

Compounded Sequence Control in Polymerization of One-Pot Mixtures of Highly Reactive Acrylates by Differentiating Lewis Pairs

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ABSTRACT: The ability to synthesize well-defined block copolymers (BCPs) from one-pot comonomer mixtures has powerful chemical and practical implications. However, controlling sequences between highly reactive, homologous comonomers such as acrylates during polymerization is challenging. Here we present a Lewis pair polymerization strategy that uniquely utilizes preferential Lewis acid coordination to differentiate between comonomers, distinctive kinetics, and compounded thermodynamic and kinetic differentiation to precisely control sequences and suppress tapering and misincorporation errors, thus achieving well-defined and resolved di- or tri-BCPs of acrylates.

Lewis pair polymerization (LPP)¹ is a versatile technique that has continuously evolved by revealing fundamental insights that translate into useful and applicable solutions to polymerization problems. By exploiting the cooperative and synergistic interplay of both Lewis acid (LA) and Lewis base (LB) components, polymerization characteristics can be targeted and manipulated with tunability, selectivity, and predictability.¹ The accumulation of research on LPP^{2–9} and frustrated Lewis pair (FLP) chemistry^{10–15} has provided a wealth of variety in Lewis pair (LP) structure and reactivity that can be exploited to solve polymerization challenges.

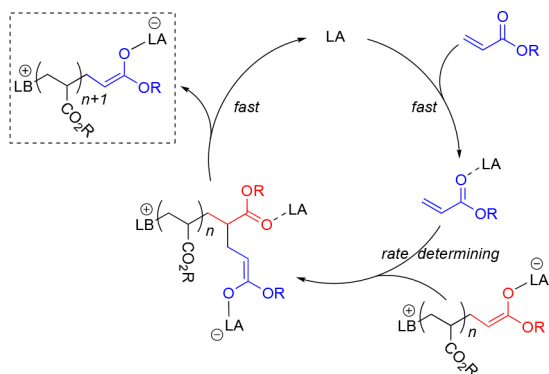
The scope of LPP has been expanded to include many types of polar monomers.^{4–6,16–22} While the reactivity varies considerably, the propagation mechanism generally remains the same, involving (rate-determining) attack on the LA-activated monomer by the LA-stabilized zwitterion (via initiation by LB) with zero-order kinetics in [monomer] (Scheme 1). Here we invoke these mechanistic nuances to demonstrate that LPP provides a unique strategy for gaining precise sequence control^{23–35} in polymerizing mixtures of

highly reactive, side-reaction prone acrylates into well-defined and resolved BCPs.

Several groups have explored methyl aluminum-di(2,6-*tert*-butyl-4-methyl-phenoxy) (MAD) as an effective bulky LA for the controlled LPP of polar monomers.^{2,3,36–41} With MAD's high acidity coupled with high steric hindrance, we hypothesized that mixing MAD with two different comonomers should result in preferential coordination of MAD to one over the other. If there is a large enough free energy difference between the two MAD/comonomer adducts, an equilibrium would be established that biases which comonomer is available for propagation before entering the rate-determining step (Scheme 1). Accordingly, we surmised that LPP could be exploited to gain precise sequence control in copolymerizing one-pot comonomer mixtures based on biased prior equilibrium differentiation (K_{eq}) during the coordination step compounding with differing monomer propagation rates (k_p) at the addition step.

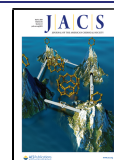
Furthermore, the unique kinetics of LPP predisposes copolymerizations to highly resolved block structures, largely absent of the common tapering effect (Figure 1). In comparison to LPP, which is zero-order with respect to monomer (rate = $k_p[LB]_0[LA]_0$),¹ conventional polymerizations are first-order in [M] (rate = $k_p[P^*]_i[M]_i$). When the rate is dependent on $[M]_i$, even when $k_A > k_B$, there will be some point in the reaction when $[A]_i$ is very low compared to $[B]_i$. At this point, rate_A will be approximately equal to rate_B, resulting in a tapering effect (Figure 1). Conversely, in LPP, there is no rate dependence on $[M]_i$. If incorporation of A is preferable to B at the start of the reaction, it will be so until A

Scheme 1. Propagation Mechanism for LPP of Acrylates (M) via Zwitterionic Intermediates with Zero-Order Kinetics in [M]



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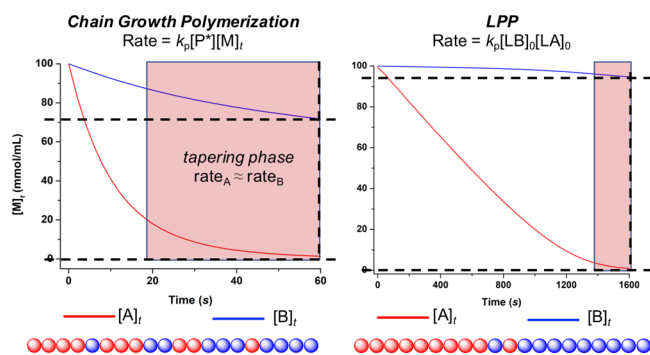


