Janus Effect of Lewis Acid Enables One-Step Block Copolymerization of Ethylene Oxide and N -Sulfonyl Aziridine

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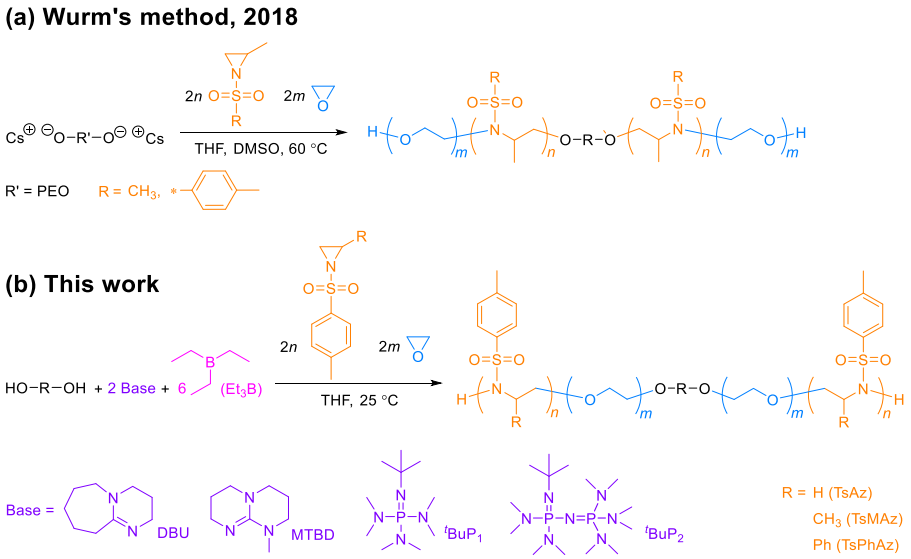
Abstract: One-step sequence-selective block copolymerization requires stringent catalytic control of monomers relative activity and enchainment order. It has been especially rare for A*n*B*m*-type block copolymers from simple binary monomer mixtures. Here, ethylene oxide (EO) and *N*-sulfonyl aziridine (Az) compose a valid pair provided with a bicomponent metal-free catalyst. Optimal Lewis acid/base ratio allows the two monomers to strictly block-copolymerize in a reverse order (EO-first) as compared with the conventional anionic route (Az-first). Livingness of the copolymerization facilitates one-pot synthesis of multiblock copolymers by addition of mixed monomers in batches. Calculation results reveal that a Janus effect of Lewis acid on the two monomers is key to enlarge the activity difference and reverse the enchainment order.

Synthetic polymers are generally inferior to natural ones in terms of precise sequence control and the resulting sophisticated functionality. In particular, precision synthesis of copolymers with strictly controlled sequence structure by classic copolymerization approach from mixed-monomer feedstocks represents a major challenge in chemistry.[1] Recently, significant progresses have been made in one-step sequence-selective block copolymerization, also frequently referred to as (self)-switchable (co)polymerization, which is constituting a new and promising section in the synthetic methodology for sequence-controlled (co)polymers.[2] The most widely reported is three-component monomer mixture comprising cyclic anhydride (A), epoxide (B), and CO_2, cyclic ester, or another cyclic anhydride (C). A diversity of metal-based catalysts and several organic/metal-free catalysts were shown effective for such monomer combinations to deliver well-defined (AB)*n*(CB)*m*- or (AB)*n*C*m*-type block terpolymers in one synthetic step.[3] The success stems mainly from the overwhelmingly high activity of cyclic anhydride (A), as compared with monomer C, towards nucleophilic attack of epoxide-derived alkoxide species. Interestingly, the same principle applies well to a two-component monomer mixture comprising only cyclic anhydride (A) and epoxide (B).[4] The catalyst allows the excess epoxide to act as "monomer C" and fulfils one-step tailored synthesis of (AB)*n*B*m*-type block copolymers. Also, (AB)*n*(AC)*m*-type block terpolymers from cyclic anhydride, *N*-sulfonyl aziridine (Az), epoxide, and A*n*(BC)*m*-type block terpolymers from *O*-carboxyanhydride, cyclic anhydrides/CO_2, epoxide, have been reported recently.[3g, 3j, 5]

