Incorporation of Large Cycloalkene Rings into Alternating Copolymers Allows Control of Glass Transition and Hydrophobicity

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S *Supporting Information*

ABSTRACT: We previously reported that cyclohexene and bicyclo[4.2.0]oct-1(8)-ene-8-carboxamides undergo efficient ruthenium-catalyzed alternating ring-opening metathesis polymerization (AROMP). Here, we demonstrate that cyclodecene and cyclododecene also function as cycloalkene monomers in the bicyclo[4.2.0]oct-1(8)-ene-8-carboxamide AROMP system, thus enabling the synthesis of linear alternating copolymers with spacers of different lengths, as demonstrated by means of NMR spectroscopy and gel permeation chromatography. The glass transition temperature and hydrophilicity of the alternating copolymers decrease as the length of the spacers increases, as determined by differential scanning calorimetry and water contact angle measurements.
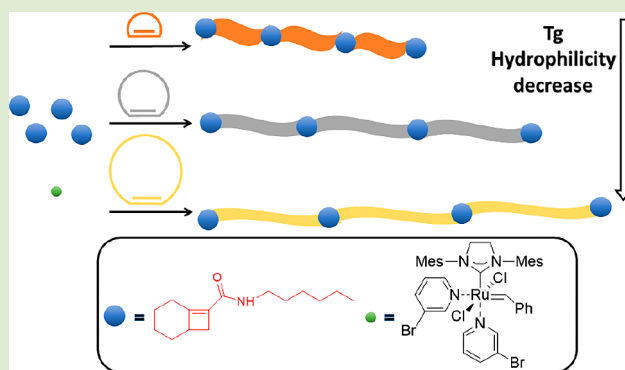
Ring-opening metathesis polymerization (ROMP) is widely used for the synthesis of macromolecules.[1−3]
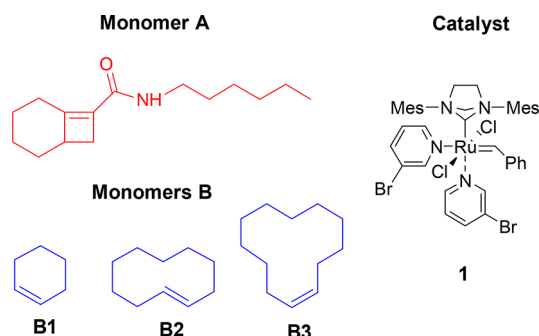
Figure 1. Monomers and catalyst used for AROMP.

This chain-growth technique, in which the driving force of polymerization is the release of ring strain in the cyclic olefin monomers, enables the synthesis of a broad range of polymers with tunable architectures and functions.[4,5] Because the molecular weights of the polymers can be controlled by varying the ratio of initiator to monomers,[6−9] ROMP presents opportunities for synthesizing well-defined and precisely controlled block copolymers[10−13] and graft copolymers[14−17] with unique structures and diverse functions.

During the past two decades, ROMP has been adapted for the synthesis of alternating AB copolymers. The preparation of an AB copolymer requires a monomer that is unable to homopolymerize and that undergoes cross-polymerization

efficiently.[18] Therefore, the primary challenge of using ROMP to achieve alternating control lies in matching an appropriate catalyst with a pair of monomers that have alternating affinities for the living metal alkylidene. Schrock et al. synthesized stereochemically controlled alternating copolymers by using molybdenum and tungsten alkylidene initiators.[19,20] However, the resulting polymers contained few heteroatoms, important components for introducing functionality into polymers.

