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Block Copolymers Synthesized by ROMP-to-Anionic Polymerization Transformation

Sasha B. Myers and Richard A. Register*

Department of Chemical Engineering, Princeton University, Princeton, New Jersey 08544-5263

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ABSTRACT: A two-step site transformation technique is presented to convert from living ring-opening metathesis polymerization (ROMP) to living anionic polymerization of unsaturated monomers. This method permits the synthesis of well-defined diblock copolymers of controllable molecular weight and narrow molecular weight distribution, combining ROMP and anionically polymerizable monomers. The technique employs a functional terminating agent to add a styryl group to the end of the ROMP chain. The end group is then metalated to yield an active site for anionic polymerization, so that the ROMP chain acts as a macroinitiator from which the anionic block is grown. Both polycyclopentene/polystyrene and polynorbornene/polystyrene diblocks were successfully synthesized, and the method should be applicable to a broad range of monomers.

Introduction

"Living" polymerization methods allow for the synthesis of polymers of controllable molecular weight and narrow molecular weight distribution (polydispersity index <1.2). The characteristics of living polymerizations (fast initiation, predictable polymerization rates, and the absence of unwanted side reactions such as chain transfer, termination, or branching) also permit the synthesis of well-defined block copolymers by simple sequential monomer addition. An important limitation is that each living technique is applicable to only a select group of monomers, so combining two or more blocks created by different polymerization chemistries can greatly expand the palette of potential block copolymers. Two such living polymerization chemistries—whose combination is the focus of the present work—are anionic polymerization (AP) and ring-opening metathesis polymerization (ROMP).

Several approaches have been explored for the synthesis of AP/ROMP diblocks. Perhaps the most obvious is to separately polymerize each of the blocks and then bond them together via reaction through their end groups. This is the route described by Notestein et al.,[1] where ω-aldehyde-functional polystyrene, synthesized by anionic polymerization, was used to terminate the living ROMP of norbornene catalyzed using a Schrock-type molybdenum initiator. Reaction of the Mo living ends with the aldehyde yields a carbon−carbon bond, robustly joining the two blocks. The principal disadvantage of this approach is the generally slow reaction of two high-molecular-weight polymers functionalized only at their ends. If an excess of the polymeric aldehyde is used to speed termination of the ROMP active sites, the excess becomes a contaminant in the product, and fractionation is required to yield the pure diblock of interest.

Alternatively, the active site present at the conclusion of one type of polymerization may be transformed to a site suitable for another class of polymerizations: a "change of mechanism" transformation.[2] The transformation may be either direct, where the active sites are converted in situ from one type to another in a "one pot" polymerization, or indirect, where the first block is isolated and its end group subsequently transformed to the complementary active site. Amass et al.[3,4] were the first to describe a direct AP-to-ROMP transformation by reacting Li carbanion living ends with WCl_6 to generate ROMP sites. However, some termination of the anionic ends also occurs, and the ROMP sites which result do not yield a living polymerization, so the block copolymers synthesized by this approach are substantially heterogeneous. Recently, Castle et al.[5,6] presented an elegant indirect AP-to-ROMP transformation, where the anionic polymer is functionalized with a styryl end group, which is then metathesized with a ruthenium organometallic to yield a Ru benzylidene active site of the Grubbs "first generation" type. Though a three-step[6] carbanionic polymerization-to-ROMP transformation process is required, this approach yields quite well-defined, narrow-distribution diblock copolymers. The literature on complementary ROMP-to-AP transformation processes, however, is quite limited. Katayama et al.[7] described the synthesis of a hydroxyl-terminated ROMP polynorbornene block via a functional chain-transfer agent and its use to initiate the anionic ring-opening polymerization of ϵ-caprolactone, but there do not appear to have been any reports of a ROMP-to-carbanionic polymerization transformation.