On the other hand, it is still rarely reported for one-step sequence-selective synthesis of classic A*n*B*m*-type block copolymers from "truly" two-component monomer mixtures. The major difficulty lies in finding two copolymerizable monomers with perfectly matching reactivity ratios and/or a proper catalytic systems to help satisfying the stringent kinetic requirements.[6] Müller *et al*. reported that the activity difference between *p*- alkylstyrene and isoprene in anionic copolymerization was large enough to achieve highly tapered sequence distribution which allowed the copolymers to exhibit microphase-segregated structures as strict block copolymers obtained via sequential monomer addition.[6a, 7] Soon after, Wurm *et al*. disclosed that the activity difference between ethylene oxide (EO) and Az in their anionic copolymerization was sufficiently large at elevated temperature. So, ring-opening polymerization (ROP) of Az occurs first from a cesium alkoxide initiator. ROP of EO was launched from the termini of PAz only after Az was fully consumed, guaranteeing one-step controlled synthesis of PAz- *b*-PEO amphiphilic block copolymers.[8] The large activity difference between Az (B) and epoxide (C) was also well utilized by Hadjichristidis *et al.* in their anionic terpolymerization with phthalic anhydride (A) to fulfil one-step synthesis of (AB)*n*(AC)*m*- type block terpolymers.[5]

Metal-free catalysts consisting of an organobase and a trialkylborane, either as two monofunctional components or as one bifunctional component, have shown high efficiency and chemoselectivity in the ROP of epoxides[9] and copolymerization of epoxides with CO_2,[10] COS,[11] cyclic anhydrides,[4a, 4b, 4d, 12] iso(thio)cyanates,[9c, 13] *etc*. Activation of epoxides through interaction with Lewis acidic boron species, among other reasons,[14] has been considered to contribute crucially to the catalytic performance. As a typical manifestation, increasing the loading of trialkylborane usually results in faster kinetics. This holds true especially for the homopolymerization of epoxides.[9a] However, it has been

observed several times that increasing the boron-to-base ratio causes faster enchainment of epoxide while slows down or even inhibits enchainment of the comonomer.[13b, 14-15] This is due to the tight coordination of the boron center with the nucleophilic chain-propagating species and the ineffectiveness of excess boron species for activating the comonomer. Here, organobases and triethylborane (Et3B) are paired for the copolymerization of EO and Az (Scheme S1 and Figure S1) at room temperature (RT), in expectation that Et3B would have an opposite (Janus) effect on their activities so that the enchainment order would be reversed to allow one-step synthesis of block copolymers with new sequence structures (Scheme 1).



Scheme 1. General scheme for one-step block copolymerization of EO and Az by (a) cesium alkoxide-initiated anionic copolymerization following an Az-first order and (b) alcohol-initiated metal-free copolymerization following a reverse (EO-first) order.