In contrast, by using a ruthenium catalyst with an N-heterocyclic carbene ligand[21,22] we were able to display heteroatom functionality on an alternating carbon backbone while maintaining monomer reactivity, by means of alternating ring-opening metathesis polymerization (AROMP) reactions between 1-substituted cyclobutenes and cyclohexene.[23,24] Importantly, we found that bicyclo[4.2.0]oct-1(8)-ene-8-carboxamides and cyclohexene undergo efficient ruthenium-catalyzed AROMP.[25,26] Long, linear, perfectly alternating copolymers are obtained, and the hexyl rings fused to the polymer backbones markedly suppress competing inter- and intramolecular cross-metathesis reactions. Our success with the unstrained monomer cyclohexene suggested that larger cycloalkenes with low strain, such as cyclodecene and cyclododecene, might work equally well in AROMP to provide even larger repeats in the polymer backbone. Different spacer lengths would offer opportunities to vary material properties

Scheme 1. Synthesis of Alternating Copolymers from Bicyclo[4.2.0]oct-1(8)-ene-8-carboxamide A and Cycloalkenes B

B1: m=3
B2: m=7
B3: m=9

poly(A-*alt*-B)$_n$
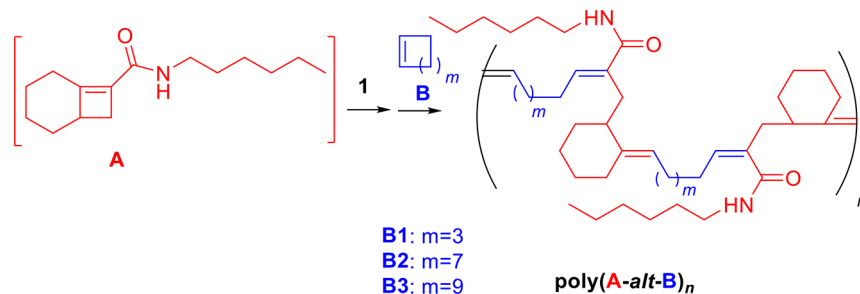
Table 1. AROMP of Bicyclo[4.2.0]oct-1(8)-ene-8-carboxamide A and Cycloalkenes B[a]

	B	[A]/[B]/[1]	temp (°C)	conv[b] (%)	$M_{n,theo}$[c] (kDa)	$M_{n,meas}$[d] (kDa)	$M_{w,meas}$[e] (kDa)	$Đ_M$	time (h)	E[f] (%)
1	B1	10:10:1	25	100	2.4	5.5	6.6	1.2	2	84
2	B1	30:30:1	25	100	7.3	7.9	9.9	1.2	6	87
3	B1	50:50:1	25	100	12.2	8.8	13.3	1.4	12	86
4	B1	100:100:1	25	100	24.2	13.0	16.5	1.3	18	86
5	B2	10:10:1	25	100	3.0	5.5	7.0	1.3	1	89
6	B2	30:30:1	25	100	9.0	9.8	13.6	1.4	4	83
7	B2	50:50:1	25	100	15.0	12.8	19.5	1.5	6	88
8	B2	100:100:1	25	100	30.0	26.9	38.5	1.4	12	87
9	B2	100:100:1	40	100	30.0	24.7	40.2	1.6	12	86
10	B3	10:10:1	25	100	3.3	6.0	7.0	1.2	6	83
11	B3	30:30:1	25	30	9.9	15.8	28.0	1.8	20	87
12	B3	50:50:1	25	20	16.4	11.8	28.9	2.4	20	89

[a]All preparative polymerization experiments were performed three times. Representative data from a single polymerization are presented. [b]Conversion was determined by monitoring the ^{1}H NMR spectrum for the disappearance of the amide resonance of monomer A. [c]Theoretical number-average molecular weight (M_n) calculated from the monomer:catalyst feed ratio. [d]Determined from GPC using refractive index detection. [e]Weight-average molecular weight. [f]Average percentage of double bonds in the backbone of the polymer that were in the *E*-configuration, as determined from the ratio of H1 and H4 values in the ^{1}H NMR spectrum.

such as conductivity, hydrophilicity, chain rigidity, thermal properties,[27] and morphology.

Herein, we describe the ruthenium-catalyzed synthesis of alternating copolymers with different spacers using cycloalkene rings (B1−B3) and bicyclo[4.2.0]oct-1(8)-ene-8-carboxamide A as monomer pairs (Figure 1), as the first step to obtaining unique polymer structures with longer repeat lengths between side-chains.