The present work demonstrates such a ROMP-to-AP transformation process, by a two-step, indirect route. A ROMP monomer of particular interest is cyclopentene, whose polymer can be converted to perfectly linear (high-density) polyethylene by hydrogenation.[8,9] For example, an efficient ROMP-to-AP change-of-mechanism polymerization would permit the synthesis of well-defined polystyrene−polyethylene (PS/PE), or poly(vinylcyclohexane)−polyethylene (PVCH/PE), block copolymers where the polyethylene blocks are free from short- and long-chain branching. Similar block copolymers have been synthesized by other routes, including a direct AP-to-Ziegler−Natta site transformation yielding PS/PE diblocks,[10,11] and the use of a PS-*block*-containing chain transfer agent in the ROMP of cyclooctene to yield PVCH/PE diblocks[12] or PVCH/PE/PVCH triblocks after hydrogenation.[13] These approaches yield rather broad molecular weight and composition distributions, often with PDI approaching or even exceeding 2. Functional chain transfer agent approaches have also been employed to synthesize difunctional poly(1,5-cyclooctadiene) chains with end groups that act as active sites for controlled radical polymerizations of styrene, using atom-transfer radical polymerization (ATRP)[14] and reversible addition fragmentation transfer (RAFT).[15] Both routes have been employed successfully to synthesize PS−poly(cyclooctadiene)−PS triblocks, but with a midblock having the most probable distribution rather than the narrow distribution characteristic of living ROMP.

Cyclopentene (CP) presents additional challenges in such a ROMP-to-AP transformation process, since its low ring strain leads to a high equilibrium monomer concentration. CP conver-

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* Corresponding author. E-mail: register@princeton.edu.

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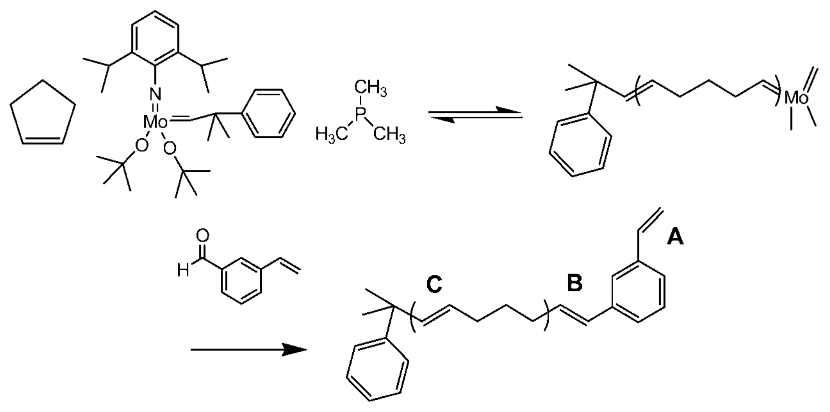

Figure 1. Synthesis of styryl-functionalized ROMP block using a Mo-based Schrock initiator and termination with 3VBA, illustrated with PCP. Three types of double bond in the product are labeled **A**, **B**, and **C**.

sion must be limited to minimize propagation−depropagation equilibration and acyclic metathesis side reactions.[9,16] A rapid ROMP-to-AP transformation is thus required, so that continued CP polymerization does not occur concurrently, which would broaden the distribution of the PCP block. For this reason, the relatively slow coupling approach described by Notestein[1] is poorly suited to the synthesis of PCP−PS diblocks.[17] The approach described herein rapidly reacts the living ROMP chains (PCP) with a large excess of a monomeric compound that caps the PCP end with a group easily converted to an AP-active living end. We demonstrate this approach through the synthesis of well-defined PCP−PS and polynorbornene−PS diblocks.

Experimental Section

Materials. Cyclopentene (96%, Aldrich Chemical Co.) and cyclohexane were dried over *sec*-butyllithium (*s*BuLi), degassed by freeze−pump−thaw cycles, and vacuum transferred prior to use. Styrene and *trans*-*β*-methylstyrene (99%, Aldrich) were dried over dibutylmagnesium, degassed by freeze−pump−thaw cycles, and vacuum transferred. Toluene and tetrahydrofuran (THF) were dried over sodium benzophenone ketyl, degassed, and vacuum transferred. Trimethylphosphine (PMe_3) and norbornene were dried over freshly cut sodium, degassed, and vacuum transferred. 3-Vinylbenzaldehyde (3VBA, 97%, Aldrich) was dried over magnesium sulfate, filtered, degassed by freeze−pump−thaw cycles, and vacuum transferred after addition of 0.2 wt % 3,5-di-*tert*-butylcatechol (99%, Aldrich), a polymerization inhibitor. Propionaldehyde, benzaldehyde, chlorotrimethylsilane, and *s*BuLi were used as received from Aldrich. The “Schrock-type” catalyst 2,6-diisopropylphenylimidoneophylidenemolybdenum(VI) bis(*tert*-butoxide) was used as received from Strem Chemicals, Inc. Methanol was degassed prior to use. All synthetic processes were performed under a nitrogen atmosphere in an Innovative Technologies glovebox (~0.7 ppm O_2, ~0.5 ppm H_2O).

