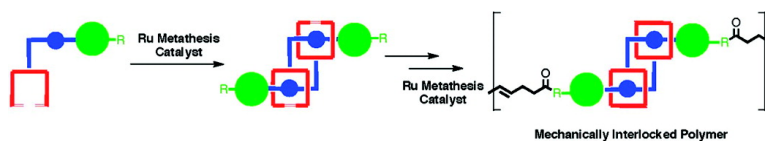


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Bifunctional [c2]Daisy-Chains and Their Incorporation into Mechanically Interlocked Polymers

Erin N. Guidry,[†] Jean Li,[†] J. Fraser Stoddart,^{*,‡} and Robert H. Grubbs^{*,†}

The Arnold and Mabel Beckman Laboratory of Chemical Synthesis, Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125, and California NanoSystems Institute & Department of Chemistry and Biochemistry, University of California, Los Angeles, 405 Hilgard Avenue, Los Angeles, California 90095

Received April 10, 2007; E-mail: rhg@caltech.edu; stoddart@chem.ucla.edu

Much attention has been devoted to the design and synthesis of linear daisy-chain polymers¹, a class of rotaxane-based polymers in which both the host and guest recognition units are coupled covalently together in the same monomer (Figure 1a). Repetitive self-assembly processes leading to daisy-chain polymers (Figure 1c) have to compete with the formation of cyclic analogues^{2,3} where the thermodynamic driving force lies in the production of small cycles, for example, the [2]daisy-chain dimer shown in Figure 1b. In addition to their appeal as challenging targets in polymer synthesis, such macromolecules would also contain mechanical links rather than covalent bonds between the monomer units. It is tempting to speculate that the incorporation of flexible mechanical links, that could also be rendered switchable, would have repercussions for the polymer-chain behavior which is expected to affect both the solid-state and solution properties.⁴ Despite the fascination of chemists with these macromolecules, few examples⁵ exist on account of the considerable challenge posed by their synthesis. Although numerous attempts have been made at their synthesis, most rely on template-directed self-assembly as the polymerization step. More often than not, however, this strategy results³ in cyclic dimer formation. While higher oligomers have been observed,^{1a–c,e} the number of repeat units is typically low. Here, we describe a strategy that relies on the polymerization of a bisfunctionalized [c2]daisy-chain monomer.

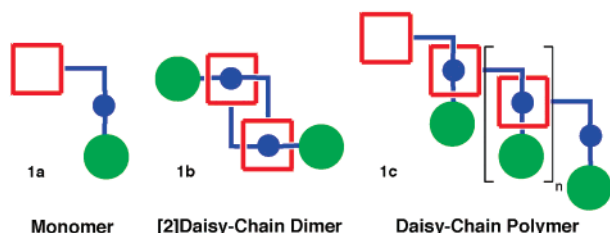
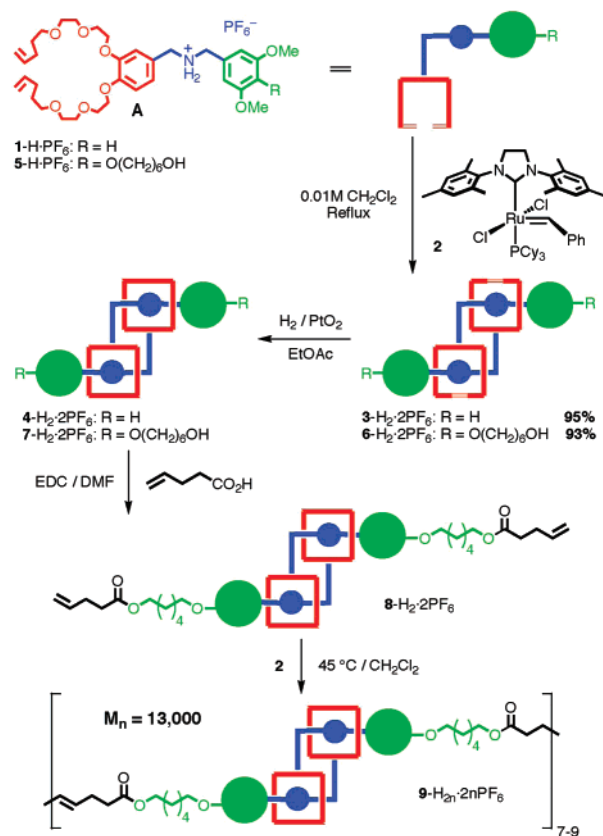


Figure 1. Graphical representation of daisy-chain monomer (**1a**), [2]daisy-chain dimer (**1b**), and daisy chain polymer (**1c**).

