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Alternating Ring-Opening Metathesis Polymerization Copolymers Containing Charge-Transfer Units

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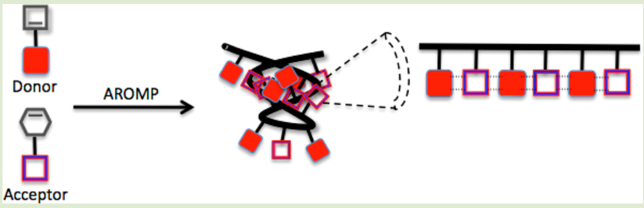
Supporting Information

ABSTRACT: Alternating copolymers derived from the ring-opening metathesis polymerization (ROMP) of functionalized cyclobutene esters (CBEs) and cyclohexenes (CHs) are described. The copolymer poly(CBE-*alt*-CH)$_n$ contains alternating side chains based on dialkoxynaphthalene (DAN) and pyromellitic dianhydride (PDI). Characterization by UV–vis spectroscopy showed that the copolymers exhibit an increase in charge-transfer intensity in comparison to previously reported alternating copolymers. The bulky side chains inhibit backbiting during the polymerization and allow for enhanced control over the polymerization in comparison to copolymers functionalized with linear alkyl groups.



Nature's uniquely sequenced polymers assume well-defined structures that are held together by noncovalent interactions such as hydrogen bonding, ionic, aromatic, hydrophobic, and van der Waals interactions.[1,2] These structures enable biopolymers to carry out sophisticated functions such as catalysis, specific binding, or directed flow of electrons.[3] Emulation of nature's affinity to engineer systems with precise structure-to-function relationships will provide new functional materials for potential applications such as synthetic enzymes.[3,4]

Alternating copolymers, in particular, provide high precision over incorporation of two different monomers into a polymer sequence. The preparation of alternating copolymers has been achieved via a variety of polymerization techniques including ring-opening metathesis polymerization (ROMP),[5] alkene polymerization,[6] and radical polymerization.[7,8] Despite the well-established implementation of ROMP that affords well-defined polymers, there are only a few reports using ROMP to obtain alternating copolymers.[9−11] This is likely due to the challenge in choosing monomer pairs with alternating affinities for the living metal alkylidene and also to appropriate catalyst selection. Employment of norbornene (NB)/cyclopentene (CPE) or NB/cyclooctene (COE) monomer pairs in alternating ROMP has been reported.[12−14] These methods rely on the slow homopolymerization of CPE or COE in combination with a significant excess of one of these monomers to obtain a high level of alternation.[9,10,15] Such strategies are chemically inefficient and risk generating homopolymer blocks of the monomer in excess. In this contribution, we report a perfectly alternating ROMP copolymer achieved using cyclobutene esters (CBE) and cyclohexenes (CH) containing bulky charge-transfer side chains.

Previously, we reported the first alternating ROMP copolymers synthesized from NB/COE monomers that were functionalized with dialkoxynaphthalene (DAN) and pyromellitic dianhydride (PDI) units, respectively.[16] This functional pair exhibits a charge-transfer absorbance (~460 nm in chloroform) when the aromatic units are properly aligned in a face-to-face geometry.[17] The charge-transfer unit provides an effective spectroscopic handle to characterize the conformational arrangement of these aromatic groups in solution.[18−20] We demonstrated that the alternating placement of the charge-transfer units along a single polymer chain provides insight into the polymer structure. However, the alternating copolymerization strategy we used required a 50-fold excess of the cyclooctene monomer, thereby yielding significant poly(COE) blocks at one end of the alternating copolymer.