Synthesis of End-Functional ROMP Polymers. A typical PCP block synthesis involved the addition of PMe_3 (5 equiv vs initiator) and initiator (2,6-diisopropylphenylimidoneophylidenemolybdenum(VI) bis(*tert*-butoxide)) to toluene, followed by the addition of cyclopentene monomer (3000 equiv, 3 M in toluene). The reaction mixture was stirred at room temperature for 60 min and terminated with 3VBA (10 equiv). The mixture was stirred for an additional 30 min and removed from the glovebox. PCP was isolated by repeated precipitation into methanol to remove all catalyst residues and excess 3VBA and subsequently dried under vacuum at room temperature. End-functional polynorbornene blocks were prepared analogously, but at 4 wt % monomer.

Diblock Copolymer Synthesis. Dry, functionalized ROMP block (PCP or polynorbornene) was dissolved in cyclohexane (1 mM) with THF (1−25 vol %). *s*BuLi (2−2.5 equiv) was added, and the reaction mixture was stirred at room temperature for 3−30 min. Styrene was then added, and the reaction mixture was stirred at room temperature for 60 min. After termination with degassed methanol, the polymer was isolated by precipitation into methanol and dried under vacuum at room temperature.

Instrumentation. Gel permeation chromatography (GPC) in THF was used to determine ROMP homopolymer and diblock molecular weights and polydispersity indices (PDI). The GPC system consists of two 30 cm Polymer Laboratories PLgel Mixed-C columns, a Waters 515 HPLC pump, a Waters 410 differential refractometer detector, and a Waters 2487 dual wavelength UV absorbance detector. As the GPC is calibrated with polystyrene standards, most of the molecular weights presented here are “polystyrene-equivalent” values. For PCP homopolymers, the PS-equivalent value was divided by the hydrodynamic volume correction factor $r_{PCP} = 1.98$ to obtain the true molecular weight.[9,17,18] For the polynorbornene homopolymer, $r_{PN} = 1.78$ was used.[19] ^1H NMR (Varian Inova-500 MHz) in $CDCl_3$ was used to determine diblock composition, from the areas of the olefinic and aromatic protons; a representative diblock spectrum is given in the Supporting Information (Figure S1). The PS block molecular weight was determined from the diblock composition and the ROMP block molecular weight. When free PS was generated by excess *s*BuLi, its molecular weight was consistent with the PS block molecular weight determined from the diblock.

Results and Discussion

ROMP-to-AP Transformation. Our change-of-mechanism polymerization technique is a two-step method: in the first step, the ROMP block is polymerized and selectively capped, and in the second step, the ROMP block’s end group is metalated to permit anionic polymerization of styrene. The ROMP block chosen for most of the present work was polycyclopentene (PCP), synthesized via the general procedure described by Trzaska et al.[9] Using the kinetic model presented there permits the synthesis of PCP of targeted molecular weight. Because the ROMP of cyclopentene is an equilibrium reaction, conversion must be limited to ≈15%, and fast termination of the polymerization is required. The preferred terminating agents for Mo-catalyzed ROMP are aldehydes, so 3-vinylbenzaldehyde (3VBA) was employed here, which places a styryl end group at the end of the PCP chain as shown in Figure 1. The external double bond **A** (Figure 1) can then be metalated to generate an active site for anionic polymerization. Typically, the molecular weight of the end-functional PCP chain was within 10% of the target value calculated via the kinetic model[9] and always showed PDI < 1.15, confirming that termination by 3VBA was rapid. ^1H NMR indicated that essentially 100% of the PCP chains bore a styryl end group, within the combined NMR and GPC measurement errors.[17] Essentially complete functionalization is also confirmed by the diblock synthesis results presented below.

To convert the styryl end group to an anionic active site, the PCP chains are reacted with *sec*-butyllithium (*s*BuLi), as

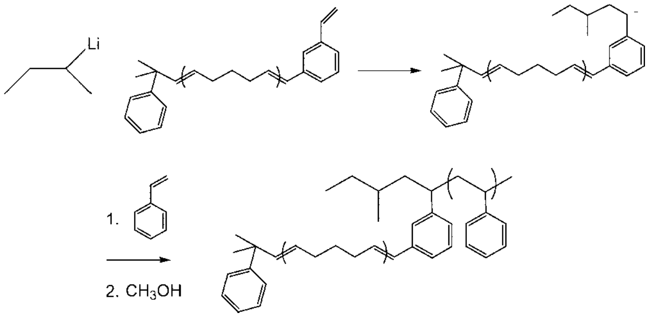

Figure 2. Second step of the ROMP-to-AP transformation route for the synthesis of diblock copolymers, illustrated for PCP/PS. The styryl end group on the PCP block is metalated with *s*BuLi, and the PS block is grown from this site.