Monomer A was synthesized according to established protocols,[25,26] and monomers B were obtained commercially. Alternating AB copolymers poly(A-*alt*-B1)$_n$ were previously prepared from A and cyclohexene (B1) with catalysis by [(H(2)IMes)(3-Br-pyr)(2)Cl(2)Ru=CHPh] (Figure 1),[23,25,26] and the same procedure was employed in this study for polymerization of A and *trans*-cyclodecene (B2) and polymerization of A and cyclododecene (B3; Scheme 1).

Specifically, polymerization of A and B1 under AROMP conditions in CHCl$_3$ at 25 °C went to completion within 18 h, affording alternating copolymers poly(A-*alt*-B1)$_n$ (n = 10, 30, 50, and 100) after quenching with ethyl vinyl ether (Table 1, entries 1−4). When B2 was subjected to the same conditions, alternating copolymers were also obtained, but the reaction time was shorter (entries 5−8). (Note that the strain energy of B2 exceeds that of B1 by 6.4 kcal/mol.[28]) It has been reported that in the presence of WCl$_6$/Et$_2$AlCl and WOCl$_4$/Et$_2$AlCl coordinate catalyst systems, *cis*-cyclodecene undergoes polymerization to form *trans*-polydecenamer.[29] However, B2 did not undergo ROMP under the conditions used in this work (see Supporting Information).

The alternating polymerization reaction of A and B3 was much slower, and achieving 100% conversion was difficult for long polymers. High concentrations of monomer required to achieve 100% conversion were limited by solubility (Table 1, entries 10−12). Commercially available cyclododecene consists of a mixture of *trans*- and *cis*-isomers (approximately 30% and 70%, respectively). Upon addition of the catalyst, *cis*-cyclododecene interconverted with *trans*-cyclododecene, and an equilibrium mixture containing 70% of the *trans*-isomer and 30% of the *cis*-isomer was obtained, as determined by NMR (Figure S5). Importantly, B3 did not undergo homopolymerization under the conditions used for AROMP (see Supporting Information). The reason that AROMP of A and B1 was faster than that of A and B3 but slower than that of A and B2 may be attributable to differences in the reactivities of the alkene-derived carbenes. The order of carbene reactivities is reported to depend on the ease with which the closest double bond in the growing polymer chain can coordinate to the metal center; specifically, the reactivities of carbenes decrease in the order cyclodecene > cyclohexene > cyclododecene.[30]
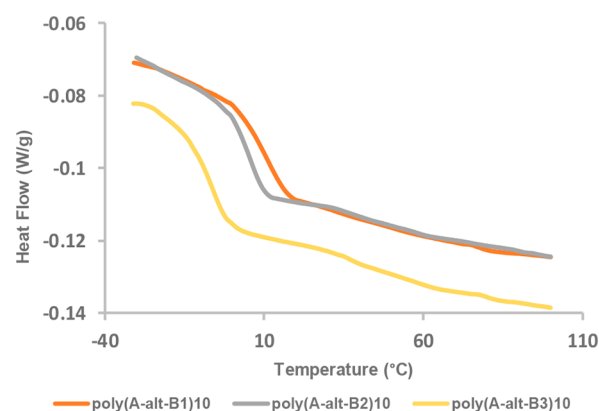
We also carried out the AROMP of A and B2 at a higher temperature (40 °C; Table 1, entries 9) and found that dispersity was lower at the lower temperature because intermolecular chain transfer reactions were suppressed.[31] In addition, the incomplete AROMP of A and B3 due to the lower reactivity of B3 derived carbene inevitably yielded broader distributions of polymer lengths.

