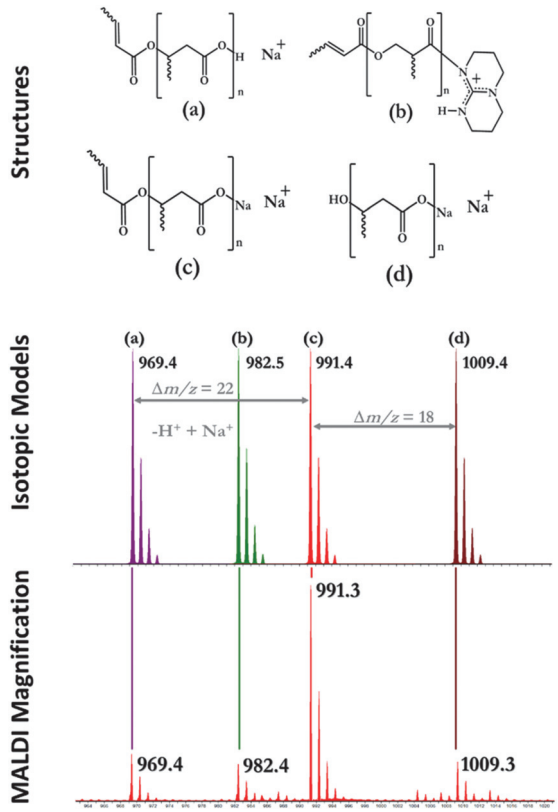


Fig. 6 Magnification of Fig. 5-b between 960 and 1020 *m/z* (bottom) exposed to adequate isotopic models (top).

α-crotonate, ω-carboxylate PBL chains carrying two sodium atoms. Such a presence of two Na^+ is the signature of a carboxylic acid extremity (here assigned to the population (a)) which is in the carboxylate form.[10e] Finally, the population (d) represents a PBL chain initiated by water and end-capped by a carboxylic acid. Note here that the low intense dehydrated species are not cationized by Na^+ in contrast to what Guillaume had proposed in her initial study.[1] In agreement to those MALDI analyses, ESI-MS spectrometry also did confirm the presence of different PBL populations (Fig. S5, ESI†).

In accordance with the ^{1}H-NMR analyses, both spectrometry techniques tend to indicate that only a very low amount of PBL chains could be assigned to *N*-acyl-α,β-unsaturated species and that the majority of those are issued from a basic activation process. To confirm this conclusion, *i.e.* most of the PBL chains are not covalently linked to a TBD residue at their extremity, NMR DOSY analyses were performed. NMR DOSY experiments allow the discrimination of different molecules according to their diffusion coefficients, and hence their molar masses. It is thus an interesting tool in the case of the present study since the small TBD "catalyst" presents a smaller molar mass than the polymer. As an effect, its diffusion coefficient should be different from that of the polymer if it is not covalently bonded. DOSY spectra were thus recorded in a solution of pristine TBD and in solutions of both PBL_8 and PBL_{48} still containing TBD (crude samples). These

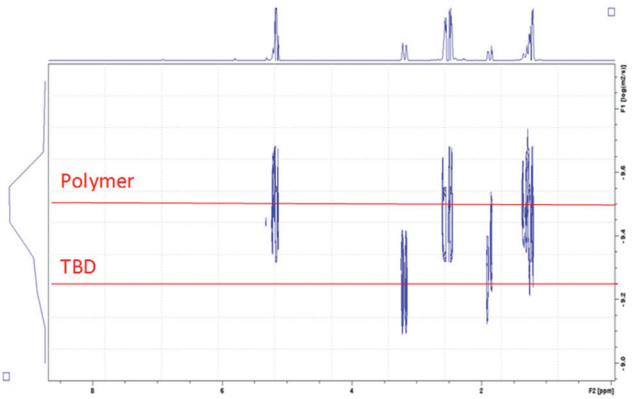


Fig. 7 DOSY spectrum recorded on a solution of PBL_8 in CD_3CN. Two sets of diffusion coefficients are clearly visible, corresponding to the peaks of TBD and of the polymer respectively.

measurements were performed in two different solvents of different polarities, *i.e.* $CDCl_3$ and CD_3CN. Fig. 7 presents the DOSY spectrum recorded in PBL_8.