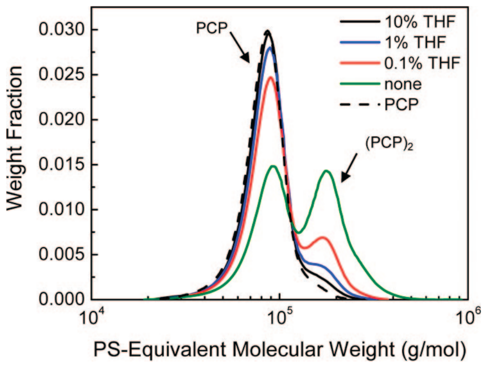

Figure 3. Molecular weight distributions of styrene-functionalized PCP (true $M_n = 40$ kg/mol, PS-equivalent $M_n = 79$ kg/mol) before and after metalation with *s*BuLi (4 equiv) and termination with degassed methanol. Increasing volume fraction of THF in the reaction solvent favors metalation over propagation.

indicated in Figure 2. Clean conversion of the end groups requires that metalation be greatly favored over propagation of the PCP macromonomers through their styryl ends. Metalation is favored by adding a stoichiometric excess of *s*BuLi (2−4 equiv). However, when the solvent is pure cyclohexane, this approach is not sufficient to suppress propagation, as shown in Figure 3. Metalation followed by immediate termination with degassed methanol reveals a substantial peak at double the starting PCP molecular weight and a shoulder near triple the PCP molecular weight. These chain populations arise by the addition of one and two styryl-functional PCP chains to the metalated PCP ends, respectively.

For comparison, we also explored the complementary approach ("grafting to" vs "grafting from"), where the styrene block is polymerized first, and the styryl-functional PCP is added to the fully formed PS block to cap the living end. Similar but more severe complications were observed,[17] with relatively slow reaction and undesired PS(PCP)$_2$ and PS(PCP)$_3$ dominating the product. In this case, it is a styryllithium anion adding a substituted styrene monomer (the PCP macromonomer), so there is little difference in reactivity between PSLi, PS(PCP)Li, and PS(PCP)$_2$Li.

However, for the route schematized in Figure 2, there is an important difference between the metalation reaction (alkyllithium adding styrene) and the concurrent but undesired propagation reaction (styryllithium adding styrene). Polar modifiers such as tetrahydrofuran (THF) are well-known to break up the aggregates typically formed by alkyllithiums in hydrocarbons,[20] which could thus favor metalation over propagation. Figure 3 shows the results of adding modest quantities (0.1−10 vol %) of THF to the cyclohexane solvent. Even 0.1 vol % THF strongly diminished the (PCP)$_2$ peak, and at 10 vol % THF, this coupling peak amounted to only 3% of the total.

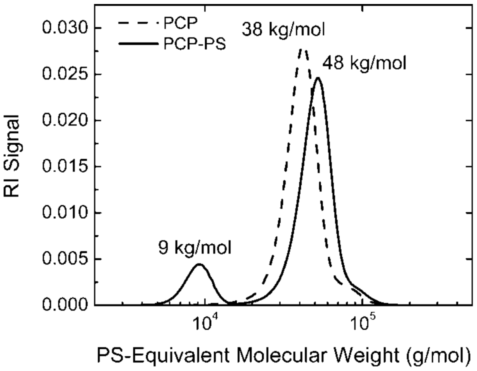

Figure 4. Molecular weight distributions of a PCP−PS block copolymer and its PCP precursor (19 kg/mol true M_n or 38 kg/mol PS-equivalent M_n) after styrene polymerization in cyclohexane with 1% THF. PS grows both from the free *s*BuLi, forming PS homopolymer (9 kg/mol), and from the ω-end of the PCP chain, forming the PCP−PS diblock (48 kg/mol PS-equivalent M_n).