Figure 1. COPASI (complex pathway simulator) simulations of typical chain-growth polymerization and LPP, illustrating the significant prior equilibrium differentiation effect in LPP (A = more reactive M, B = less reactive M, $K_{eq} = 16$).

is at a concentration comparable to $[LA]_t$, at which point the K_{eq} of the prior equilibrium between comonomer/LA adducts begins to shift in favor of B (Figure S23). If the initial K_{eq} is considerably high, the aforementioned shift in K_{eq} will be negligible and block resolution will approach ideal (Figure S24). LA–monomer binding affinity was exploited in copolymerization of lactones, but no block copolymer (BCP) was generated.^{16,17}

To test this hypothesis, we chose acrylates as they are industrially important but their high reactivity and propensity for termination or transfer side reactions presents a challenge to control, especially in BCP synthesis by anionic or coordination polymerization methods.⁴² Specifically, we chose a comonomer pair of *n*-butyl acrylate (^hBA) and *tert*-butyl acrylate (^tBA), with their corresponding polymers P^hBA and P^tBA serving as soft and hard blocks.^{43,44} Acrylates also present challenges to LPPs⁶ due to the facile Claisen-type backbiting termination.^{9,45–47} Although BCPs have been synthesized by sequential additions of acrylates/methacrylates^{46,48} or acrylates⁴⁹ by carbene- or LA-mediated group-transfer polymerization, and methacrylates by LPP,^{3,40} the synthesis of all acrylate tri-BCP containing both ^hBA (highly reactive) and ^tBA (prone to decomposition)^{47,49,50} has remained a challenge, not to mention via more difficult one-pot additions. All these factors make these acrylates ideal candidates to showcase the unique capability of LPP with specially designed LPs.

We found that, using MAD and less hindered (mesityloxy)-diisobutylaluminum (**1**) and (2,6-di-*tert*-butyl-4-methylphenoxy)diisobutylaluminum (**2**) LAs, combined with sterically unhindered LB PMe_3 , ^hBA was effectively polymerized, yielding full conversion in seconds (Table S1). Near ideal initiation efficiency and low dispersity (\mathcal{D}) values were obtained from ^hBA/2/ PMe_3 = 200/2/1, and using MAD as the LA, high molecular weight P^hBA (M_n = 256 kg/mol, \mathcal{D} = 1.02) was obtained in just 100 s. A kinetic profile of ^hBA/MAD/ PMe_3 = 400/4/1 showed a linear curve in the conversion–time plot (Figure S2), consistent with the general mechanism of LPP (Scheme 1) that exhibits zero-order dependence on $[M]$. The challenge associated with ^tBA is its extreme reactivity, making its polymerization harder to control and prone to chain termination with less hindered LAs **1** and **2**. With MAD, full conversion with ^tBA/MAD/ PMe_3 = 800/2/1 can be achieved in seconds, but bimodal molecular-weight distributions were observed (Table S2).

Next, we investigated sequential block copolymerizations of ^hBA with ^tBA (Table S3). The 300/300 and 300/300/300 block copolymerizations afforded well-defined di- and tri-BCPs, P^hBA-*b*-P^tBA and P^hBA-*b*-P^tBA-*b*-P^hBA, with M_n = 128 kg/mol, \mathcal{D} = 1.07 and crossover efficiency = 91%, and M_n = 200 kg/mol, \mathcal{D} = 1.08 and crossover efficiency = 96%, respectively. However, gel-permeation chromatography (GPC) traces of the aliquots of the BCPs exhibited a low molecular weight shoulder (Figure 2a), representing terminated P^hBA.

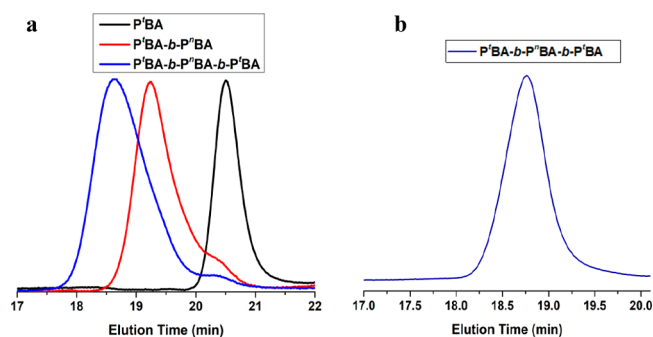
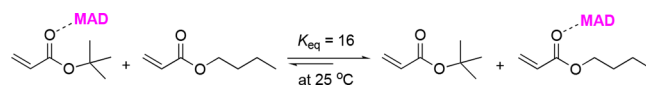


Figure 2. GPC traces of monoblock, diblock, and triblock aliquots of (a) ^hBA/^hBA/^tBA sequential triblock copolymerization (300–300–300) and (b) P^hBA-*b*-P^tBA-*b*-P^hBA synthesized by mixed addition.