Although [c2]daisy-chains, based on hydrophobic, hydrogen bond, and metal-coordination templating motifs have been produced, all these approaches involve irreversible stoppering events as the final mechanical bond-forming reactions. On account of the accompanying formation of unwanted byproducts, this strategy does not always result in high yields of mechanically interlocked products. An alternative strategy exploits dynamic covalent chemistry,⁶ an approach that relies on reversible reactions in which the product distribution depends on thermodynamic rather than kinetic control. Examples of reversible reactions employed as the final bond-forming steps in the synthesis of catenanes and rotaxanes

Scheme 1. Synthesis of [c2]Daisy-Chain Dimers Using RCM and Their Subsequent ADMET Polymerization to Form An Interlocked Polymer.



include the formation of imines,⁷ disulfides,⁸ and cyclic acetals⁹ as well as olefins.¹⁰ The use of functional group tolerant ruthenium alkylidene catalysts has been applied¹¹ successfully to the synthesis of [2]catenanes¹² and [2]rotaxanes.¹³ Previously, we have demonstrated that the ring-closing of appropriate bisolefin-containing polyether substrates around disubstituted dibenzylammonium ions result in the reversible formation of [2]catenanes¹⁴ and [2]rotaxanes.¹⁵ We now describe how we have extended this ring-closing metathesis methodology to the synthesis of [c2]daisy-chains.

The formation of [c2]daisy-chains necessitates that both recognition units reside within the same molecule such that it will not undergo self-complexation but rather form a dimeric daisy-chain. The precursor **1-H**·PF₆ was prepared (Supporting Information) in seven steps. Ring-closing of the terminal olefin functions present in **1-H**⁺ using the ruthenium catalyst **2** afforded (Scheme 1) the [c2]daisy-chain **3-H**·2PF₆ in near quantitative conversion and as a 95% yield, isolated as a mixture of (*E*) and (*Z*) isomers, a situation which confers considerable complexity upon the ¹H NMR spectrum (SI). Hy-

[†] California Institute of Technology.

[‡] University of California, Los Angeles.

drogenation of the olefinic bonds in $3\text{-H}_2\cdot 2\text{PF}_6$ to give $4\text{-H}_2\cdot 2\text{PF}_6$ simplifies the spectrum, and the characteristic signals for the methylene protons associated with the $-\text{CH}_2\text{NH}_2^+\text{CH}_2-$ units encircled by [24]crown rings are evident in the range 4.25–4.68 ppm. Since this [c2]daisy-chain compound is a mixture of three stereoisomers, on account of the breaking of constitutional symmetry in the central benzene ring (A in Scheme 1), the ^1H NMR spectrum is particularly complex in the region where these aromatic protons resonate. Crystallization, however, leads to the fractional separation of the meso-form, which remains dissolved in the mother liquor, and the racemic mixture, which forms single crystals suitable for X-ray crystallography.¹⁷ The solid-state structure is illustrated in Figure 2.

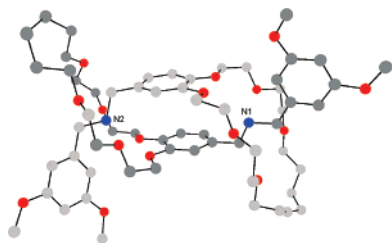


Figure 2. Ball and stick representation of $4\text{-H}_2\cdot 2\text{PF}_6$ generated from a low-resolution X-ray crystal structure. Hydrogen atoms have been omitted for clarity.

Functionalization of the stoppers in these [c2]daisy-chains could provide an alternative means to synthesize mechanically interlocked polymers. Acyclic diene metathesis (ADMET) chemistry looked promising to us since it requires only functionalization of the [c2]-daisy-chain as a bisolefin which can be polymerized under mild conditions catalytically using **2** and is driven by the removal of ethylene. The synthesis of the [c2]daisy-chain $6\text{-H}_2\cdot 2\text{PF}_6$, containing olefinic terminal groups on both stoppers was accomplished (Scheme 1), starting from $5\text{-H}\cdot \text{PF}_6$ in 93% yield using the ruthenium catalyst **2**. The diol $6\text{-H}_2\cdot 2\text{PF}_6$ was hydrogenated using Adams' catalyst (Pt_2O) to afford the saturated derivative $7\text{-H}_2\cdot 2\text{PF}_6$. EDC coupling of this diol with 4-pentenoic acid gave the [c2]daisy-chain monomer $8\text{-H}_2\cdot 2\text{PF}_6$. Since this monomer is a solid, the polymerization was run in a minimal amount of solvent (CH_2Cl_2) under an Ar purge to aid the removal of the ethylene. When the ADMET polymerization of $8\text{-H}_2\cdot 2\text{PF}_6$ was performed (monomer/catalyst loadings of 20:1) in CH_2Cl_2 at 45 °C, a polymer $9\text{-H}_2\cdot 2\text{nPF}_6$ with a molecular weight of 13000, determined by ^1H NMR spectroscopy using end-group analysis, was isolated.

Metathesis, in two different guises is making a hitherto unreachable goal in synthesis a reality. Ring-closing olefin metathesis has been shown to provide a very high yielding route to [c2]daisy-chains suitably functionalized to allow their one-step conversion to bisolefins which can be used as monomers in ADMET polymerizations to afford mechanically interlocked polymers. While the properties of these polymers are being investigated, their potential for applications is also being explored.

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Supporting Information Available: Complete experimental procedures as well as full characterization. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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