Diblock Synthesis. Although THF speeds metalation relative to propagation, our typical reaction procedure still involved the addition of excess *s*BuLi (2 equiv) to ensure that all PCP ends were metalated, as there is always the possibility of some trace contaminants (e.g., atmospheric water) in the PCP, which could consume a fraction of the *s*BuLi. As a result, upon addition of styrene, PS chains grew simultaneously from the excess *s*BuLi and the metallated PCP end groups. This gave a reaction mixture as shown in Figure 4, containing both the desired PCP−PS diblock and PS homopolymer. In the particular case shown in Figure 4, the PS homopolymer could be removed from the product mixture by simple solvent−nonsolvent (toluene−methanol) fractionation, which is straightforward when $M_{w,PCP} \gg M_{w,PS}$. But for the opposite case ($M_{w,PS} \gg M_{w,PCP}$), fractionation would be more difficult, motivating the development of an alternative procedure which yields "clean" diblock directly and eliminates the need for fractionation.

It is well-known that THF can react with, and gradually terminate, living anions.[21] Leveraging the fact that the rate of free *s*BuLi termination is much faster than that of styryllithium,[21,22] we selectively terminate the excess *s*BuLi by allowing a controlled interval (30 min) to elapse between metalation and styrene addition. Typically, 25 vol % THF was required to terminate a 1.5× molar excess of *s*BuLi in ~30 min, as evidenced by the fact that subsequent styrene addition results in the formation of only the desired PCP−PS diblock. A risk in this approach is potential termination of the metalated PCP, producing "dead" PCP homopolymer. However, no substantial termination of metalated PCP was in fact observed, as revealed in Figure 5. Here, *s*BuLi (2.5 equiv) was added to the styryl-functionalized PCP and stirred at room temperature for 30 min to decompose the excess *s*BuLi. Styrene was added, and the reaction mixture was stirred for an additional 60 min before termination with degassed methanol. The final reaction product is principally the desired PCP−PS diblock, with a barely detectable PCP homopolymer peak. Parenthetically, this result also confirms essentially complete functionalization of the PCP by 3VBA, as any unfunctionalized PCP would not be able to grow a styrene block and would reveal itself in the GPC of the diblock product as a contaminant at the elution time of the starting PCP block.

Table 1 lists a selection of block copolymers synthesized by these approaches, using either 1% THF, which allows the growth

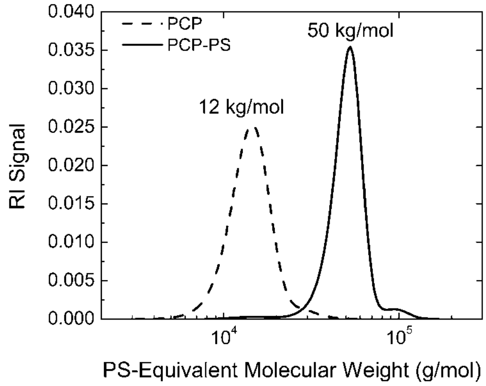

Figure 5. Molecular weight distributions of a PCP−PS diblock copolymer and its PCP first block (5.8 kg/mol true M_n, 12 kg/mol PS-equivalent M_n) after styrene polymerization in 75/25 v/v cyclohexane/THF. 30 min was allowed to elapse between PCP metalation and styrene addition, to decompose the excess *s*BuLi; PS grows only from the PCP chain end, forming the desired PCP−PS diblock.

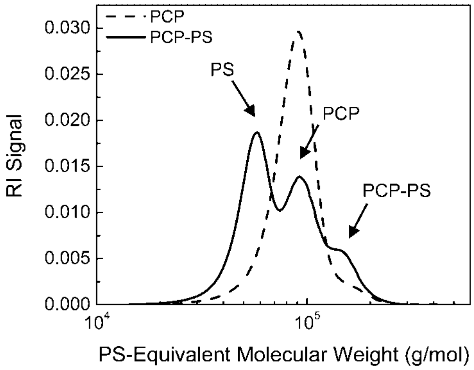

Figure 6. Molecular weight distribution of benzaldehyde-terminated PCP (38 kg/mol true M_n, 75 kg/mol PS-equivalent M_n) after metalation and immediate termination (dashed curve) and after metalation and styrene addition (solid curve), both in 90/10 v/v cyclohexane/THF. Partial metalation of internal conjugated double bonds and styrene addition results in a trimodal molecular weight distribution consisting of PCP and PS homopolymers and PCP−PS diblock copolymer.

