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Norbornadiene Endcapping of Cross-Coupling Polymerizations: A Facile Route to Triblock Polymers

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Supporting Information Placeholder

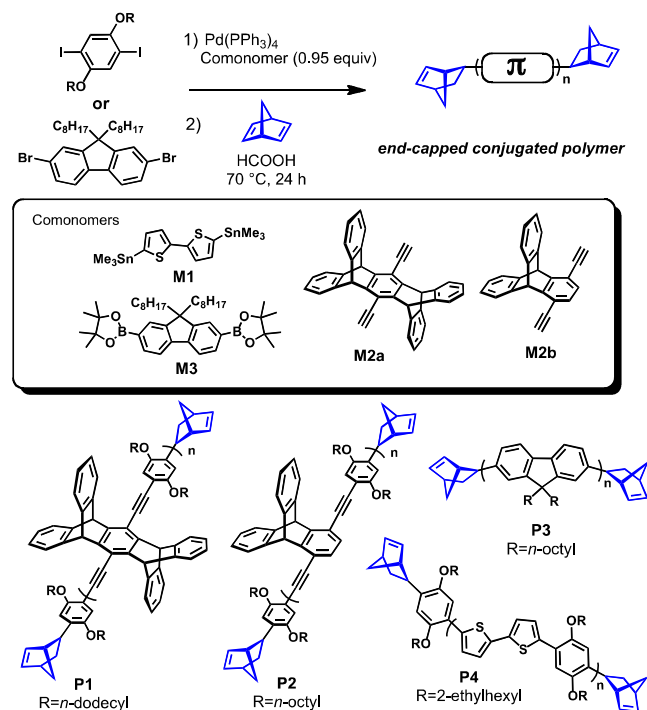
ABSTRACT: The potential use of conjugated polymers in device applications is often limited by their less than optimal physicochemical properties. This work describes an efficient protocol to end-cap conjugated polymers synthesized via palladium catalyzed cross-coupling polymerization with norbornene groups. Specifically, the hydroarylation of norbornadiene is shown to be a high-yielding end-capping method. These strained bicyclic alkenyl end-groups can be transformed into macroinitiators via ring-opening metathesis polymerization and can polymerize other strained monomers such as norbornene yielding elastomeric triblock copolymers.

The rigidity and self-associating properties of π -conjugated materials limits the utility of these building blocks in materials exhibiting the full spectrum of mechanical properties.¹ Specifically, the low molecular weights of these materials limits the mechanical durability necessary to realize the often-stated goal of enabling flexible electronic/photonic devices.²⁻⁶ The creation of block copolymers is a powerful method by which a multifunctional polymeric material can be designed to exhibit diverse mechanical and organizational properties.⁷ In spite of the potential of block copolymers to extend the scope of conjugated polymer applications, there are only a few methods for the creation of these materials. Prior to our work, these materials have been limited,⁸ with the best known examples being the end-capping of polythiophenes with groups that can initiate a controlled radical polymerization.⁹⁻¹¹ Recognizing that the vast majority of soluble poly(arylene)s are synthesized via cross-coupling methods,¹² we expected that an end-capping method that is compatible with these polymerization conditions could find significant utility. Herein, we describe a modular approach to the formation of triblock copolymers using the hydroarylation of norbornadiene as the pivotal end-capping step in a cross-coupling polymerization. Conjugated polymers capped with strained bicyclic alkenes permits the formation of ruthenium alkylidene macroinitiators that are capable of propagating a polynorbornene segment via ring-opening metathesis polymerization (ROMP) to generate triblock copolymers.

Strained bicyclic alkenes such as norbornene and norbornadiene have enjoyed success in hydroarylation reactions.¹³⁻¹⁵ Much of this interest stems from two points: (1) carbopalladation of norbornene/norbornadiene is accelerated due to relief of ring strain and (2) intermediates derived from the carbopalladation of these strained substrates lack a properly oriented β -hydrogen atom, thus giving rise to additional reaction pathways. In many of these methods the alkene is used as an *ipso*-

carbon placeholder and is not incorporated into the final product.¹⁶ Less work has focused on the incorporation of norbornene in the final product using reductive conditions. Recognizing the synthetic potential of polymers bearing norbornene end-caps, we embarked on a study to test the efficiency of the hydroarylation reaction as an end-capping step.