We also reported the perfectly alternating ring-opening metathesis polymerization (AROMP) between cyclobutene (CB) and CH.[21] We demonstrated that CB derivatives substituted at the 1-position, that have a similar strain energy to NB,[22,23] undergo ruthenium-catalyzed ROMP.[24] Introduction of an ester functional group at the 1-position leads to a loss of homopolymerization ROMP activity.[21,25] In contrast to CBE, the strain energy of CH is close to zero and is not a suitable monomer for ROMP. However, CH was found to react with the enoic carbene generated from the ring-opened CBE.[21] In turn, the regenerated Ru alkylidene reacts with an equivalent of CBE. This alternating reactivity of the ruthenium catalyst provides alternating copolymers irrespective of the monomer feed ratio. The alternating copolymers, however, were found to display a bimodal molecular weight distribution due to intramolecular chain transfer, i.e., "backbiting". Herein we address both the limitation of the NB/COE ROMP, i.e., the

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formation of COE homoblocks, as well as the intramolecular chain transfer of current AROMP by utilizing CBE/CH monomers containing the DAN−PDI pair to achieve perfectly alternating copolymers. We show that these polymers exhibit a higher intensity charge-transfer absorbance than analogous poly(NB-*alt*-COE) polymers.

The target monomers and catalyst are shown in Figure 1. The syntheses of the side chains are in close analogy to published methods[16] and are described in the Supporting Information. On the basis of previous studies,[21] synthetic route 1 (Scheme 1) was first investigated for the alternating copolymerization of the DAN and PDI functionalized CBE and CH monomers, respectively. This route successfully afforded poly(**1**-*alt*-**2**)$_5$. However, longer polymerization times were required due to the significant steric hindrance presented by the side-chain units. This resulted in a decrease in the rate of polymerization inhibiting the formation of higher molecular weight polymers.

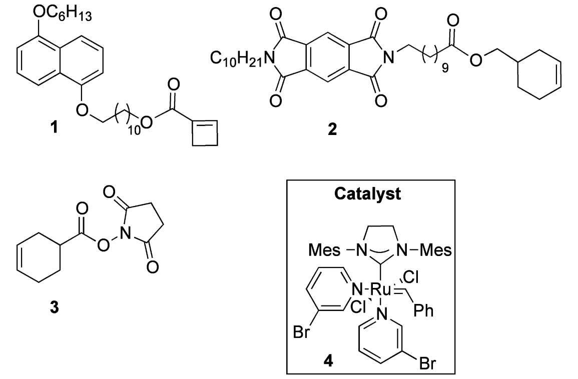


Figure 1. Chemical structures of monomers and catalyst (box) used for AROMP.

To minimize steric hindrance and to achieve a higher degree of polymerization, a revised synthetic route was applied using DAN−CBE **1** and a cyclohexene functionalized with *N*-hydroxysuccinimide (NHS) (compound **3**) for AROMP (Scheme 2). The NHS group is less bulky than the PDI and is not reactive during the polymerization. The PDI ester can then be formed via a postpolymerization functionalization strategy to generate poly(**1**-*alt*-**5**)$_{10}$. This modified route not only allowed for a higher degree of polymerization but also provided an alternative strategy for the incorporation of the PDI moiety.