Table 1. Characteristics of ROMP/Anionic Block Copolymers

ROMP block			anionic (PS) block M_n (g/mol)	diblock PDI	metalation method (% THF)
monomer	M_n (g/mol)	PDI			
cyclopentene	5 300	1.11	5 500	1.10	25
cyclopentene	5 800	1.09	38 100	1.07	25
cyclopentene	10 200	1.08	25 900	1.11	25
cyclopentene	14 000	1.10	16 200	1.07	1
cyclopentene	18 800	1.09	10 300	1.08	1
cyclopentene	23 200	1.10	5 800	1.09	1
norbornene	24 100	1.04	17 500	1.04	1

of PS homopolymer, or 25% THF, resulting in free *s*BuLi decomposition and no PS homopolymer. The block copolymers span a broad range of molecular weights and compositions, and all exhibit narrow molecular weight distributions for both blocks. ROMP monomers other than cyclopentene may be used, as the reaction of 3VBA with the Mo ROMP active site does not depend significantly on the polymer chain to which it is attached. The last entry in Table 1 corresponds to a polynorbornene−PS diblock synthesized by this ROMP-to-AP transformation approach. A low PDI = 1.04 was achieved, equivalent to that obtained by Notestein[1] via the chain-coupling route.

Internal Metalation. Though Figures 4 and 5 and Table 1 demonstrate the utility and range of this ROMP-to-AP transformation approach, it is important to identify and assess any side reactions which could compromise the block architecture in these materials. One such side reaction—propagation of the styryl-functional PCP—has already been identified in Figure 3 and ameliorated by adding THF to the reaction mixture. Another potential side reaction is metalation of double bonds other than the terminal bonds **A** (Figure 2). Such metalation, if it occurs, could lead to the growth of two or more PS chains from a single PCP. Though metalation of the **A** double bonds should be strongly favored over **B** or **C**, the internal end group double bond **B** (one per PCP) is also conjugated; it is essentially a substituted β-alkylstyrene. In benzene, *trans*-β-methylstyrene is slowly metalated by BuLi through abstraction of a β-methyl proton; the resulting phenyl-substituted allyl anion is relatively stable toward further reaction.[23] By contrast, in THF, BuLi rapidly initiates *trans*-β-methylstyrene, which polymerizes through the usual addition of a carbanion to the C═C bond; however, chain transfer to monomer by abstraction of a β-methyl proton also occurs, eventually generating the stable phenyl-substituted allyl anion.[23]

In cyclohexane/THF mixtures, one might expect that metalation of β-alkylstyrenes or their polymeric analogues would yield a mixture of unreactive allylic anions and styryl anions capable of initiating polymerization of less-hindered monomers. We confirmed this possibility directly for the small molecule β-methylstyrene: in 90/10 v/v cyclohexane/THF, adding *s*BuLi to *trans*-β-methylstyrene (110 equiv vs sBuLi) led to the immediate development of yellow/orange color, but no polymerization even after 60 min. Styrene was then added: the color remained yellow/orange, and the styrene polymerized within 30 min to yield narrow-distribution polymer of nearly double the molecular weight expected from the styrene:*s*BuLi ratio. This indicates that half the metalated *trans*-β-methylstyrene sites formed by *s*BuLi under these conditions were reactive styryl anions and half unreactive allyl anions.

We next examined a polymeric analogue, simpler in structure than our styryl-terminated PCP: namely benzaldehyde-terminated PCP (M_n = 38 kg/mol), which has the internal conjugated double bond (**B**) but not the external one (**A**). Ideally, no metalation would occur in this case, but in 90/10 v/v cyclohexane/THF, adding 4 equiv of *s*BuLi turned the reaction solution pale yellow, indicating some metalation, analogous to the results of the *trans*-β-methylstyrene experiment discussed above. Styrene was subsequently added and polymerized to yield three peaks in the GPC trace of the reaction product (Figure 6): PS homopolymer from the excess *s*BuLi, unreacted PCP homopolymer, and a PCP−PS diblock product. On the basis of the relative intensities of the peaks and the refractive index increments of the polymers[17] ($(dn/dc)_{PS}$ = 0.188 mL/g, $(dn/dc)_{PCP}$ = 0.122 mL/g), 9% of the PCP chains propagated into PCP−PS diblocks. Control reactions[17] in pure cyclohexane (no THF) using this same polymer showed no color change 30 min after adding *s*BuLi to PCP and no propagation to diblock. The same null result was found,[17] even in the presence of 10 vol % THF, for reaction of *s*BuLi with propionaldehyde-terminated PCP, which contains only the nonconjugated double bonds **C**. These results confirm the expected inertness of the backbone double bonds (**C**) to metalation, but they also indicate that some metalation of the internal double bonds **B** can occur and that some of these metalated sites are of the reactive styryl type.

