Living Ring-Opening Metathesis Polymerizations of 3,4-Disubstituted Cyclobutenes and Synthesis of Polybutadienes with Protic Functionalities

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ABSTRACT: The compounds bis(phenylmethyl) *cis*-cyclobutene-3,4-dicarboxylate (**1**) and *cis*-3,4-bis(2-oxa-3-phenylpropyl)cyclobutene (**2**) were polymerized by ring-opening metathesis polymerizations using $Mo(CHC(CH_3)_2R^1)(NC_6H_3\text{-}2,6\text{-diisopropyl})(OR^2)_2$ ($R^1 = Ph$, $R^2 = C(CH_3)_3$, **I**; $R^1 = CH_3$, $R^2 = C(CF_3)_2CH_3$, **II**) as the initiator. For **I** as initiator, no chain termination or chain transfer processes were observed during the lifetime of the polymerization, showing that the polymerizations of **1** and **2** by **I** are living. Block copolymers containing **1** and **2** and diethyl *cis*-cyclobutene-3,4-dicarboxylate (**5**) were synthesized. The double bonds of the poly-**2** and poly-**3** ranged from 70% *trans* to 92% *cis* depending on the initiator and monomer used. Poly-**1** and poly-**2** were treated with iodotrimethylsilane and converted to the acid-functionalized and alcohol-functionalized poly-**4** and poly-**6**, respectively. Block copolymers were treated with iodotrimethylsilane and converted to materials with blocks bearing protic functionalities and blocks bearing polar aprotic groups.

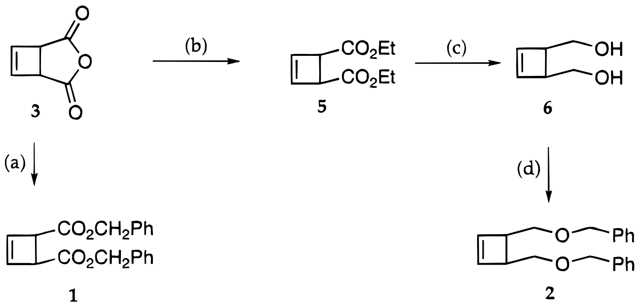
Introduction

The development of initiators for the living ring-opening metathesis polymerization (ROMP) of cyclic olefins has opened a new chapter in the field of controlled-architecture polymers.[1−12] These initiators have been shown to be tolerant of a wide variety of functionalized monomers,[7,13−15] thus offering well-defined polymers with varying polarity, solubility, and reactivity. Functional groups can have a strong effect on polymer crystallinity, strength, adhesive potential, barrier phenomenon, and many other useful real-world properties. Protic functionalities, particularly acidic and alcoholic groups, can change a material drastically. Unfortunately most ROMP-initiating systems are extremely intolerant of acidic protons, being based on early and middle transition metals. To circumvent this problem, and to explore the controlled synthesis of protic ROMP polymers, we have developed living syntheses of polybutadienes bearing pendant benzyl-substituted esters and ethers. In a quantitative postpolymerization reaction, the benzyl groups can be deprotected to yield the nascent protic functionality.

Results and Discussion

The monomers polymerized in this study were bis(phenylmethyl) *cis*-cyclobutene-3,4-dicarboxylate (**1**) and *cis*-3,4-bis(2-oxa-3-phenylpropyl)cyclobutene (**2**) (Scheme 1). The cyclobutenes were synthesized in two or four steps, respectively, from commercially available sources, using the anhydride-functionalized cyclobutene **3** as the cyclobutene source.[16] Additionally, the diethyl ester-substituted cyclobutene **5** was included as a comonomer for block copolymerization studies. As we reported earlier, **3** is a convenient precursor to many functionalized cyclobutenes, and **5** can be polymerized in a living fashion.[17] It would seem logical that **3** would be a useful source of acid-functionalized polymers via polymerization and subsequent hydrolysis. However the polymerization of **3** is nonliving, and poly-**3** appears to be unstable and not a useful source of acid-functionalized materials.[18]

Scheme 1. Monomer Synthesis[a]



[a] (a) $PhCH_2OH$, diisopropylcarbodiimide, (dimethylamino)pyridine, CH_2Cl_2, 0 °C, 64%; (b) EtOH, HCl, 82%; (c) $LiAlH_4$, THF, 69%; (d) KH, $PhCH_2Br$, THF, 94%.

