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Communication

Synchronous Control of Chain Length/Sequence/Topology for Precision Synthesis of Cyclic Block Copolymers from Monomer Mixtures

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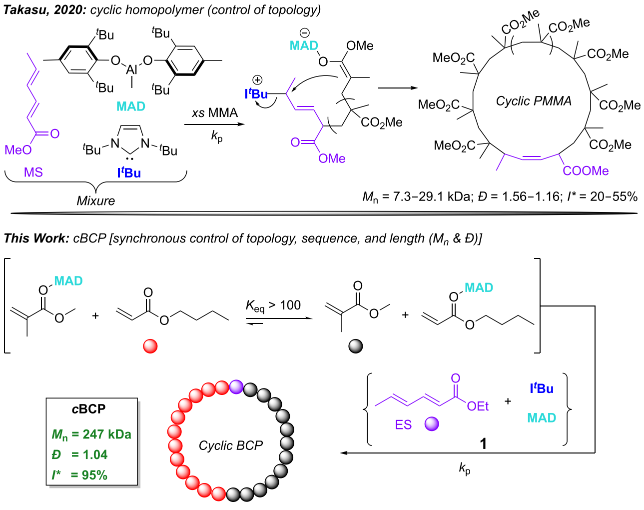
ABSTRACT: Precision synthesis of cyclic polymers with predictable molecular weight and low dispersity is a challenging task, particularly concerning cyclic polar vinyl polymers through a rapid chain-growth mechanism and without high dilution. Harder yet is the precision synthesis of cyclic block copolymers (*c*BCPs), ideally from comonomer mixtures. Here we report that Lewis pair polymerization (LPP) capable of thermodynamically and kinetically compounded sequence control successfully addressed this longstanding challenge. Thus, LPP of acrylate/methacrylate mixtures under ambient temperature and normal concentration conditions rapidly and selectively affords well-defined *c*BCPs with high molecular weight (M_n = 247 kg/mol) and low dispersity ($Đ$ = 1.04) in one step. Such *c*BCPs have been characterized by multiple techniques, including direct structural observation by imaging.

Lewis pair polymerization (LPP) utilizes both Lewis acid (LA) and Lewis base (LB) components to cooperatively facilitate polymerization reactions, delivering exquisite control and tunability.[1−3] Recent LPP examples that have noticeably advanced the polymerization methodology include living and immortal polymerizations,[4−6] polymerizations of bio-based monomers with high functionality,[7−10] and precise comonomer sequence[11] and topological[10−14] control. Most recently, Takasu utilized LPP to synthesize cyclic polar vinyl polymers.[12] During the LPP of methyl sorbate (MS) by LA methyl aluminum di(2,6-di-*tert*-butyl-4-methylphenoxy) (MAD) and LB 1,3-di-*tert*-butylimidazolin-2-ylidene (I^{t}Bu) pair, cyclization takes place, which is proposed to proceed by S_N2 attack from the enolate at the ω-terminus to the carbon bonded to the cationic LB initiating group at the α-terminus.[10] When excess methyl methacrylate (MMA) was added to a stoichiometric MS/MAD/I^{t}Bu mixture, LPP took place followed by ring closure, presumably through S_N2 attack from the polymeric MMA (PMMA) enolate anion to the MS/I^{t}Bu cation, to form cyclic PMMA with number-average molecular weight (M_n) ranging from low (7.3 kDa) to medium (29.1 kDa), dispersity ($Đ$) from 1.56 to 1.16, and initiation efficiency (I^*) from ∼20 to 55%[12] (Scheme 1). This strategy suppressed H-transfer events encountered in the direct MMA polymerization by I^{t}Bu alone, which limited cyclic PMMA formation.[15] Herein we disclose our findings that Takasu's sorbate-based methodology for cyclic vinyl polymers coupled with our LPP methodology for compounded sequence control (CSC)[2,11] enables the exquisite chain length-, sequence-, and topology-controlled synthesis of well-defined cyclic block copolymers (*c*BCPs) with high values of M_n (247 kDa), low $Đ$ (1.04), and high I^* (95%) from one-pot monomer mixtures using premixed ethyl sorbate (ES)/MAD/I^{t}Bu mixture **1** (Scheme 1).