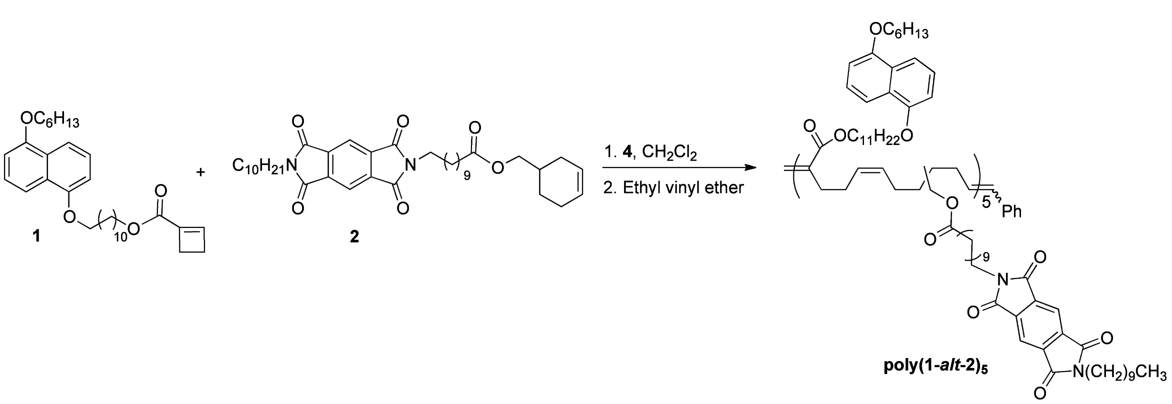
The previously reported studies on poly(CBE-*alt*-CH)$_n$ revealed signals in the ^{1}H NMR spectrum corresponding to concentration-independent intramolecular backbiting of the enoic ruthenium carbene on the unhindered disubstituted alkenes in the polymer backbone.[21] As a result, polydispersity indices of unfunctionalized poly(CBE-*alt*-CH)$_n$ were larger than 2, and a significant fraction of the polymer was cyclic. In our case, poly(**1**-*alt*-**2**)$_{10}$ and poly(**1**-*alt*-**5**)$_{10}$ did not show any proton resonance signals due to backbiting had PDIs lower than 1.3, and displayed a monomodal distribution. We hypothesize that backbiting is inhibited by the increased steric hindrance at the enoic carbene and disubstituted alkene in combination with the restricted flexibility of the polymer backbone upon modification with larger substituents. As a consequence, longer AROMP copolymers were obtained than previously reported.

UV−vis spectroscopy was utilized to investigate the charge-transfer between the side chains of the alternating copolymers in solution. The UV−vis spectrum of poly(**1**-*alt*-**5**)$_{10}$ (3 mM in chloroform) shows a charge-transfer absorbance at the characteristic wavelength (Figure 2a − light blue trace), indicating that the side chains are able to favorably orient to transfer energy in this system. A concentration study from 3 mM to 100 μM was carried out to determine if these interactions occur inter- or intramolecularly. As shown in Figure 2a, the charge-transfer absorbance signal was persistent even at low concentrations. Moreover, the absorbance followed Beer−Lambert behavior based on the concentration of polymer (Figure 2b), which demonstrated that the charge transfer is intramolecular. Additionally, the ^{1}H NMR spectrum of poly(**1**-*alt*-**5**)$_{10}$ shows upfield shifting of the aromatic signals in comparison to the individual monomers (Figure S10, Supporting Information). These shifts further indicate the $\pi-\pi$ stacking of the donor−acceptor aromatic units and are consistent with similar previously reported partially folded polymers.[18]

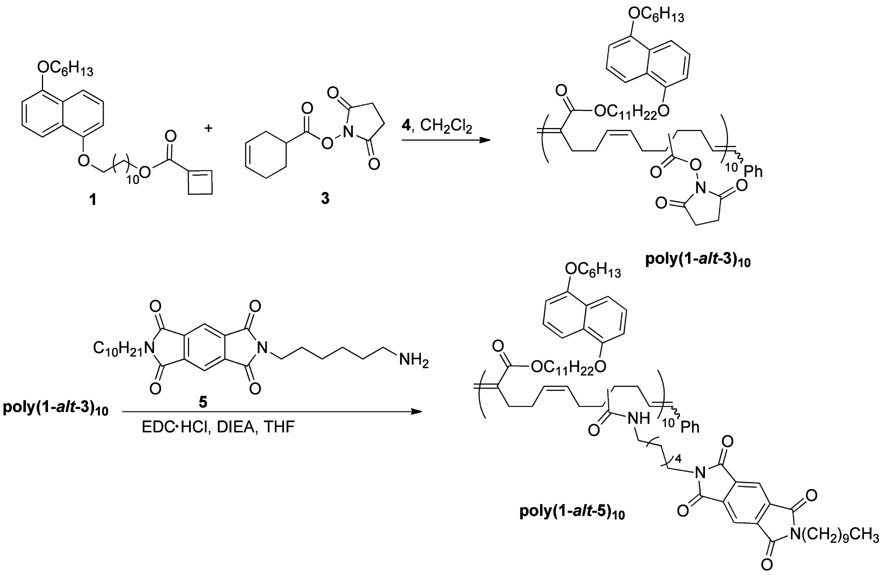
We compared the charge-transfer absorbance of the functionalized poly(CBE-*alt*-CH)'s to the previously reported functionalized poly(NB-*alt*-COE)-*block*-COE. As shown in Figure 2, poly(**1**-*alt*-**5**)$_{10}$ exhibits a higher charge transfer absorbance intensity in comparison to the NB/COE polymers at the same concentration, which indicates that the new poly(**1**-*alt*-**5**)$_{10}$ polymers more favorably align the aromatic units of the donor and acceptor moieties.