The ester **1** may be formed from **3** (or *cis*-cyclobutene-3,4-dicarboxylic acid (**4**), derived from **3** by hydrolysis) by a mild coupling reaction (Scheme 1). The ether **2** is synthesized in three steps: First, esterification to the diethyl ester **5**, followed by reduction to 3,4-bis(hydroxymethyl)cyclobut-1-ene (**6**) and finally protection as the dibenzyl ether **2** (Scheme 1). Although distillation from metal hydrides is the preferred method of purification to obtain scrupulously air- and moisture-free monomers, **1** and **2** are not thermally robust enough for distillation. The only products afforded from attempted distillation (10^{-4} Torr, 70−100 °C) were ring-opened substituted butadienes, arising from the known pericyclic reaction of cyclobutenes.[19] For both **1** and **2**, purification via flash chromatography followed by repeated freeze-drying from anhydrous benzene yielded polymerization grade monomer.

Polymerization of 1 and 2. Polymerizations were successful only with the specific and tolerant molybdenum initiators $Mo(NAr)(CHCMe_2Ph)(OCMe_3)_2$, **I**, or $Mo(NAr)(CHCMe_3)(OCMe(CF_3)_2)_2$, **II** (Ar = 2,6-diisopropylphenyl).[8,20] As we have seen with other substituted cyclobutenes,[17] classical ROMP initiators[21−23] are ineffective, as was the initiator $Ru(CHCHCPh_2)(PR_3)Cl_2$ (R = cyclohexyl) reported recently by Grubbs *et al.*[4] In

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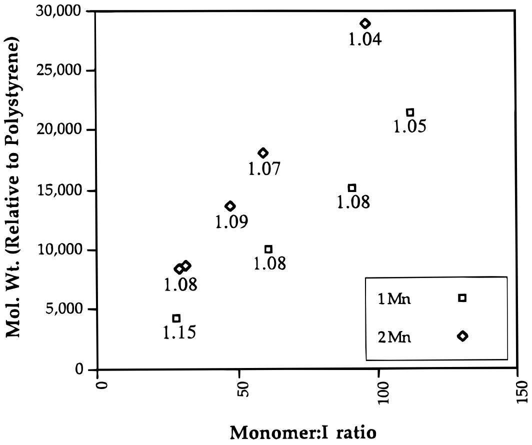


Figure 1. GPC molecular weight (relative to polystyrene) of poly-**1** and poly-**2** vs monomer:I ratio. Points are labeled with the polydispersity of the sample.

contrast, polymerization reactions initiated with **I** or **II** resulted in a quantitative yield of polymer. Reactions were successful in a variety of anhydrous, degassed aromatic, chlorinated, and ether solvents. The living endgroup could be removed in a controlled fashion by the addition of an aldehyde (pivaldehyde, benzaldehyde, and 2-naphthaldehyde were used equally successfully). Oxygen was rigorously excluded from the polymerization medium until termination was complete, to avoid a bimolecular termination process that occurs between living endgroups and oxygen.[24]

Poly-**1** was synthesized by the addition of either a solution of **1** or solid **1** to a rapidly stirring solution of **I** (or **II**). The reaction medium slowly changed from the yellow/orange solution typical of the initiators to a reddish solution consistent with active polymerization centers. Using **I**, quantitative conversion from **1** to poly-**1** was observed in 1−24 h, depending on initiator concentration. The catalyst centers remained active at the completion of polymerization, allowing the controlled termination (with an aldehyde) or the synthesis of block copolymers (see below). Poly-**1** initiated by **I** yielded monodisperse material with a polydispersity index (PDI) of 1.05−1.1. The more active initiator **II** also resulted in quantitative yields of unimodal poly-**1** but with a higher PDI of 1.3−1.4. Polymerization was successful in a variety of organic solvents (benzene, toluene, THF, methylene chloride, chloroform, etc.); however, aromatic solvents generally gave the most monodisperse polymer. With the initiator **I**, the molecular weight of poly-**1** was directly dependent on the monomer:initiator ratio (Figure 1).