In the ^{1}H NMR spectra of poly(A-*alt*-B1)$_n$, peaks for H1 and H4 appeared in the expected chemical shift regions (δ =
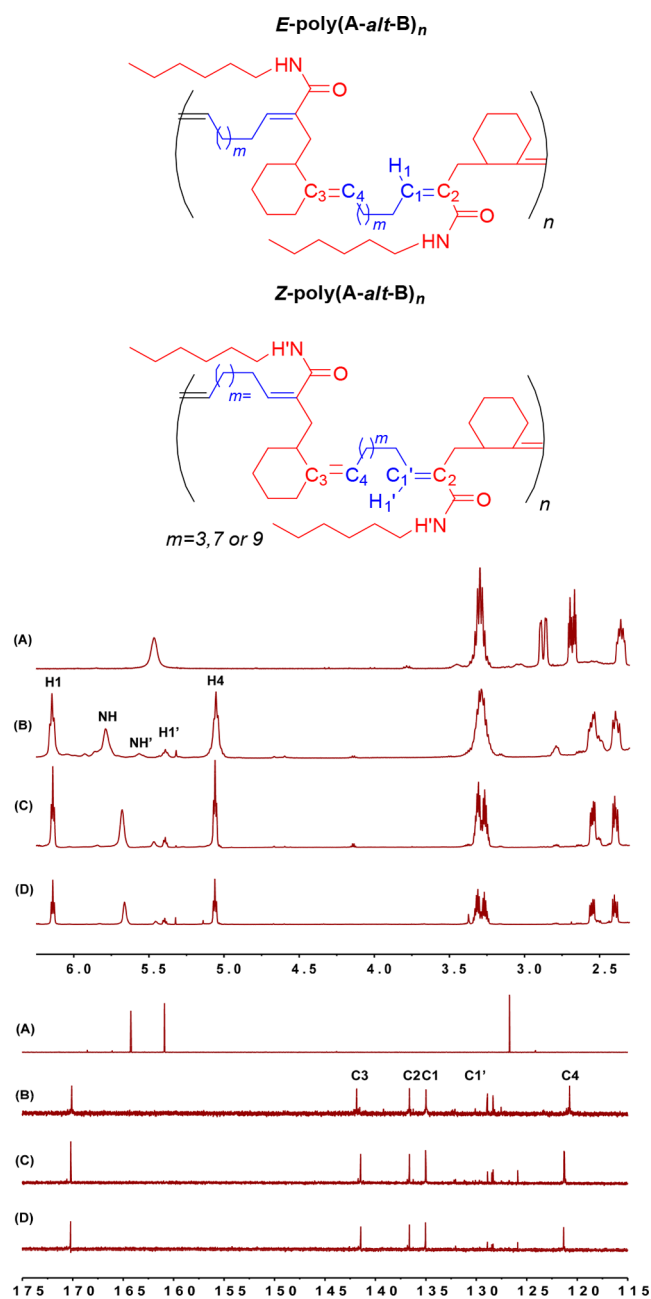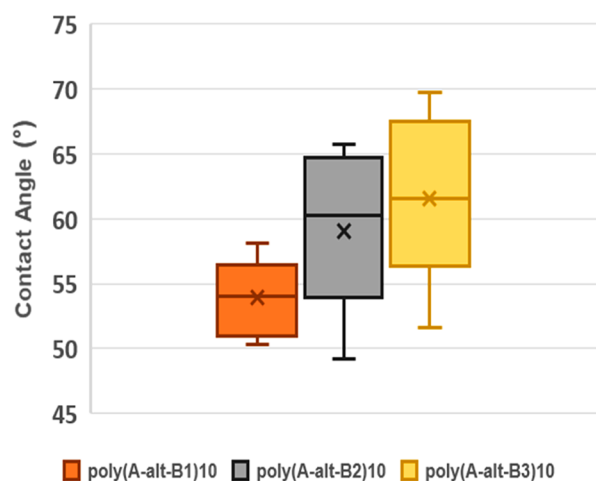
Figure 2. ^{1}H NMR spectra (top) and ^{13}C NMR spectra (bottom) of (A) monomer **A**, (B) poly(**A**-*alt*-**B1**)$_{10}$, (C) poly(**A**-*alt*-**B2**)$_{10}$, and (D) poly(**A**-*alt*-**B3**)$_{10}$ in CDCl$_3$.

Figure 3. Glass transition temperature decreases with increasing spacer length. DSC scans of second heat runs for polymers were obtained at a heating rate of 5 °C min^{-1}.