Since PEO ends with alcoholic hydroxyl groups, it is a prerequisite that controlled ROP of Az could be accomplished from hydroxy initiators. A series of experiments were first performed with 1,4-benzenedimethanol (BDM) as a representative hydroxy initiator for the ROP of *N*-tosyl-2-methyl aziridine (TsMAz) in tetrahydrofuran (THF) at RT (*ca*. 25 °C) using a phosphazene base (PB) as the catalyst either alone or in cooperation with Et3B (Scheme S2). It was found that the weakest PB (^{t}BuP1)[16], with or without BDM and 1.0 eq. of Et3B, was inactive as no TsMAz conversion was detected in 24 h (entry S1~S3 in Table S1). A stronger PB, ^{t}BuP2,[16] triggered the ROP of TsMAz when used alone in 1 eq. of BDM hydroxyl group (OH; entry S4 Table S1). However, the number-average molar mass ($M_{n,SEC}$) obtained from size exclusion chromatography (SEC) was much higher than the theoretical value calculated from monomer-to-initiator ratio ($M_{n,th}$). ROP of TsMAz also occurred when ^{t}BuP2 was used without an added initiator, but $M_{n,SEC}$ was significantly higher and broader (entry S5 Table S1). These results suggest that ^{t}BuP2-activated OH could initiate the ROP of TsMAz but in a slow-initiation-fast-propagation mode, probably because of the large acidity difference between OH and sulfonamide group at the propagating chain end.[17] When Et3B was used in 1 eq. of ^{t}BuP2, $M_{n,SEC}$ agreed well with $M_{n,th}$ and $Đ_M$ was 1.16 at full TsMAz conversion (entry S6 Table S1). Only one distinct mass population was shown in the matrix assisted laser desorption/ionization time of flight mass spectrometry (MALDI-TOF

MS) corresponding to the expected BDM-initiated PTsMAz (Figure S2). It is thus indicated that the initiation efficiency can be significantly enhanced in the presence of Et3B to afford highly controlled ROP of TsMAz from a hydroxy initiator. Controlled ROP of TsMAz was also achieved when the loading of Et3B was increased to 3 eq. of ^{t}BuP2 but without noticeably accelerated kinetics (entry S7 in Table S1 and Figure S3). This is distinct from the ROP of epoxides[9a] and implies that the catalysts take effects in the two ROPs very differently. Controlled ROP of a bulkier Az, *N*-tosyl-2-phenyl aziridine (TsPhAz), also occurred when [^{t}BuP2]/[Et3B] was 1/1, though in a much slower rate (entry S8 in Table S1, Figure S4).[18] The feed ratio of OH, TsMAz, and EO was first kept at 1/12/57 aiming at a total molar mass of 10 kg mol^{-1} (Table 1). When Et3B was used in 1 eq. of ^{t}BuP2 (entry 1 in Table 1), conversion of EO reached 88% in 50 min when the conversion of TsMAz was only 9%, demonstrating significantly faster enchainment of EO than TsMAz. In 5 h, EO was exhausted and only 5% of TsMAz was left (Figure S5), suggesting the formation of a high-gradientcopolymer with EO units enriched around the center and TsMAz units enriched at both ends. Molar mass distribution was narrow and unimodal, and ^{1}H NMR spectrum of the isolated product exhibited signals from both EO and TsMAz monomeric units (Figure S6). Both $M_{n,SEC}$ and $M_{n,NMR}$, calculated by comparing the proton signals of BDM residue and monomeric units, were in good agreement with $M_{n,th}$. Unlike PTsMAz, the copolymer clearly presented methylene signals from BDM residue, revealing that EO had the priority to react with the initiating OH.[9a] ^{1}H DOSY NMR spectrum showed a single diffusion coefficient for all these protons, further confirming successful initiation and copolymerization (Figure S7).[8]

Table 1. Conditions and results of the copolymerization of EO and Az[a]