The polymerization of the benzyl ester **1** is very slow on typical ROMP time scales.[13] In side by side experiments at the same initiator and monomer concentrations, **1** is consumed at 1/7 the rate of the ethyl ester **5**, a similarly substituted cyclobutene. Yet **5**, itself, is polymerized much slower than norbornenes and norbornadienes bearing equivalent functionalities,[17] which further illustrates the sluggishness of **1** toward polymerization initiated by **I**. This is most likely caused by two effects: First, the presence of a strong electron-withdrawing substituent on the β-carbon of the incoming monomer suppresses coordination and therefore reaction of the monomer. This would explain the slow polymerization of **1** and **5** relative to equivalent norbornadienes. Additionally, the large steric volume of the benzyl ester (which is attached to the β-carbon of the growing polymer chain) increases the steric congestion along the reaction pathway and further retards the polymerization process, and we use this to explain the slow rate of the polymerization of **1** relative to **5** (although a wider variety of ester-substituted cyclobutenes would need to be studied to show this conclusively). Increasing the size of substituents on norbornadienes has been shown to completely shut down the polymerization process.[25]

Similarly, addition of a solution of **2** to the initiator **I** in a variety of organic solvents rapidly and quantitatively resulted in poly-**2** as a soluble, linear high polymer. Monodisperse polymer was routinely obtained with **I** as the initiator (PDI of 1.04), choice of solvent played less of a role for **2** as for **1** above, and equally monodisperse material was obtained in toluene, THF, and methylene chloride. As with **1**, the active initiator **II** rapidly resulted in a quantitative yield of poly-**2** but with a slightly broader molecular weight distribution (PDI of 1.2−1.3). The molecular weight of poly-**2** obtained with **I** was also directly dependent on the **2**:**I** ratio chosen for the reaction (Figure 1).

In contrast to the ester cyclobutenes, **2** is polymerized rapidly by the molybdenum initiator **I** (and even more rapidly by **II**). Reactions at 1−10 mM initiator concentrations are complete in 10 min or less. These conditions are much the same as has been reported for functionalized norbornenes polymerized by **I**.[13] On a relative scale **2** is consumed 56 times as fast as **1** and 9 times as fast as **5** (side by side experiments, using the same solvent, monomer, and **I** concentrations). We attribute the rapid polymerization of **2** mainly to the electronic character of the β-side chains of the monomer. Cyclobutenes **1** and **5** bear esters, strongly electron-withdrawing substituents (positive Hammett σ), whereas **2** bears an ether-substituted alkyl side chain which is electron donating in character (negative σ).[26] Thus **2** possesses an electron rich olefin relative to **1** (or **5**), and electron rich monomers have been previously shown to polymerize faster than electron poor monomers.[25] The difference in steric contribution between a methylene and carbonyl moiety on the γ-carbon of the growing polymer chain is harder to quantify but probably also affects the rate of polymerization. The Taft steric parameter (E_s) for an unsubstituted alkyl chain is one-half the magnitude of the E_s parameters for α-substituted chains[26] (treating the carbonyl moiety as an α-substituted chain, as E_s values remain undetermined to the best of our knowledge). Thus the $-CH_2OCH_2Ph$ γ-side chain of living poly-**2** is sterically smaller than the $-C(O)OCH_2Ph$ γ-side chain of living poly-**1**. This decrease in side chain bulk would lower the free energy of intermediates along the polymerization pathway (reduced steric congestion), which would increase the rate of polymerization of **2** relative to **1**. Thus both steric and electronic factors explain the observed rate increase going from the polymerization of **1** to the polymerization of **2** by **I**.

To show that a given polymerization system is living, one must prove the absence of chain transfer and chain termination reactions. There are many ways of doing this as discussed in the literature.[27−33] The ROMP of **5** by **I** has already been shown to be a living polymerization;[17] we show herein that the polymerizations of **1** and **2** by **I** are also living. The linear nature of the plot of monomer:initator vs molecular weight of polymer obtained (Figure 1) shows that no chain transfer is occurring during the polymerization of **1** (or **2**) initiated by **I**.[32,33] Quantitative conversion of monomer shows that termination is essentially[34] not present during the lifetime of polymerization.[33] Even at extremely high monomer:initiator ratios of 500:1, we have observed >99% consumption of **1** (and **2**) by **I**, as evidenced by the complete disappearance of monomer in the ^{1}H NMR spectrum of the crude polymerization medium, as well as the quantitative production of poly-**1** (and poly-**2**) by comparison to an internal standard (mesitylene). This shows the absence of termination reactions in the polymerization of **1** (or **2**) initiated by I.