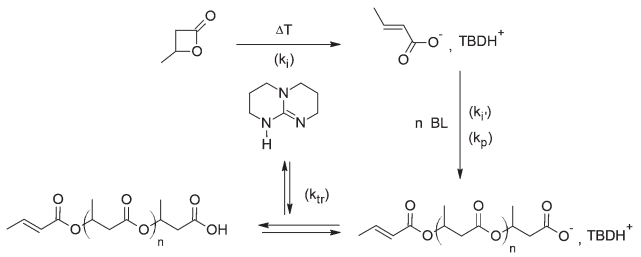
As expected, a difference between the diffusion coefficients of the TBD and the polymer chain is clearly visible. Nevertheless, as stated in the experimental part, precise diffusion coefficients were obtained by extracting the diffusion curves (Fig. S6-a and S6-b, ESI†) on 3 different peaks of the polymer and of TBD. Results are shown in Table 1. First, it is clearly visible that all the measured diffusion coefficients are higher in CD_3CN than in $CDCl_3$ by a factor of 1.6 in average. This can easily be explained by the difference of viscosity between the 2 solvents. Secondly, the comparison between the diffusion coefficients of the polymer and the TBD – for both solutions of polymer in the 2 solvents – shows that TBD is diffusing more rapidly than the polymer. This difference tends to confirm that TBD is not covalently bonded to the polymers. Nevertheless, the comparison between the diffusion coefficients of TBD in the solutions of the polymer and alone in the solvents shows a slower diffusion of TBD in the solutions of the polymer.

This tends to prove that there is, for the major part of the PBL samples, a non-covalent interaction between the polymer and the TBD, with an exchange between the bonded and the free form of TBD which is rapid on the NMR timescale, as suggested by the linear evolution of the diffusion curves. As rationalized in the experimental part, a linear evolution of the natural logarithm of the signal intensity *versus* the square of the gradient is typical of a mono-diffusing species, which allows us to suggest that the obtained diffusion coefficient is a weighted average between the diffusion coefficients of the bonded and of the free form of the TBD.[14,15] Moreover it has to be noted that, the trend being the same in both solvents, the non-covalent interaction between TBD and the polymer does not seem to depend on the solvent polarity.

In accordance with an anionic process in which the protonated TBD plays the role of a counterion (Scheme 3), adding exogenous carboxylic acid in the course of a reaction might

Table 1 Averaged diffusion coefficients extracted from the diffusion curves obtained on 3 different peaks of the polymer and TBD in both $CDCl_3$ and CD_3CN. Unit: $m^2\ s^{-1}$

	TBD	PBL_8	PBL_{48}
$CDCl_3$	$D_{TBD} = 9.50 \times 10^{-10}$	$D_{polymer} = 4.30 \times 10^{-10}$ $D_{TBD} = 5.95 \times 10^{-10}$	$D_{polymer} = 1.94 \times 10^{-10}$ $D_{TBD} = 3.16 \times 10^{-10}$
CD_3CN	$D_{TBD} = 1.98 \times 10^{-9}$	$D_{polymer} = 7.00 \times 10^{-10}$ $D_{TBD} = 9.45 \times 10^{-10}$	$D_{polymer} = 2.68 \times 10^{-10}$ $D_{TBD} = 4.75 \times 10^{-10}$



Scheme 3 AROP of BL explained by TBD basic activation (transfer reactions have been omitted for more clarity).

lead to an "active-dormant" polymer chain equilibrium. In contrast, if the TBD is covalently linked to the PBL chains, such an equilibrium does not happen and the extra carboxylic acid moieties should only act as spectators being then unable to initiate any polymerization. Accordingly, 1-pyreneacetic acid (PyCOOH) has been selected as a transfer agent.[16] Practically, a BL polymerization was initiated by TBD at 60 °C for a $[BL]_0/[TBD]_0$ ratio of 50. After 10 minutes, the medium was cooled down to 21 °C and charged with one equivalent of PyCOOH (pre-solubilized in BL) relative to the TBD initial content. The reaction was then thermally treated (60 °C) for an extra hour. Fig. 8 presents the SEC curves of the crude medium right after the addition of the PyCOOH (sample 1) and after the extra 1-hour treatment (sample 2). As expected, adding the PyCOOH slows down the process but does not terminate it. The PBL chains obtained in the early stage of the reaction (before the addition of the transfer agent) still grow after the addition of PyCOOH while this last clearly initiates the polymerization of new chains. The UV detection of the SEC also attests that the chromophore is only end-capping the freshly initiated PBL chains while the pre-formed ones do not present any pyrene incorporation. Such a result is in perfect agreement with an ionic polymerization in which the TBD goes from one carboxylic acid end-group to another.