entry	[base]/[Et_3B]/[OH]/[Az]/[EO][b]	base	time (h)	conv. (EO) (%)	conv. (Az) (%)	$M_{n,th}$[c] (kg mol^{-1})	$M_{n,NMR}$[d] (kg mol^{-1})	$M_{n,SEC}$[e] (kg mol^{-1})	$Đ_M$[e]
1	1/1/1/12/57	^{t}BuP$_2$	5/6	88	9	5.0	–	8.1	1.06
			5	100	95	10.0	11.3	9.9	1.11
2	1/3/1/12/57	^{t}BuP$_2$	1/60	100	0	5.0	–	7.5	1.06
			5	100	94	10.2	10.3	11.4	1.05
3	1/3/1/12/57	DBU	24	100	88	9.6	11.3	5.9	1.15
4	1/3/1/12/57	MTBD	24	100	92	9.8	11.9	7.5	1.16
5[a]	1/3/1/13/57	^{t}BuP$_2$	48	100	57	8.1	10.1	10.9	1.11
6[a]	1/1/1/9/57	^{t}BuP$_2$	96	100	94	9.7	11.5	12.3	1.07
7[a]	1/3/1/9/57	^{t}BuP$_2$	192	100	15	5.9	7.4	10.6	1.07
8	1/3/1/25/226	^{t}BuP$_2$	6	100	100	30.6	36.7	26.3	1.12
9	1/3/1/50/113	^{t}BuP$_2$	24	100	100	31.2	34.4	25.9	1.09
10-1[f]	1/3/1/12/57	^{t}BuP$_2$	6	100	100	10.2	–	11.1	1.11
10-2[f]	0/0/0/12/57	^{t}BuP$_2$	6	100	85	19.7	–	19.9	1.09
10-3[f]	0/0/0/24/114	^{t}BuP$_2$	12	100	87	38.7	41.7	31.6	1.17
11-1[g]	1/3/1/12/57	^{t}BuP$_2$	6	100	100	10.2	–	11.0	1.11
11-2[g]	0/0/0/12/40	^{t}BuP$_2$	24	100	68	19.3	15.3	15.7	1.11

[a] $[Az]_0 = 0.45$ M, $[EO]_0 = 0.7$–1.2 M; TsMAz is used for entry 1–4 and 8–11, TsAz is used for entry 5, TsPhAz is used for entry 6 and 7. [b] Feed ratio of base, Et_3B, OH, and monomers. [c] Theoretical number-average molar mass. [d] Number-average molar mass calculated from ^{1}H NMR spectra of the isolated product. [e] Number-average molar mass and molar mass distribution from SEC analysis (THF, 35 °C, PS standards). [f] EO/TsMAz mixtures were added in three batches. [g] EO and TsMAz were copolymerized first, and a batch of PO/TsMAz mixture was added after 6 h.

When the loading of Et3B was increased to 3 eq. of ^{t}BuP2 (entry 2 in Table 1), the difference in enchainment rates of the two monomers was further magnified. Conversion of EO reached 100% in 1 min when TsMAz had barely reacted (Figure 1). In another 5 h, full consumption of TsMAz was detected. SEC showed controlled and increased molar mass, narrow and unimodal molar mass distribution in the two stages ($Đ_M$ = 1.05 for the final

copolymer). It is thus explicit that a well- defined PTsMAz-*b*-PEO-*b*-PTsMAz triblock copolymer was one-step synthesized.

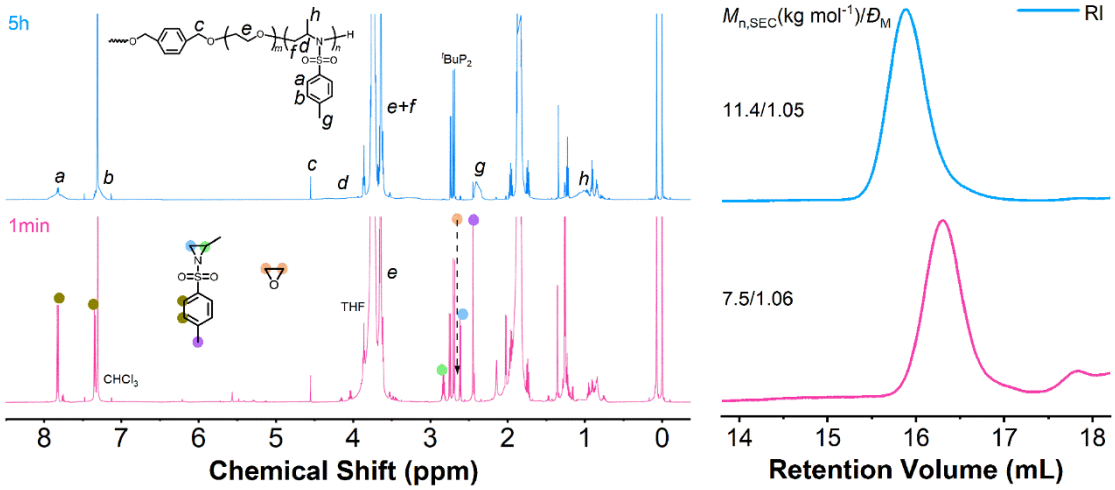


Figure 1. ^{1}H NMR spectra (left) and SEC traces (right) of the aliquots withdrawn at different reaction times for entry 2 in Table 1.