Scheme 1. Synthesis of End-Capped Polymers.



Model reactions employing the dihaloarenes shown in Scheme 1 were used to gauge the efficiency of the hydroarylation reaction under conditions typically used for Stille, Sonogashira-Hagihara, and Suzuki-Mizoroki cross-coupling polymerizations (see Supporting Information). The model reactions proceeded in excellent yields (82-97%), and the conditions were repeated for polymerizations using comonomers M1, M2a, M2b, and M3 to generate the end-capped conjugated polymers depicted in Scheme 1. A slight excess of the dihaloarene was employed to ensure that the polymer chains are terminated with an aryl halide prior to addition of norbornadiene. The end-capping step was carried out under reductive conditions – employing formic acid as a hydride source to permit reductive elimination. It is noteworthy that the conditions could potentially give rise to hydrodehalogenated products;¹⁷ however, we did not observe this secondary pathway in

our model studies nor does it appear to interfere with the polymer end-capping reaction. One possible explanation is that relief of ring-strain accelerates the carbopalladation step thereby limiting other pathways.

^1H NMR analyses of the resulting polymers (see Supporting Information) contained proton resonances associated with norbornene end-caps – an example spectrum is shown in Figure 1. Two methine resonances associated with the bridgehead positions of norbornene, as well as a benzylic methine are visible in the spectrum (for comparison see ^1H NMR spectra of model compounds and gCOSY analysis of **P2** in Supporting Information). Of particular note is the good correlation in the ratio of end-cap resonances (red integral/protons) to the near end-cap α -methylenes on the dialkoxy comonomer (small blue integral/protons). A perfectly efficient end-capping reaction would yield a ratio of 3:4 (red:blue), our ratio of 3:5 suggests that the reaction proceeded in a highly efficient manner.

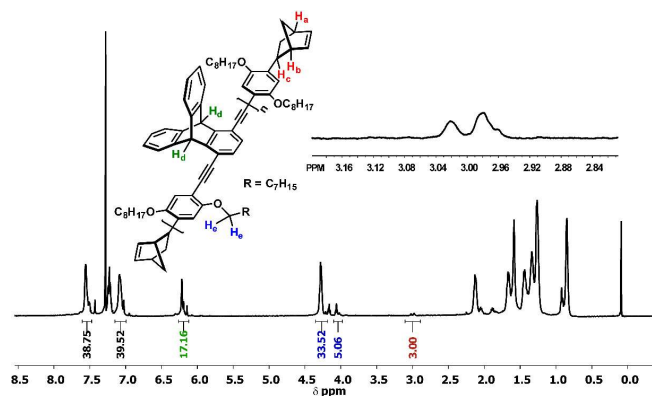


Figure 1. ^1H NMR spectrum of polymer **P2**. Included is the molecular structure of **P2** with appropriate protons highlighted as well as a magnified region of the spectrum as an inset.

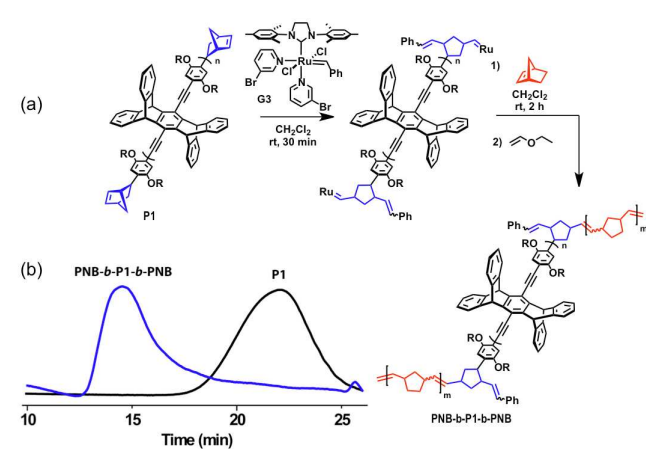


Figure 2. (a) Synthesis of **PNB-b-P1-b-PNB**. (b) THF SEC (UV detection 450 nm) traces of **P1** (black) and **PNB-b-P1-b-PNB** triblock copolymer (blue).