Scheme 1. (top) General Synthetic Route to Cyclic Polar Vinyl Homopolymers[12] and (bottom) Synthetic Route to *c*BCPs by CSC-LPP



A classic strategy for cyclic polymer[16] synthesis[17−19] involves anionic polymerization wherein the initiating species acts not only as a nucleophilic initiator but also as a leaving group for ring closure. This strategy works well for coordinative[20−24] and zwitterionic[25−27] ring-opening polymerization (ROP). In this case, if the activity of ring closure (which is usually considered a chain transfer) is similar to the activity of propagation, then

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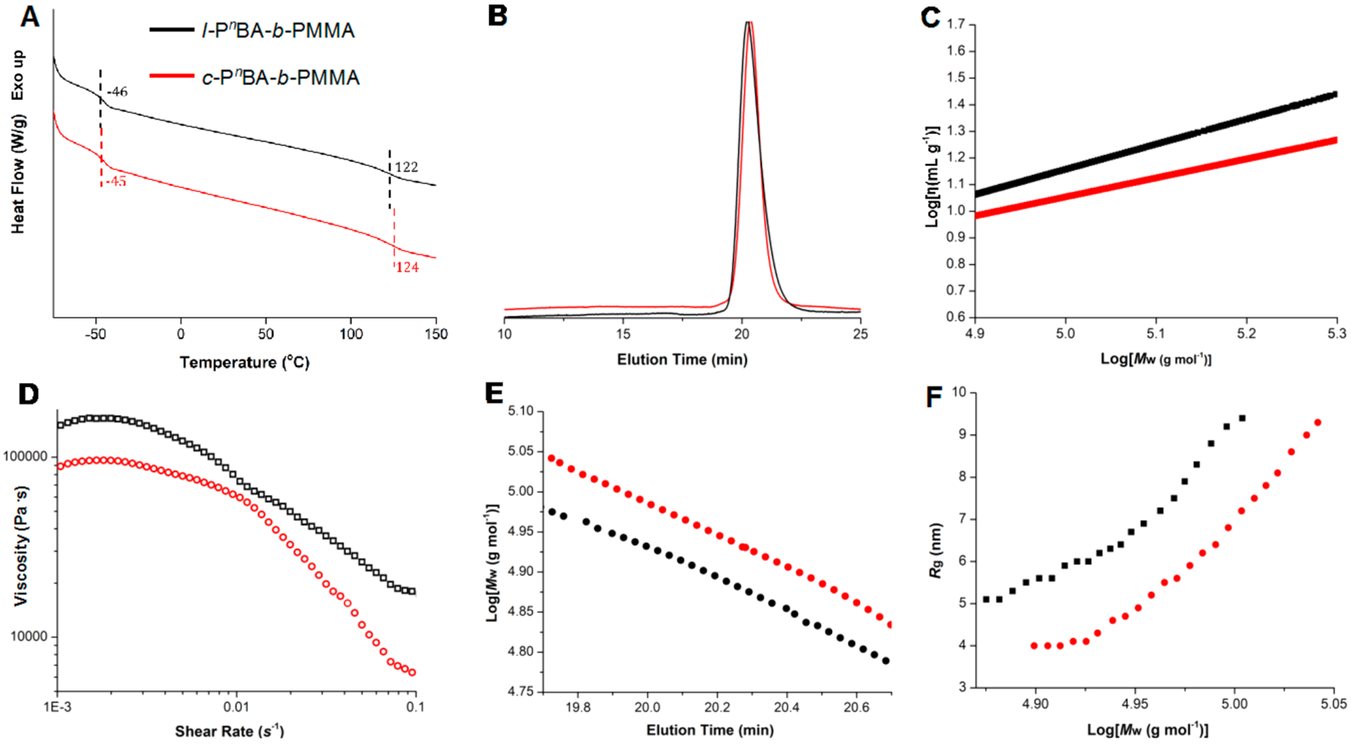

Figure 1. Comparative characterizations of linear (run 1, black) and cyclic (run 2, red) diblock P^{n}BA-*b*-PMMA counterparts. (A) DSC traces of linear (*l*) and cyclic (*c*) P^{n}BA-*b*-PMMA showing two T_g values corresponding to P^{n}BA (−45 to −46 °C) and PMMA (122 and 124 °C) domains. (B) GPC elution times for *l*- and *c*-P^{n}BA-*b*-PMMA showing narrow molecular weight distributions for both topologies. (C) Mark−Houwink−Sakurada plots for *l*- and *c*-P^{n}BA-*b*-PMMA showing higher $[\eta]$ for the *l* structure, especially in the higher-M_w region. (D) Rheological viscosities of *l*- and *c*-P^{n}BA-*b*-PMMA. (E) Plots of $\log(M_w)$ vs elution time for *l*- and *c*-P^{n}BA-*b*-PMMA. (F) Plots of R_g vs $\log(M_w)$ showing higher R_g for the *l* structure.