In conclusion, we have demonstrated the AROMP of CBE and CH monomers containing bulky DAN/PDI side chains.

Scheme 1. Original Synthesis Scheme of Poly(1-*alt*-2)$_5$



Scheme 2. Revised Synthetic Scheme for the Preparation of poly(1-*alt*-5)$_{10}$ Using a Postpolymerization Functionalization Step



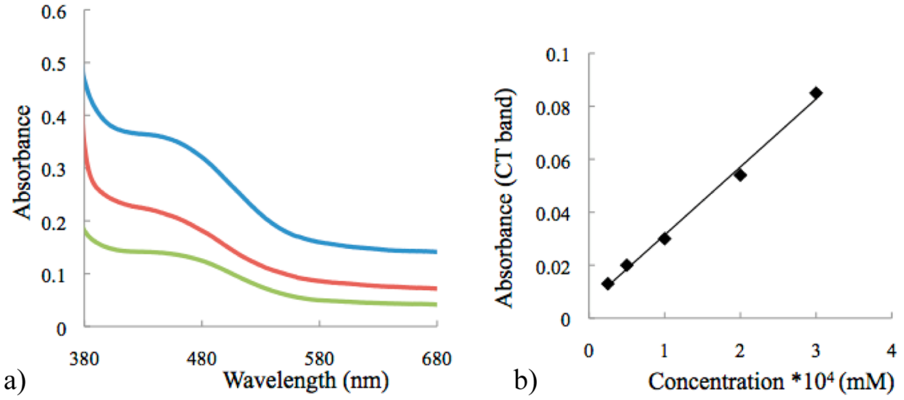


Figure 2. Partial UV−vis spectra of the charge-transfer region in chloroform. (a) Comparison of alternating copolymers. Blue trace = 3 mM poly(**1**-*alt*-**5**)$_{10}$, red trace = 100 μM poly(**1**-*alt*-**5**)$_{10}$, green trace = 3 mM poly(NB-*alt*-COE)-*block*-poly(COE). (b) Plot of charge-transfer absorbance versus concentration of poly(**1**-*alt*-**5**)$_{10}$.

We attribute inhibition of backbiting to the steric hindrance provided by bulky side chains around the carbene and the polymer alkenes. UV−vis spectroscopic analysis shows a charge-transfer absorbance signal for the perfectly alternating copolymers signifying the alignment of the side chains. The new polymers demonstrate an enhancement of charge-transfer in comparison to previously studied polymers, indicating that the sequence specificity in alternating CBE−CH copolymers provides efficient energy transfer. These results will guide the direction of future monomer designs to provide backbiting-free AROMP and toward efficient materials for charge-transfer. Precise control of the monomer sequence presents a viable handle toward regulating polymer assembly, a step toward advanced material properties.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures for the synthesis of monomers and polymers, including NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions

§The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. These authors contributed equally.

Notes

The authors declare no competing financial interest.

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