We reasoned that this termination occurs only after monomer is completely consumed and not during the polymerization. The aforementioned backbiting termination requires the LA to activate an in-chain ester carbonyl. If there is free monomer left in solution, the LA will preferentially coordinate to it instead. This hypothesis has been confirmed by a more convenient mixed monomer addition strategy detailed below.

On the basis of the following three arguments, here we present the corresponding evidence to support our original hypothesis that LPP can be used to differentiate between multiple comonomers in a one-pot mixture to yield highly resolved BCPs. The first argument, preferential coordination of the LA to one comonomer over the other, was quantified for a ^hBA/^hBA/MAD (1/1/1) mixture by variable temperature ¹H NMR in toluene-*d*₈ between –70 and –30 °C. A Van't Hoff plot yielded $K_{eq} = 16$ and $\Delta H_{rxn} = -2.3$ kJ/mol for the equilibrium between ^hBA/MAD and ^tBA/MAD adducts at RT (Scheme 2). Thus, in a LPP where ^hBA and ^tBA are mixed with

Scheme 2. Prior Equilibrium Differentiation between ^hBA and ^tBA Biased by MAD



MAD, initially 94% of the MAD is occupied by ^hBA, and that amount gradually decreases as ^tBA is preferentially consumed. Therefore, when both monomers are present, there is approximately a 1/17 probability that the LPP will misincorporate a ^tBA unit into the growing polymer chain based on this argument alone.

For the second argument, differing monomer k_p , we can compare turnover frequencies (TOFs) of the LPP of each monomer. The kinetic profile (Figure S2) of a polymerization with ^hBA/MAD/ PMe_3 = 400/4/1 gave a TOF of 10.3 s^{–1}. An identical experiment with ^tBA gave a TOF of 310 s^{–1}. Thus, the k_p for ^tBA is ~30-times greater than that of ^hBA, implying

Table 1. Results of Diblock and Triblock Copolymerizations^a

run	LA	[^t BA]/[ⁿ BA]/[LA]/[PMe ₃]	time (s)	conv. (%)	M _n (kg/mol)	Đ (M _w /M _n)
1	I	100/100/2/1	4	100	32.3	1.68
2	MAD	400/400/2/1	59	100	109	1.05
3	MAD	100/900/2/1	15	100	127	1.02
4	MAD	300/300/6/1	40	100	90.1	1.06
5	MAD	800/800/8/1	20 ^b	100	272	1.03
6	MAD	600/300/6/1	50 ^b	100	204	1.02

^aConditions: 23 °C, for diblock copolymerizations (runs 1–4), [M]₀ = 0.59 M in toluene ([M]₀ = [ⁿBA]₀ + [^tBA]₀), ^tBA, ⁿBA, and LA premixed, followed by addition of PMe₃. For triblock copolymerizations, [M] = 1.18 M (run 5) and [M] = 0.59 M (run 6). ^tBA and LA were premixed, followed by addition of PMe₃. ^bTime corresponds to the approximate time of 50% conv of ^tBA when ⁿBA was added.

that there is roughly a 1/30 probability that the LPP will make the mistake of incorporating a ^tBA unit into the growing PⁿBA chain based on kinetics. However, for a ^tBA unit to be mistakenly incorporated into the growing chain while the ⁿBA block is polymerizing, two mistakes must be made consecutively: MAD must coordinate to ^tBA followed by chain addition to the ^tBA/MAD adduct. Hence, both probability values compound to establish roughly a 1/510 chance (without considering cross-propagation rates) of misincorporation.

For the third argument, suppressed tapering, since LPP does not have kinetic dependence on [M], these assumptions are true throughout the linear course of the polymerization and are not subject to the tapering effect until very late in the reaction. The simulated LPP curve shape (Figure 1) was experimentally confirmed by monitoring the polymerization of the ^tBA + ⁿBA (1/1) mixture with MAD/PMe₃. Figure S25 gives a realistic picture of the polymer structure and an approximation for block resolution of a ⁿBA/^tBA diblock with ⁿBA/^tBA/MAD/PMe₃ = 100/100/2/1, where by the time the first aliquot was taken at 2.7 s, the ⁿBA reservoir was completely depleted, while only 3.0% of the ^tBA reservoir had been consumed. Therefore, it can be assumed that an amount less than 3.0% of ^tBA misincorporates into the ⁿBA block.