the M_n and $Đ$ values of the polymerization will be uncontrolled because of a reliance on the proportionality shown in eq 1:[2]

$$M_n \propto \frac{k_p[\mathrm{M}]_t[\mathrm{I}]_0}{k_{ct}[\mathrm{I}]_0} \tag{1}$$

where k_p and k_{ct} are the activities of propagation and chain transfer (cyclization), respectively, $[\mathrm{M}]_t$ is the time-dependent monomer concentration, and $[\mathrm{I}]_0$ is the initial initiator (I) concentration (a reasonable proxy for the number of propagating species). Since this logic gives an average molecular weight, it should rather be understood as a statistical likelihood of chain transfer distributed across a broad range of molecular weights (that average to M_n). Moreover, the time-dependent nature of $[\mathrm{M}]_t$ means that the statistically predicted M_n will be variable with respect to time. Thus, M_n and $Đ$ can hardly be controlled in a reaction governed by the proportionality shown in eq 1.

In contrast, LPP is well-equipped to control M_n and $Đ$ of the cyclic polymer because of its unique zeroth-order in $[\mathrm{M}]_t$ propagation kinetics, as shown by the absence of $[\mathrm{M}]_t$ in the numerator of the proportionality given by eq 2:

$$M_n \propto \frac{k_p[\mathrm{LA}]_0[\mathrm{LB}]_0}{k_{ct}[\mathrm{LB}]_0} \tag{2}$$

Therefore, the propagation rate (numerator) can be tuned independently with respect to the chain transfer (ring-closure) rate by manipulation of $[\mathrm{LA}]_0$. If the propagation rate is considerably higher than the chain transfer rate, the proportionality in eq 2 can be completely circumvented because chain transfer will statistically occur long after monomer depletion. *Thus, cyclic polymers with specific M_n values and low $Đ$ indices can be targeted and achieved by LPP.*

Likewise, *c*BCPs are challenging to synthesize by chain-growth methods, especially with the classical sequential addition method, because of the event that cyclization can occur prematurely after the first comonomer sequence, resulting in either a mixture of cyclic homopolymers or *c*BCPs contaminated with cyclic homopolymers. We are aware of only a few examples involving ROP,[21,22] and to our knowledge, *c*BCPs obtained from olefinic monomers by pure chain-growth methodologies are absent from the literature, with the exception of postfunctionalized ring closing by click reactions or other privileged processes and highly dilute conditions.[28−34] To this end, a one-pot sequence-controlled methodology would seamlessly transition from one comonomer to the next, thereby minimizing the total polymerization time during which cyclization can occur prematurely. We recently devised a one-pot sequence-controlled diblock copolymerization of *n*-butyl acrylate (^{n}BA) and *tert*-butyl acrylate (^{t}BA) based on constructive compounding of the thermodynamic bias (K_{eq}) between the two monomers during the first step (LA activation) with the kinetic bias (k_p) during the second step (conjugate addition), hence the name CSC.[2,11] The result was rapid polymerization of ^{n}BA with exclusion of ^{t}BA until ^{n}BA was near depletion, followed by eventual polymerization of ^{t}BA.

Upon optimization of the LB, we found that tricyclohexylphosphine ($\mathrm{PCy_3}$) works for the synthesis of the linear di-BCP via CSC diblock polymerization of ^{n}BA/MMA mixtures