With an adequate end-capping reaction in hand, we turned our attention to the formation of ruthenium based macroinitiators via the ring opening metathesis reaction of polymers **P1-P4**. The end-capped polymers were exposed to an excess of Grubbs' 3rd generation catalyst (**G3**), reprecipitated in cold hexanes to remove the unreacted catalyst, and subsequently

used as macroinitiators for the ROMP of norbornene monomers (see Figure 2). Grubbs' 3rd generation catalyst was chosen because it has been shown to exhibit an excellent initiation to propagation ratio.¹⁸ The formation of triblock copolymers was verified using ^1H NMR analysis (see Supporting Information) as well as SEC (size-exclusion chromatography).

The key advantage of using Ru-alkylidene based macroinitiators lies in the functional group tolerance, high-yielding nature, and practicality of ROMP.¹⁹ To showcase the modularity of this approach we used strained monomers **5** and **6** (see Scheme 2 for molecular structures). These readily accessible monomers are highly active in ROMP and also possess functional group handles for further derivitization. Table 1 displays the results of the triblock copolymerizations. Of particular note are the high molecular weights of the block copolymers demonstrating the activity of the macroinitiators in propagating strained bicyclic alkenes via ROMP. Despite these advantages, there are two drawbacks of using high molecular weight macroinitiators, (1) the decreased solubility and slow diffusion rates increase the PDI's of the resulting triblock copolymers, and (2) the high metathesis reactivity of norbornene end-caps causes oligomerization of the macroinitiator in some cases.

Scheme 2. Synthesis of Triblock Copolymers.

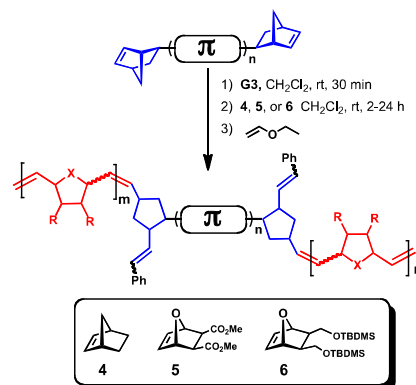


Table 1. Selected results of triblock copolymerizations^a.

CP	macroinitiator		Monomer	block copolymer	
	Mn ^b (g/mol)	PDI		Mn ^b (g/mol)	PDI
P1	130,900	2.5	5	511,200	6.3
P1	36,400	1.9	4	140,300	2.1
P3	29,000 ^c	1.69	5	528,300	2.52
P4	23,600	1.8	6	26,900	4.0
P4	23,600	1.8	5	701,200	5.1

^aConditions: See Scheme 2 for general conditions, specific conditions are outlined in the Supporting Information. ^bDetermined using SEC relative to polystyrene standards in THF. ^cThis macroinitiator was formed using Grubbs' 2nd generation catalyst. **G3** exhibited significant oligomerization of the end-capped polymer.

In addition to functioning as macroinitiators, the end capped polymers can also be employed as crosslinkers. Polynorbornene, commercially known as Norsorex®, is an elastomeric material with a tunable glass transition temperature

(T_g) that can vary from 35 °C to -60 °C.²⁰ When the material is plasticized with a hydrocarbon or aromatic additive the T_g drops below room temperature and the material behaves as an elastomer. We envisioned using polymers **P1-P4** as crosslinkers for the formation of functionalized elastomers - materials that exhibit the mechanical properties of polynorbornene and the optical properties of the conjugated crosslinker.