We then examined the efficacy of 1,8- diazabicyclo[5.4.0]undec-7-ene and 7-methyl-1,5,7-triazabicyclododecene as the basic catalytic component (Scheme 1; entry 3 and 4 in Table 1). When Et3B was used in 3 eq. of the bases, EO was also polymerized and exhausted first followed by the enchainment of TsMAz (see Figure S8~S11, entry S9 and S10 in Table S2 for details). However, $M_{n,SEC}$ was remarkably lower than $M_{n,th}$, indicating the copolymerization was also initiated directly by the bases, in addition to OH, because of their nucleophilicity.[11a] Apparently, the non- nucleophilic nature of PB was indispensable to the success of controlled one-step block copolymerization.

TsAz, with smaller bulkiness than TsMAz,[19] could copolymerize together with EO when Et3B was used in 1 eq. of ^{t}BuP2 to form a statistical copolymer (entry S11 in Table S2, Figure S12 and S13). Similarly, strict block copolymerizationoccurred when Et3B was used in 3 eq. of ^{t}BuP2, resulting in a well-defined PTsAz-*b*-PEO-*b*-PTsAz triblock copolymer (entry 5 in Table 1; also see entry S12 in Table S2, Figure S14 and S15 for details). In the second stage, TsAz polymerized much slower as compared with TsMAz, which might be due to tighter coordination of the less bulkier sulfonamide anion with Et3B (see below).[19] TsPhAz, with larger bulkiness than TsMAz,[20] could strictly block-copolymerize with EO when Et3B was used in either 1 or 3 eq. of ^{t}BuP2 (entry 6 and 7 in Table 1; also see entry S13 and S14 in Table S2, Figure S16~S19 for details), though it polymerized extremely slow in the latter case. These results have clearly shown that Et3B accelerates the enchainment of EO while decelerates that of Az. Such a Janus effect allow their one-step sequence-selective (EO-first) block copolymerization. By changing the monomer-to-initiator ratios, we targeted triblock copolymers with higher and similar molar mass (*ca*. 30 kg mol^{-1}) but different block lengths (PTsMAz^{5K}-*b*- PEO^{20K}-*b*-PTsMAz^{5K} and PTsMAz^{10K}-*b*-PEO^{10K}-*b*-PTsMAz^{10K}). The results showed successful control of these macromolecular characters as well as complete monomer conversions (entry 8 and 9 in Table 1, Figure S20 and S21).

Chain extension was conducted by addition of EO/TsMAz mixtures in three batches (entry 10-1/2/3 in Table 1). Full monomer conversions were reached each time. SEC peaks remained

unimodal and narrow with a constant shift to high molar mass (Figure 2a~c), demonstrating "livingness" of the one-step block copolymerization and one-pot three-step synthesis of a (PTsMAz-*b*-PEO)5-*b*-PTsMAz undecablock copolymer. The living block copolymerization was further utilized, with propylene oxide (PO) as the second epoxide, for one-pot two-step synthesis of a PTsMAz-*b*-PPO-*b*-PTsMAz-*b*- PEO-*b*-PTsMAz-*b*-PPO-*b*-PTsMAz heptablock terpolymer by addition of mixed PO/TsMAz after the block copolymerization of EO/TsMAz (entry 11-1/2 in Table 1 and Figure 2d~e). It needs to be noted that copolymerization of PO and TsMAz under the same conditions was also sequence-selective (PO-first) but led to relatively high $Đ_M$ most probably because of insufficient initiation efficiency of the secondary hydroxy ends of PPO for TsMAz, as will be detailed in a separate study.