To further test our hypothesis, diblock copolymerizations of the ^tBA + ⁿBA mixture were compared with nondifferentiating I and differentiating MAD (Table 1, runs 1–4). Predominantly due to no differing *k_p* for ⁿBA and ^tBA, I yielded a random copolymer (P^tBA-*ran*-PⁿBA), as evidenced by both differential scanning calorimetry (DSC) (Figure 3) and ¹³C NMR (Figure S17). The ¹³C spectrum of P^tBA-*ran*-PⁿBA shows two unresolved peaks in the carbonyl region corresponding to randomly incorporated ^tBA and ⁿBA units, while the DSC trace shows a single glass-transition temperature (*T_g*) at −15.3 °C, which lies between the *T_g* values of the

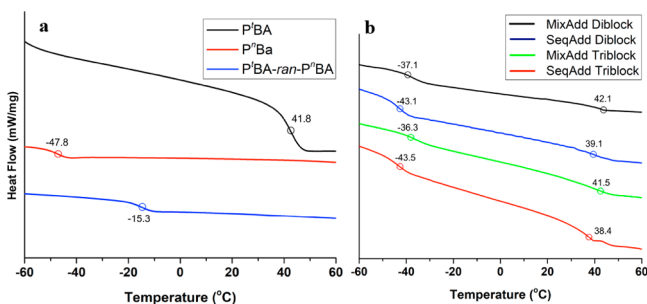


Figure 3. DSC plots (endo down) of (a) P^tBA, PⁿBA, and P^tBA-*ran*-PⁿBA and (b) P^tBA-*b*-PⁿBA synthesized from sequential addition (SeqAdd) and mixed addition (MixAdd), and P^tBA-*b*-PⁿBA-*b*-PⁿBA synthesized from SeqAdd and MixAdd.

two homopolymers at 41.8 °C for P^tBA and −47.8 °C for PⁿBA. In contrast, MAD led to well-resolved di-BCPs. The high resolution of these diblocks is supported by the above arguments as well as DSC (Figure 3) and ¹³C NMR (Figure S17). Thus, P^tBA-*b*-PⁿBA synthesized from sequential and mixed additions both exhibit two *T_g* values with values close to their homopolymers. The ¹³C NMR also indicates independent ^tBA and ⁿBA domains as signatures nearly identical to the homopolymers were observed. Furthermore, P^tBA-*b*-PⁿBA (M_n = 127 kg/mol, run 3) showed a unimodal GPC, symmetric bell curve with essentially ideal initiation efficiency (100%) and Đ (1.02) values, suggesting that when ^tBA is present in the ⁿBA polymerization, it prevents a bimodal distribution.

With well-defined di-BCPs synthesized by mixed comonomer addition, we reasoned that tri-BCP P^tBA-*b*-PⁿBA-*b*-PⁿBA should be made in two addition steps by initiating LPP on the entire sum of less reactive ^tBA, and adding the more reactive ⁿBA at ~50% conversion of ^tBA, at which point the more reactive monomer will selectively polymerize until depleted. Then the remaining fraction of the less reactive comonomer will continue to polymerize to yield tri-BCP. Indeed, this strategy produced well-defined tri-BCP with high M_n (272 kg/mol) and low Đ (1.03, run 5) values. The high resolution of these triblocks is supported again by DSC (Figure 3) and ¹³C NMR (Figure S17). Furthermore, P^tBA-*b*-PⁿBA-*b*-PⁿBA (run 6, Figure 2b) showed a symmetric GPC bell curve without shouldering, unlike the tri-BCP prepared by sequential addition. This result further highlights an important advantage of this strategy that can prevent LA-activated chain termination by occupying the free LA with a comonomer at all block-constructing stages.

In summary, we have established LPP as a unique and powerful method to polymerize one-pot comonomer mixtures of highly reactive and side-reaction prone acrylates into well-defined and resolved di- or tri-BCPs. A preliminary result also indicated this method can be applied to acrylate/methacrylate mixtures. Three distinctive features of LPP have been exploited to accomplish this challenging task. First, preferential coordination of the LA to one comonomer over the other imposes the significant prior equilibrium differentiation (*K_{eq}*) effect. Second, zero-order kinetic dependence on [M] substantially suppresses tapering in BCP formation. Third, compounding the biased *K_{eq}* with differing monomer *k_p* further diminishes the probability for misincorporation errors. The principles described in this report should be generally applicable to catalysis and other polymerization systems, especially concerning sequence control, kinetic resolution, and block resolution.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/jacs.0c01127>.

Experimental details and additional figures (PDF)

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Notes

The authors declare no competing financial interest.

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■ NOTE ADDED AFTER ASAP PUBLICATION

K_{eq} was recalculated and Van't Hoff plot was revised in the Supporting Information. The values associated with K_{eq} in the main text were changed accordingly. We thank Professor Jerome Robinson of Brown University for bringing the K_{eq} issue to our attention.