(Table S1, runs 1 and 2) since ^{n}BA is predisposed to termination during the course of polymerization. We found that sterically hindered LBs greatly diminish the activity of the Claisen-type termination common among acrylic monomers. I^{t}Bu works well for the linear copolymerization as well, but since it has a tendency to cyclize and undergo H-transfer reactions, we opted to use PCy_3 to ensure that we had a reliable linear comparison. Our attempt to measure the K_{eq} value for the ^{n}BA/MAD versus MMA/MAD equilibrium showed that the equilibrium bias is shifted so far in favor of ^{n}BA/MAD that MMA/MAD could not be detected (see Figure S1). Thus, we postulated that a heavily biased K_{eq} for the ^{n}BA/MAD adduct compounded with the heavy k_p bias of ^{n}BA vs MMA (acrylates by MAD/LB convert on the order of seconds, while methacrylates convert on the order of minutes) would result in a high degree of block resolution in the mixed one-pot copolymerization. Indeed, the one-pot CSC method works well for the ^{n}BA/MMA mixture, as evidenced by the presence of two glass transition temperature (T_g) values (−46 and 122 °C) observed by differential scanning calorimetry (DSC) (Figure 1A), suggesting the presence of individual P^{n}BA and PMMA domains, and by well-resolved ^{13}C NMR peaks of the BCP, which strongly resemble the signatures of the individual homopolymers (Figure S3). The polymer sequencing can actually be observed qualitatively by a color change that occurs a few seconds after initiation from brilliant yellow to light yellow (signaling full conversion of ^{n}BA) followed by a color change from yellow to clear after a few minutes (signaling full conversion of MMA). Thus, high-M_n P^{n}BA-*b*-PMMA (up to 286 kDa) was synthesized in one pot in one step with low $Đ$ values (1.06−1.12) rapidly (in minutes).

Next, we endeavored to synthesize the postulated cyclic ^{n}BA/MMA di-BCPs by initiating the same polymerization with the sorbate-derived mixture **1**. Here we simply dissolved MAD into a mixture of ^{n}BA and MMA in toluene and added initiator **1** to reach the predetermined ^{n}BA/MMA/MAD/**1** molar ratio (Table S1, runs 3 and 4). The polymerization was complete in less than 5 min (as indicated by a color change), but the reaction mixture was left to stir for 3 h to ensure complete cyclization before quenching with benzoic acid in MeOH. As with the linear BCPs, the resulting cyclic analogues also exhibited two distinct T_g values, and the polymer M_n could be controlled by the ^{n}BA/MMA/MAD/**1** molar ratio, producing BCPs with M_n = 82.6 and 247 kDa (Table S1, runs 3 and 4, respectively). Noteworthy also is the extremely low $Đ$ value of 1.04 for the resulting *c*BCPs. The presumed *c*BCPs were further characterized using hydrodynamic volume (V_h) and intrinsic viscosity ([η]) measurements by triple-detection gel-permeation chromatography (GPC) to determine the polymer topology since cyclic polymers are known to have lower V_h and thus lower [η] than their linear counterparts.[35] A d*n*/d*c* method was used to determine absolute molecular weight data for both linear and *c*BCPs, and therefore, the individual d*n*/d*c* values were measured and were indeed found to be different. For example, a linear BCP (run 1) and cyclic analogue (run 3) containing the same comonomer ratio eluted at nearly the exact same time (Figure 1B). However, the measured d*n*/d*c* value for the cyclic polymer (0.0643 mL/g; Figure S14) was considerably lower than that of its linear counterpart (0.0737 mL/g; Figure S6). When the weight-average molecular weights (M_w) of these linear and cyclic analogues are compared per elution volume (as functions of hydrodynamic radius), the *c*BCPs have higher M_w than their linear analogues by a factor of 1.14 on average and thus a lower V_h (Figure 1E,F), supporting the cyclic structure of the BCPs. The radius of gyration (R_g) per M_w measured by multiangle light scattering was also higher for linear polymers than for their cyclic analogues. Lastly, we compared the [η] per M_w and the bulk rheological viscosity (Figure 1C,D), and in both cases the cyclic polymers exhibited lower viscosity since they have a lower degree of chain entanglement.[35]

High-molecular-weight *c*BCPs can be made by simply decreasing the LP loading, as judged by all lines of evidence, including M_w versus elution time, R_g versus M_w, a similarly lower d*n*/d*c*, higher T_g values, and lower bulk rheological viscosity for the *c*BCPs compared with the linear BCP counterparts (Figures S24−S27). However, for the high monomer/initiator ratio run, ^{n}BA/MMA/MAD/**1** = 1200/800/10/1 (run 4), we opted to use a 10/1 MAD/LB ratio to increase the polymerization activity relative to the cyclization activity (eq 2), which increases the likelihood of Claisen termination (as MAD is required to catalyze termination). Thus, one might expect that this *c*BCP may contain some unquantified linear contaminant. However, the identically low $Đ$ value (1.04) of this BCP compared to that produced by the 2/1 MAD/LB ratio (run 3) appears to indicate that the two *c*BCPs are similarly well-controlled. Lastly, we included a five-point demonstration of control over M_n and $Đ$ by this system (Table S2 and Figure S28).