The narrow polydispersity index of the polymers produced (PDI of 1.04−1.05 at high monomer:initator ratios, Figure 1) provides collaborative evidence to the lack of chain termination and transfer reactions. The PDI of polymers is subject to debate and confusion, as outlined and discussed by Quirk and Lee,[32] as well as Penczek *et al.*[33] The essence is that a narrow PDI is not required of a living polymerization (other factors such as slow initiation and reversible propagation can increase the molecular weight distribution without affecting the living nature of the polymerization), but a narrow PDI is strongly indicative of a living polymerization, as chain transfer and chain termination reactions will both serve to increase the polydispersity. This is subject to the constraint that the PDI is checked at high conversion of monomer, early in the reaction chain transfer, and termination reactions may not be observable. Additionally, the gel permeation chromatogram (GPC) of the final polymer must be examined closely for traces of low molecular weight components. Even base-line amounts of low molecular weight polymer indicate termination reactions. Taking all of this into account, in the polymerization of **1** (or **2**) by **I**, we have seen no trace of low molecular weight components and narrow PDI at high conversion of monomer, and this experimental evidence is consistent with a living polymerization. Therefore by showing the absence of chain transfer and termination reactions by the arguments outlined above, **I** is an initiator for the living polymerization of both **1** and **2**.[27−31]

Polymer Characterization. Physically, poly-**1** is a tacky solid at room temperature, highly soluble in most organic solvents (exceptions being hexane and methanol). The microstructure of the polymer is highly dependent on the initiator used. Reaction of **1** with **I** typically results in a material with 60% *trans* double bonds, while polymerizations initiated with **II** give polymer with up to 91% *cis* double bonds. The signals for each carbon on the backbone in the ^{13}C NMR spectrum are split into multiple peaks which indicates an atactic microstructure (in addition to the multiplicity of peaks due to *cis* and *trans* double bonds).[22] No further information on tacticity is available, due to a lack of comparison materials. Since the monomer is symmetric, there is no chance of head to tail bias or selection. Poly-**1** shows a T_g at 21 °C and decomposes upon heating under nitrogen (onset T = 277 °C, 10 °C/min, ash level = 10.5% at 500 °C).

Poly-**2** is a white powdery material highly soluble in toluene, chloroform, methylene chloride, and THF, with a narrower range of good solvents than poly-**1**. As with the other monomers, the olefin microstructure of the double bonds is dependent on initiator used, with **I** giving 70% *trans* and **II** giving 92% *cis* olefins along the backbone of the polymer. The solubility of the high *cis* material is much lower than that of the *trans* polymer, with good solubility in chlorinated solvents but limited solubility in toluene and THF (in contrast to high *trans* poly-**2**). Tacticity of the polymer has not been determined, but again, multiple ^{13}C resonances for most atoms in the repeat unit indicate an essentially atactic structure. The material is thermally stable to 308 °C (under nitrogen), at which point near complete decomposition sets in (3% ash at 500 °C). Poly-**2** is partially crystalline, with a melt transition observed at 124 °C, and shows a T_g at −4 °C.

Table 1. Molecular Weights and Percent Compositions of Block Copolymers

first monomer	equiv[a]	M_n[b]	second monomer	equiv[a]	M_n[b]	PDI[a]
2	56	14 253	**5**	124	36 264	1.15
5	55	10 369	**2**	73	33 563	1.07
5	110	20 696	**2**	37	34 667	1.07
5	55	10 369	**1**	77	37 250	1.12
5	110	20 696	**1**	41	32 016	1.13

[a] Relative to amount of initiator **I** added. [b] Determined by GPC in THF relative to narrow molecular weight polystyrene standards.