Figure 4. Increased spacer length results in increased thin film hydrophobicity. Thin polymer films were prepared by spin coating 1 wt % solutions onto silica wafers. Contact angles were measured by CAM 200 optical Contact Angle Meter. Average pure water droplet contact angles for two preparations for each of four batches of polymer are reported. Box plots are 25%ile and 75%ile; whiskers are 10%ile and 90%ile.

5.0 and 6.2 ppm, respectively; Figure 2 and Supporting Information). We also observed a signal for H1′, which could not be removed by precipitation or column chromatography of the copolymer. In addition, substitution of vinylene carbonate[32] for ethyl vinyl ether as the quenching agent did not affect the integration value for H1′(Figure S10), and the value remained constant even when the spacer length was AROMP (see Supporting Information). Therefore, H1′ was not due to impurities, polymer terminal groups, or residues resulting from catalyst decomposition. The sum of the integration values for H1 and H1′ was equal to the value for H4. We observed this same proton signal in the NMR spectra of AROMP products in our previous work.[23,25] Comparison of the spectrum of poly(**A**-*alt*-**B1**)$_n$ with the spectra of model compounds 2-methyl-but-2-enoylamino]-acetic acid methyl esters[33] indicated

that different configurations may exist in the conjugated polymer alkenes. This possibility was supported by inspection of the ^{13}C, HSQC, and HMBC NMR spectra (Figures 2, S9, and S11), which indicated that H1′ is attached to C1′ and that H1 is attached to C1. On the basis of these results, we propose that polymer backbone structures with different configurations were formed, as indicated by the compound labels in Figure 2. The percentage of *E*-alkene in the polymer backbone was approximately 85% in the AROMP system consisting of bicyclo[4.2.0]oct-1(8)-ene-8-carboxamide and **B1**, regardless of polymer length. Peaks for H1′ were also seen in the spectra of poly(**A**-*alt*-**B2**)$_n$ and poly(**A**-*alt*-**B3**)$_n$, and *E*/*Z* ratios of the alkenes in the polymer backbones were similar to the ratio in poly(**A**-*alt*-**B1**)$_n$.

All polymers were stable below 200 °C based on thermogravimetric analysis (Figure S39). Glass transition temperatures (T_g) were determined by differential scanning calorimetry (DSC). T_g's for poly(**A**-*alt*-**B1**)$_{10}$, poly(**A**-*alt*-**B2**)$_{10}$ and poly(**A**-*alt*-**B3**)$_{10}$ were 11.1, 5.7, and −6.1 °C respectively (Figure 3). Based on the reduced transition temperatures, flexibility of the polymer backbone increases when larger

cycloalkene rings are incorporated by AROMP, as expected based on the increased degrees of freedom in the polymer chain.

Water contact angles of polymer thin films prepared through spin coating were measured to evaluate whether hydrophobicity can be controlled by AROMP spacer. The average water contact angle increased as the length of the spacer increased from 6 to 12 carbons (Figure 4). Incorporation of larger spacers results in a lower density of side chain functionality. Increasing the spacing of the hydrophilic amide side chains decreases the interfacial energy and the thin film surface formed becomes more hydrophobic. The frequency of hydrophilic side chain functional groups can be tuned by the length of spacers, thus affecting the hydrophilicity of corresponding alternating copolymers.

To summarize, alternating copolymers with spacers of different lengths were synthesized through ruthenium-catalyzed AROMP. The NMR spectra are consistent with a purely alternating backbone of approximately 85% *E*-configuration. The dispersities were acceptable indicating that molecular weights could be controlled. The combination of large cycloalkene monomers and bicyclo[4.2.0]oct-1(8)-ene-8-carboxamide provides alternating all carbon backbones with different spacings between heteroatom functionalities on the side chains, leading to copolymers with tunable glass transition behavior and hydrophobicity, as demonstrated by DSC and contact angle measurements.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsmacro-lett.8b00510.

Experimental details and supporting figures (PDF).

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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