Figure 3 displays optical images of polynorbornene cross-linked with **P1** under both ambient and UV (365 nm) irradiation. The material shows elastomeric behavior while also exhibiting the optical characteristics of **P1**. The material exhibited greater than 80% recovery after being uniaxially stretched to six times its initial length.

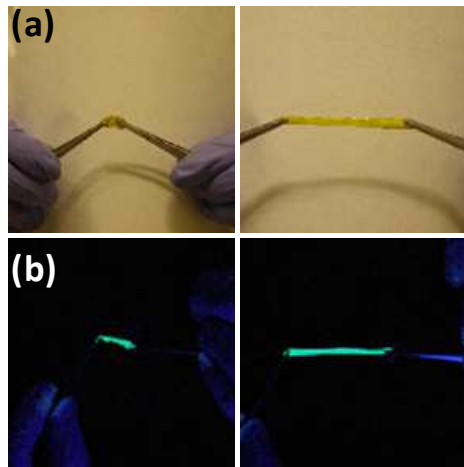


Figure 3. (a) Optical micrographs of **PNB** crosslinked with **P1** in unstretched (left) and stretched (right) states. (b) Optical micrographs with 365 nm excitation light of the same material in unstretched (left) and stretched (right) states.

P2 is a soluble conjugated polymer that exhibits red-shifted photoluminescence in thin-films as a result of π - π interactions. We surmised that **PNB** rubber crosslinked with **P2** would exhibit photophysical perturbations as a result of swelling in the presence of organic solvents, possibly acting as a sensor for detection of volatile organic compounds (VOCs) in water. Figure 4 displays the photoluminescence spectra of this material in aqueous solutions with or without tetrahydrofuran (THF). In water, the film exhibits broad red-shifted emission consistent with interpolymer interactions such as π - π stacking. After addition of a small amount of THF (1% v:v) the emission shifts to higher wavelengths suggesting that the material is swelling with concurrent loss of interpolymer interactions. In addition, exposure of this material to the saturated vapor of THF shows a similar response and the emission decay at 450 nm is depicted in Figure 4b.

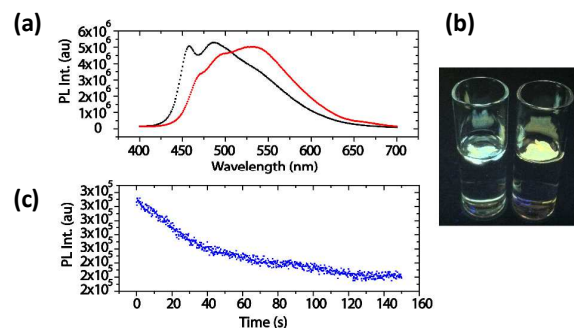


Figure 4. (a) Photoluminescence spectra of **PNB** crosslinked with **P2** in water (red) and 1% THF:water (v:v) (black). (b) Optical micrograph (UV excitation at 365 nm) showing **PNB** crosslinked with **P2** films in water (right) and 1% THF:water (v:v) (left). (c) Photoluminescence intensity decay (monitored at 450 nm) of the same film after exposure to the saturated vapor of THF.

In conclusion, we have shown the utility of the hydroarylation of norbornadiene in the context of multiblock copolymer synthesis. The end-capping protocol is compatible with standard conditions used to synthesize common conjugated polymers, uses cheap and abundant materials, and can be accomplished in a one-pot fashion. The resulting end-functionalized polymers were converted to alkylidene macroinitiators that were shown to act as competent catalysts in ROMP. This approach yielded triblock copolymers with mechanical properties similar to the peripheral units and optical properties associated with the parent conjugated polymer unit. Future work using this method towards the synthesis of highly functionalized nanoparticles is currently underway in our laboratory.

Supporting Information. Detailed synthetic procedures and NMR spectra. This material is available free of charge via the Internet at <http://pubs.acs.org/journal/amlccd>.

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