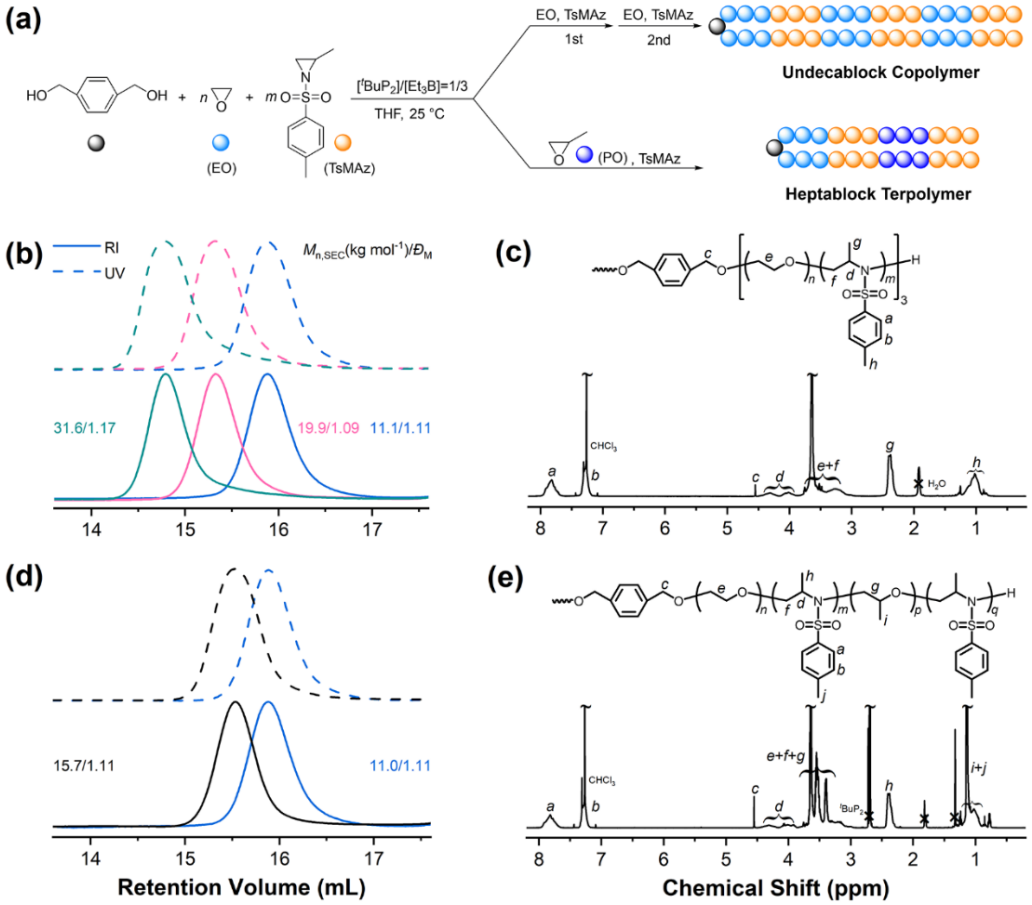


Figure 2. (a) One-pot multiblock co-/terpolymer synthesis (entry 10 and 11 in Table 1); (b) SEC traces after full consumption of each batch of EO/TsMAz; (c) ^{1}H NMR spectrum of the undecablock copolymer; (d) SEC traces after full consumption of EO/TsMAz and PO/TSMAz; (e) ^{1}H NMR spectrum of the heptablock terpolymer