Returning to the styryl-functional PCP of interest, its UV absorbance at 254 nm is a sensitive probe of the end group density and conjugation state, since the PCP backbone has negligible absorbance at this wavelength, and the absorbance of a π-conjugated phenyl ring at 254 nm is typically at least an order of magnitude higher than that for an unconjugated phenyl ring.[24] Thus, if the end group conjugation is destroyed

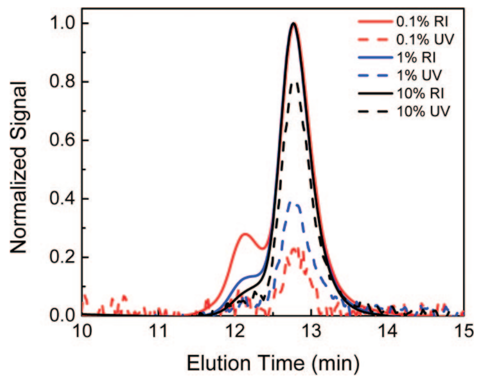

Figure 7. GPC chromatograms of styrene-functionalized PCP (M_n = 40 kg/mol) after metalation with 4 equiv of *s*BuLi and termination with degassed methanol. Each plot contains RI (solid) and UV (254 nm, dashed) traces for test metalations run in 0.1, 1, and 10 vol % THF. UV signals are normalized to equal the RI signal when one internal conjugated end group double bond is present. Observed UV signals are attenuated relative to this reference, indicating metalation of internal double bonds **B**; metalation is reduced but not eliminated by adding THF.

by metalation and simple termination (e.g., with methanol), the UV absorbance will decrease strongly while the refractive index increment will be essentially unchanged. This can be monitored directly in the GPC by taking the ratio of the UV (254 nm) to RI signal intensities, when analyzing the products of metalation test reactions on a single styryl-functionalized PCP (M_n = 40 kg/mol). Metalation of only the external double bond **A**, followed by termination with methanol, should yield a UV/RI ratio similar to that of the benzaldehyde-terminated PCP, which we will take as the reference (UV/RI ≡ 1, normalizing by M_n^{-1}).

Prior to metalation, the styryl-functional PCP shows UV/RI = 1.33, slightly greater than the benazaldehyde-terminated reference case because of the second double bond conjugated to the phenyl ring. Figure 7 shows the GPC RI and UV traces which result after metalation with 4 equiv of *s*BuLi, and termination with methanol, for various contents of THF in the reaction solution. In all cases, the UV signal traces are normalized so that they would superpose on the RI traces for the benzaldehyde-terminated reference case (UV/RI ≡ 1). With 10% THF in the reaction solution, the UV absorbance is only 80% of the expected value, suggesting that along with destroying all of the external double bonds **A**, ca. 20% of the internal double bonds **B** were destroyed through addition of *s*BuLi to the C=C bond and subsequent termination with methanol. Note that any metalation by β-methylene proton abstraction, which yields the allylic anion, would not be detected by this method, as the double bond is preserved through the metalation-termination cycle. As the THF content is reduced, the residual UV absorbance drops, indicating the destruction of 60% of the internal end group double bonds at 1 vol % THF and 75% at 0.1 vol % THF. Varying the Li:end group molar ratio over the range 2−20× produced only modest differences in these fractions.[17] While all these results indicate some addition of *s*BuLi to the **B** double bonds, note that the effect of THF is opposite to that found for *trans*-β-methylstyrene[23] and benzaldehyde-terminated PCP, where THF *promotes* addition of the anion to the C=C bond. This difference indicates that the conversion of the external double bonds **A** to the styryl anion changes the reactivity of the internal double bonds **B**.

Though Figure 7 indicates that *s*BuLi adds to a fraction of the double bonds **B** in our styryl-functional PCP, the reactivity of these sites appears to be quite low. Using the same conditions described above, we added a 10-fold excess of the highly reactive $(CH_3)_3SiCl$ to the metalated styryl-functional PCP. The red/orange color typical of a living conjugated styryl anion diminished when $(CH_3)_3SiCl$ was added but did not disappear until the subsequent addition of degassed methanol. Analysis of the product polymers[17] by ^{1}H NMR revealed that the number of $-Si(CH_3)_3$ groups per chain was 1.07, 0.87, and 0.89 for reactions in 0.1, 1, and 10 vol % THF—all within measurement error of unity—and not equal to the expected values of 1.75, 1.6, and 1.2 based on the UV/RI results, if all of the sites formed by addition of *s*BuLi to the double bonds **B** are able to react. We conclude that while a fraction of the internal double bonds **B** do metalate, these low-reactivity metalated sites lead to at most a small fraction of PCP chains which grow two PS blocks from their end groups, to yield $PCP(PS)_2$ miktoarm star polymers. This is confirmed by the GPC traces in Figure 5, which show only a minute high-molecular-weight shoulder at the position expected for $PCP(PS)_2$, amounting to <3% of the total product.