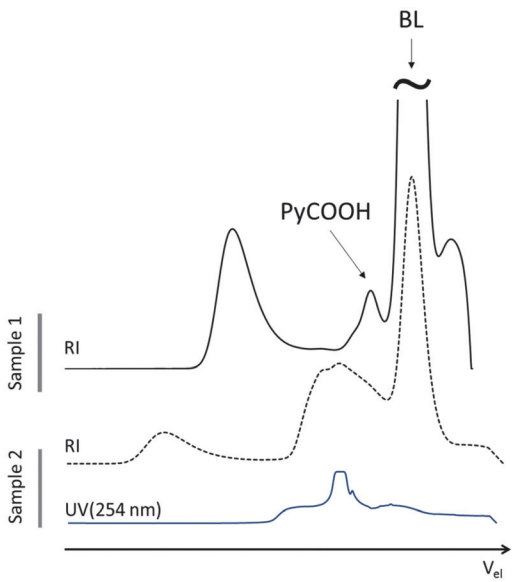


Fig. 8 SEC analyses using both RI and UV detectors of samples 1 and 2 (see main text).

The above-presented results indicate that carboxylate anions, issued from a BL basic activation from TBD, might constitute the main growing species in BL polymerization leading, at 60 °C and in bulk, to α-crotonate, ω-carboxylate, $TBDH^+$ PBL chains.

Conclusions

The bulk ROP of BL from TBD at 60 °C has been reinvestigated. The gathered results tend to prove that the polymerization process is majorly due to an initial deprotonation of the monomer from the guanidine base generating *in situ* crotonate initiators for which the carboxylate ($-C(O)O^-$) is compensated for by the protonated TBD ($TBDH^+$). Model experiments indicate that only a part of the TBD activates the polymerization in the early stage of the process and that potent initiators are produced all along the ROP course, especially at high temperature. Under such conditions, most of the produced PBL chains are end-capped by both crotonic and $-C(O)O^-$, $TBDH^+$ moieties as proven by DOSY NMR experiments. While MALDI/ESI-MS analyses confirm that most of the PBL chains are indeed obtained from an AROP, kinetic experiments clearly demonstrated the uncontrolled behaviour of such a process.

Experimental

Materials

(*R*,*S*) β-Butyrolactone (BL, +98% Aldrich) and (*R*,*S*)-benzylcarbonyl-3,3-dimethyl-2-oxetanone (dMMLABe) were purified and synthesized as reported in ref. 8*h* and 11, respectively. 1-Pyreneacetic acid (PyCOOH, 98%, Aldrich) and 1,5,7-triazabicyclo-[4.4.0]dec-5-ene (TBD, 98%, Aldrich) were dried overnight at 80 °C under vacuum. Crotonic acid (99%, Fluka) was used

as received. Chemicals were stored and manipulated in a glovebox (H_2O < 3 ppm, O_2 < 1 ppm).

General polymerization procedure

In a glovebox, a vial with a stir bar was charged with BL and TBD (regarding the targeted DP). The sealed vial was stirred at 60 °C in an oil bath out of the glovebox. After adequate reaction time, the reaction was cooled down to room temperature and crude mixtures were analysed by ^{1}H-NMR and SEC analyses.

Methods

^{1}H NMR-spectra were recorded using Bruker AVANCEII 500 apparatus at r.t. in $CDCl_3$ (10 mg per 0.6 mL) or at different temperatures in CD_3CN (2 mg per 0.6 mL). Temperature-dependent experiments were performed between 25 °C and 70 °C thanks to a BVT-3200 unit, with a 5 min stabilizing time between each temperature.