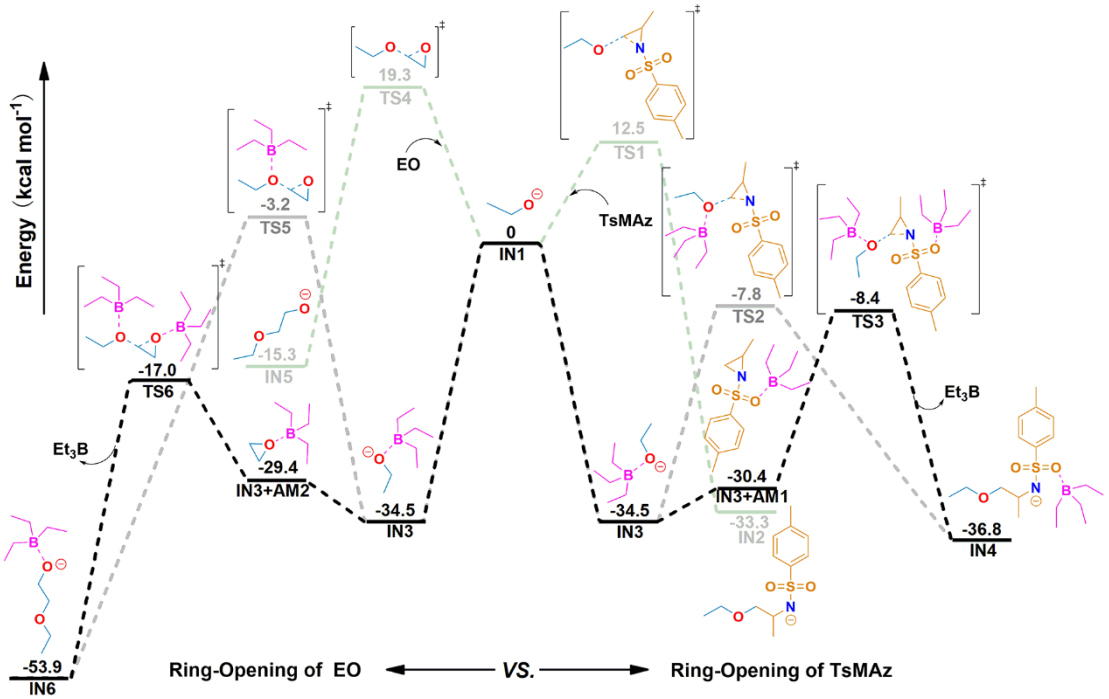


Figure 3. Modelling of the reaction between an oxyanion and EO (left) or TsMAz (right) in the presence of different amounts of Et3B. Light grey line: [Et3B] = 0; dark grey line: [Et3B]/[oxyanion] = 1, black line: [Et3B]/[oxyanion] = 3.

Properties of tri- and undecablock copolymers with the same composition (products of entry 2 and entry 10 in Table 1) are preliminarily investigated and compared. Both two exhibit higher decomposition temperatures (>350 °C) than the PTsMAz homopolymer (Figure S22). Crystallization of PEO segments in the cooling processes is prohibited, while cold crystallization is observed during heating (Figure S23). The undecablock copolymer shows higher crystallinity probably owing to enhanced intramolecular ordering.[21] The reverse sequence structure ensures that these amphiphilic block copolymers are insoluble in water, which is distinct from Wurm's products (Scheme 1)[8] and desirable for use as antifouling materials.[22] In quartz crystal microbalance studies, the spin-coated films of both tri- and undecablock copolymers exhibit complete resistance to a large protein (fibrinogen), with PTsMAz homopolymer as a reference (Figure S24). Lysozyme, a much smaller protein, is also greatly though not fully resisted. Interestingly, the undecablock copolymer outperforms the triblock one in this case. Water contact angles (62° and 64°, Figure S25) indicate that the difference is not related to the surface hydrophilicity. Atomic force microscopy images imply that the multiblock structure inhibits microphase separation more profoundly thus better preventing the adsorption of small protein (Figure S25).[23] The slightly higher elasticity of the undecablock copolymer film, as reflected by the lower elastic modulus, may also contribute to its better protein resistance performance (Figure S26).[24] To shed light on the key mechanistic aspects, DFT computations were carried out for the copolymerization of EO and TsMAz on simplified models (see Experimental Section for details). In the absence of Et3B (light grey lines in Figure 3), ring opening of TsMAz by the oxyanion shows a lower energy barrier (**IN1**→**TS1**; ΔG = 12.5 kcal mol^{-1}) than that of EO (**IN1**→**TS4**; ΔG = 19.3 kcal mol^{-1}), which accords with the discovery of Wurm *et al*. that TsMAz