Direct observation of the *c*BCP topology by high-resolution transmission electron microscopy (TEM) would provide more direct evidence for not only cyclization but also block resolution enabled by CSC. By using the method employed by Takasu[13] and utilizing the exquisite chemoselctivity of LPP,[1,2,36−38] we substituted allyl methacrylate (AMA) for MMA in the block copolymerization and synthesized cyclic P^{n}BA-*b*-PAMA (M_n = 170 kDa, $Đ$ = 1.28). Next, we grafted octadecanethiol onto the pendent allyl groups of the *c*BCP via the thiol−ene click reaction to obtain the corresponding grafted brush *c*BCP, P^{n}BA-*b*-PAMA$_g$ (M_n = 720 kDa, $Đ$ = 1.39) (Figure 2A). Now, expecting the octadecanethiol-grafted block to be visible by TEM, we anticipated seeing “half-circle”-shaped *c*BCP images. Indeed, we were able to directly observe half-circles with a diameter of 50 nm (Figure 2B). Because of the packing of the octadecanethiol-grafted BCP into crystalline domains (Figure S35), we could more easily observe large polymer crystalline domains that intriguingly retained the half-circle shape from 0.5 to 1 μm in diameter (Figure 2C). To ensure that these “half-circle” shapes were a consequence of the *c*BCPs topology, we synthesized the linear BCP P^{n}BA-*b*-PAMA$_g$ analogue using PCy_3 instead of **1** and subsequently observed columns of linear “wormlike” polymer domains of various sizes (Figures 2D, S36, and S37).

In summary, we have developed a general method for making well-defined *c*BCPs selectively and precisely from a one-pot monomer mixture. Acrylic *c*BCPs were expediently (in minutes), conveniently (one pot, room temperature, normal concentration), and efficiently (I^* = 95%) synthesized to medium and high molecular weight (M_n = 247 kDa) with low dispersity ($Đ$ = 1.04). In view of the well-recognized challenges of controlling M_n and $Đ$ values of cyclic homopolymers by rapid chain-growth polymerizations, not even mentioning *c*BCPs, this method showcases the potential of LPP to conquer longstanding precision polymer synthesis challenges and also the broad applicability of the CSC methodology.

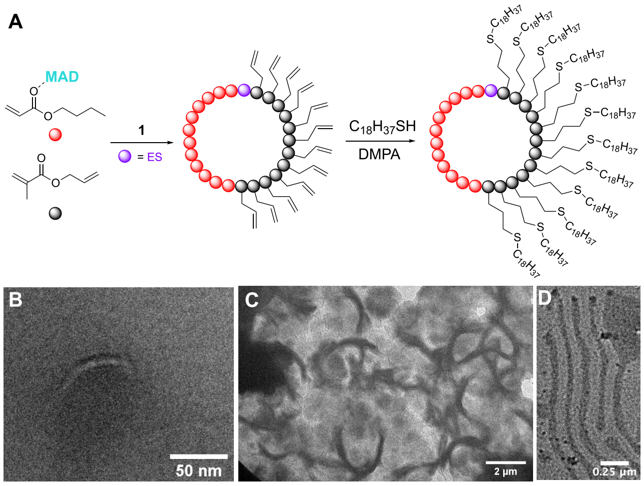

Figure 2. Direct observation of cyclic and linear BCP morphologies by TEM. (A) Synthetic route to cyclic "half-circle" brush copolymers. (B) TEM image of a single cyclic half-circle $\mathrm{P}^n\mathrm{BA}$-*b*-PAMA_g chain. (C) TEM image of large half-circle-shaped crystalline cyclic $\mathrm{P}^n\mathrm{BA}$-*b*-PAMA_g domains. (D) TEM image of a self-organized linear $\mathrm{P}^n\mathrm{BA}$-*b*-PAMA_g analogue for comparison.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.1c00561.

Experimental details and supporting figures and tables (PDF)

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Notes

The authors declare no competing financial interest.

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