Conclusions

We have demonstrated a simple, two-step method for the synthesis of ROMP/AP diblock copolymers through a macroinitiator approach. The ROMP block is synthesized using a Mo-based initiator and terminated with 3VBA to give a polymer with a styryl end group, which is then metalated to yield a site for living carbanionic polymerization. The method yields well-defined ROMP/AP diblock copolymers with narrow molecular weight distributions. Though excess metalating agent (*s*BuLi) is used to ensure complete crossover, the formation of homopolymer of the second block can be avoided simply by allowing the excess *s*BuLi to decompose prior to adding the second-block monomer. PCP−PS diblock copolymers with a broad range of molecular weights and compositions were synthesized. These materials could serve as precursors to well-defined diblocks containing linear (high-density) polyethylene via catalytic hydrogenation.

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Supporting Information Available: ^{1}H NMR spectrum of a polycyclopentene−polystyrene diblock copolymer, with relevant peak assignments. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Notestein, J. M.; Lee, L.-B. W.; Register, R. A. *Macromolecules* **2002**, *35*, 1985–1987.
(2) Hillmyer, M. *Curr. Opin. Solid State Mater. Sci.* **1999**, *4*, 559–564.
(3) Amass, A. J.; Bas, S.; Gregory, D.; Mathew, M. C. *Makromol. Chem.* **1985**, *186*, 325–330.
(4) Amass, A. J.; Gregory, D. *Br. Polym. J.* **1987**, *19*, 263–268.
(5) Castle, T. C.; Khosravi, E.; Hutchings, L. R. *Macromolecules* **2006**, *39*, 5639–5645.
(6) Castle, T. C.; Hutchings, L. R.; Khosravi, E. *Macromolecules* **2004**, *37*, 2035–2040.
(7) Katayama, H.; Fukuse, Y.; Nobuto, Y.; Akamatsu, K.; Ozawa, F. *Macromolecules* **2003**, *36*, 7020–7026.
(8) Dounis, P.; Feast, W. J. *Polymer* **1996**, *37*, 2547–2554.
(9) Trzaska, S. T.; Lee, L.-B. W.; Register, R. A. *Macromolecules* **2000**, *33*, 9215–9221.
(10) Cohen, R. E.; Bellare, A.; Drzewinski, M. A. *Macromolecules* **1994**, *27*, 2321–2323.
(11) Drzewinski, M. A. *Polymer* **1994**, *35*, 5024–5034.
(12) Switek, K. A.; Bates, F. S.; Hillmyer, M. A. *PMSE Prepr., Am. Chem. Soc, Div. Polym. Mater. Sci. Eng.* **2005**, *93*, 585–585.
(13) Switek, K. A.; Chang, K.; Bates, F. S.; Hillmyer, M. A. *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *45*, 361–373.
(14) Bielawski, C. W.; Morita, T.; Grubbs, R. H. *Macromolecules* **2000**, *33*, 678–680.

(15) Mahanthappa, M. K.; Bates, F. S.; Hillmyer, M. A. *Macromolecules* **2005**, *38*, 7890–7894.
(16) Lee, L.-B. W.; Register, R. A. *Polymer* **2004**, *45*, 6479–6485.
(17) Myers, S. B. Ph.D. Thesis, Princeton University, **2008**.
(18) Sebastian, J. M.; Register, R. A. *J. Appl. Polym. Sci.* **2001**, *82*, 2056–2069.
(19) Hatjopoulos, J. D.; Register, R. A. *Macromolecules* **2005**, *38*, 10320–10322.
(20) Morton, M. *Anionic Polymerization: Principles and Practice*; Academic Press: New York, 1983; p 123.
(21) Honeycutt, S. C. *J. Organomet. Chem.* **1971**, *29*, 1–5.
(22) Ogle, C. A.; Strickler, F. H.; Gordon, B. *Macromolecules* **1993**, *26*, 5803–5805.
(23) Okamoto, Y.; Yuki, H.; Murahashi, S. *Bull. Chem. Soc. Jpn.* **1968**, *41*, 197–203.
(24) Pasto, D. J.; Johnson, C. R. *Laboratory Text for Organic Chemistry*; Prentice-Hall: Englewood Cliffs, NJ, 1979; p 119.

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