polymerized before EO in the conventional anionic route (Scheme 1).[8] The dark grey lines in Figure 3 show that when the oxyanion is strongly coordinated with Et_3B (also see Figure S27), the energy barriers for reacting with TsMAz (**IN3→TS2)** and EO (**IN3→TS5)** increase to 26.7 and 31.3 kcal mol^{-1}, respectively. This seems to contradict the results of entry 1 in Table 1 and suggest that *B-O* coordination is not strictly quantitative when the oxyanion needs to be generated through deprotonation of a hydroxyl group. Most importantly, when there are excess Et_3B to form the "activated monomer" (**AM1** and **AM2**; black lines in (Figure 3), the energy barrier for ring opening of TsMAz changes little (**IN3→TS3**; ΔG = 26.1 kcal mol-1) while that for EO drops drastically (**IN3→TS6**; ΔG = 17.5 kcal mol-1), which agrees well with the experimental results (*e.g.* entry 2 in Table 1) that EO polymerized before TsMAz when Et_3B was in large excess of $^{t}BuP_2$.

It is therefore clear that the reverse enchainment order and strict sequence selectivity stems mainly from the different effects of Lewis acidic Et_3B on the two monomers. Formation of **AM2** (ΔG = 5.1 kcal mol^{-1}) can be easily overcompensated for by the coordination (stabilizing effect) of Et_3B with the newly forming oxyanion ($\Delta G \approx -34.5$ kcal.mol-1), thus greatly promoting the ring opening of EO. However, formation of **AM1** (ΔG = 4.1 kcal mol^{-1}; also see Figure S28) can barely be equalized by the coordination of Et_3B with the newly forming sulfonamide anion ($\Delta G \approx -3.2$ kcal mol^{-1}; Figure S29), thus providing no extra driving force for the ring opening of TsMAz. The futility of "activated monomer" in the case of TsMAz is also reflected in its self-propagation as the energy barriers are quite similar with or without **AM1** (Figure S29), and may also explain for the slow ROP of Azs observed above (*e.g.* entry 5 and 7 in Table 1). It is also interesting that Et_3B-coordinated sulfonamide anion reacts much more smoothly with **AM2** (ΔG = 12.3 kcal mol^{-1}; Figure S30) than with **AM1** (ΔG = 23.2 kcal mol^{-1}; Figure S29), which indicates that ROP of EO in the first stage of the block copolymerization could benefit from "automatic error correction" if TsMAz was occasionally enchained. This also supports the sequence selectivity (EO-first) of the second and third steps of the one-pot multiblock copolymers synthesis in which the copolymerization was initiated by sulfonamide anions (Figure 2).

In summary, we have fulfilled one-step synthesis of A*n*B*m*- type block copolymers from mixed EO and Az using $^{t}BuP_2$ with excess Et_3B as the catalyst. The PAz-*b*-PEO-*b*-PAz triblock copolymers features a distinct sequence structure as compared with those obtained by the conventional anionic route because of the reverse enchainment order of the two monomers. Calculation results attribute the sequence selectivity to the Janus effect of Lewis acidic Et_3B, *i.e.* it accelerates the enchainment of EO and decelerates that of Az because of its much stronger coordination with the oxyanion than the sulfonamide anion. Livingness of the one-step block copolymerization allows convenient one-pot synthesis of multiblock copolymer which appears superior to the triblock copolymer for use as antifouling material. The concept of using tunable bicomponent catalyst to enlarge and/or reverse the activity discrepancy of copolymerizable monomers is expected to further expand the scope of sequence-controlled copolymerization.

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