Size exclusion chromatography (SEC) was performed in THF (+2 vol% NEt_3) at 35 °C using a Triple Detection Polymer Laboratories liquid chromatograph equipped with a refractive index (ERMA 7517), a UV detector (254 nm), a capillary viscometry, a light scattering RALS (Viscotek T-60) (Polymer Laboratories GPC-RI/CV/RALS) and an automatic injector (Polymer Laboratories GPC-RI/UV) and four columns: a PL gel 10 μm guard column and three PL gel Mixed-B 10 μm columns (linear columns for separation of MWPS ranging from 500 to 10^6 daltons).

Positive-ion MALDI-Mass Spectrometry (MALDI-MS) experiments were recorded using a Waters QToF Premier mass spectrometer equipped with a Nd:YAG (third harmonic) operating at 355 nm with a maximum output of 65 μJ delivered to the sample in 2.2 ns pulses at 50 Hz repeating rate. Time-of-flight mass analyses were performed in the reflectron mode at a resolution of about 10 000. All the samples were analyzed using *trans*-2-[3-(4-*tert*-butylphenyl)-2-methylprop-2-enylidene] malononitrile (DCTB) as the matrix. This matrix was prepared as 40 mg mL^{-1} solution in $CHCl_3$. This matrix solution (1 μL) was applied to a stainless steel target and air-dried. Polymer samples were dissolved in THF to obtain 1 mg mL^{-1} solutions and 50 μL of 2 mg mL^{-1} NaI solution in acetonitrile has been added to the polymer solution. Therefore, 1 μL of this solution was applied onto the target area already bearing the matrix crystals, and air-dried. For the recording of the single-stage MS spectra, the quadrupole (rf-only mode) was set to pass all the ions of the distribution, and they were transmitted into the pusher region of the time-of-flight analyzer where they were mass analyzed with 1 s integration time. Data were acquired in continuum mode until acceptable averaged data were obtained.

The electrospray ionization mass spectrum was recorded using a Waters Synapt G2-S*i* mass spectrometer. The solution (~10–6 mol L^{-1} in acetonitrile) is directly infused in the ESI source with a typical flow rate of 5 μl min^{-1}, with a capillary voltage of 3.1 kV, a source temperature of 100 °C and a desolvation temperature of 200 °C. The quadrupole was set to pass ions from 100 to 2000 Th and all ions were transmitted into the pusher region of the time-of-flight analyzer (resolution ~20 000) for mass-analysis with 1 s integration time. Data were acquired in continuum mode until acceptable average data were obtained.

NMR DOSY experiments were recorded on an AVANCEII 500 spectrometer equipped with a superconducting magnet of 11.75 T (Bruker, Karlsruhe, Germany). Bipolar gradient pulses with two spoil gradients were used to measure the diffusion coefficients (BPP-LED pulse sequence). The value of the gradient pulse length δ was 2 ms, while the value of the diffusion time Δ was set to 200 ms or 250 ms depending on the polymer size. The pulse gradients were incremented in 16 steps from 2% to 95% of the maximum gradient strength (53.5 G cm^{-1}) in a linear ramp and the temperature was set at 25 °C. The DOSY spectra were obtained from the TOPSPIN 2.1 software and the diffusion curves were extracted on 3 different peaks of the polymer and of the catalyst to measure precisely their respective diffusion coefficients. In each case, the mono-exponential diffusion curves were fitted with the well-known eqn (1) to extract the diffusion coefficients. The averaged diffusion coefficient was then calculated for the polymer and for TBD based on these 3 measurements.[17,18]

$$I = I_0 \exp[-\gamma^2 g^2 D \delta^2 (\Delta - (\delta/3) - (\tau/2))] \quad (1)$$

where I_0 is the intensity at 0% gradient, γ is the gyromagnetic ratio, g is the gradient strength, D is the diffusion coefficient, δ is the gradient pulse length, Δ is the diffusion time and τ is the interpulse spacing in the BPP-LED pulse sequence.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was supported by the Science Policy Office of the Belgian Federal Government (PAI 7/5) and by a grant from the Belgian FRFC-FNRS (no. 2.4508.12). O. C. is a Research Associate of the F.R.S.-FNRS. The UMONS MS laboratory acknowledges the "Fonds National de la Recherche Scientifique (FRS-FNRS)" for its contribution to the acquisition of the Waters QToF Premier and Synapt G2-S*i* mass spectrometers and for continuing support.

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