Table 2. Glass Transitions and Melt Transitions of Polymers and Block Copolymers

wt %[a]				
1	**2**	**5**	T_g (°C)[b]	T_m (°C)[b]
100			21	
	100		−4	124
		100	6	
71		29	−0.1	94
42		58	~1, ~7[c]	110
	74	26	17	
	41	59	11	

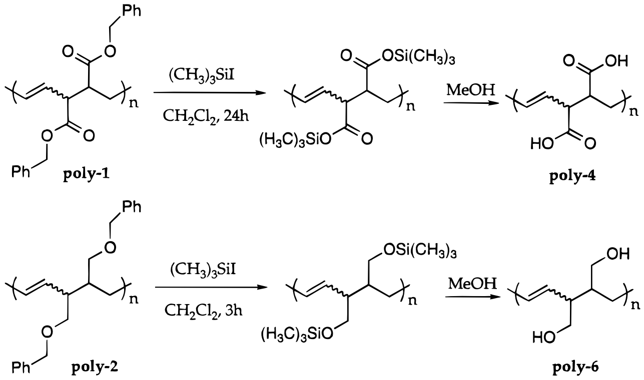
[a] Determined by ^{1}H NMR on purified products. [b] Heating rate 10 °C/min under N_2 flow. [c] Thermogram appears to show two overlapping glass transitions, one centered around 1 °C and one centered around 7 °C.

Block Copolymers. Both monomers **1** and **2** were combined in AB block copolymers, with each other, as well as AB blocks with diethyl cyclobut-3-ene-3,4-dicarboxylate, **5** (Table 1). Addition of a second aliquot of monomer to the living polymerizations (instead of a quenching reagent like pivaldehyde) resulted in complete consumption of the second monomer and the synthesis of a linear block copolymer. Polydispersities of the block copolymer were low, and no homopolymers (of either monomer) were observed in the final product.

The block copolymers between the ethyl ester **5** and the benzyl ester **1** do not show apparent phase separation between the homopolymer segments, as evidenced by one single glass transition at an intermediate temperature between that of the homopolymer constituents (Table 2). Thermograms of block copolymers between the ether **2** and the ester **5** are less conclusive. The presence of a crystalline melt transition around 95−110 °C indicates phase-separated domains of poly-**2**, but only one glass transition is seen for these materials (Table 2), which indicates a homogeneous solid state. It may be that the glass transitions of the respective homopolymers (−4 and 6 °C) are too close to allow resolution. We are currently investigating electron microscopy and solid state NMR methods to resolve the solid state structure of these block copolymers.

Deprotection Chemistry. We have synthesized polymers with benzyl-protected side chains, as there are a variety of methods known in the organic chemistry literature for the selective removal of benzyl groups.[35] This unmasks the protic alcohol or acid functionality that was protected in the monomer. Thus, the protection/polymerization/deprotection route affords polymers

Scheme 2. Removal of Benzyl-Protecting Groups



with protic alcohol and acid functionalities that are unavailable by direct polymerization of the corresponding monomer. Standard methods for the removal of benzyl protection groups were tried, including reduction with sodium in liquid ammonia[36] and hydrogen over Pd or Pd(OH$_2$) supported on carbon.[37] These methods were found to be ineffective or gave very poor conversion. In the case of the liquid ammonia reaction, insolubility of the macromolecular reagent precludes reaction, and in the Pd/H$_2$ case, the polymer precipitates from solution after 5−10% conversion.

Trimethylsilyl iodide (TMSI) in methylene chloride has been shown to be a useful reagent for the conversion of ordinary ethers[38] and esters[39] to silyl ethers and silyl esters, respectively. TMSI will eventually react with most ethers or esters, but a benzyl group reacts orders of magnitude faster than simple primary ethers,[38,39] allowing the selective conversion of benzyl groups in the presence of other functionalities. Similarly, ethers react with TMSI much faster than esters in general. In principle, the silyl intermediate can be isolated, but silyl esters and silyl ethers are very sensitive to traces of moisture and can be hydrolyzed quantitatively upon treatment with methanol. We have successfully converted poly-**1** to poly-**4**[40] and poly-**2** to poly-**6**[40] using TMSI in methylene chloride (Scheme 2). Poly-**1** is converted in about 24 h, whereas poly-**2** reaches quantitative conversion in 2−3 h. It is interesting to note that the polymeric substrates poly-**1** and poly-**2** are much less reactive than the reported small molecule analogs, which react in <1 min in the case of ethers[38] and 30 min in the case of esters.[39]

As would be expected for the introduction of protic, polar functionality to a hydrocarbon backbone, both poly-**4** and poly-**6** are very different than their precursor polymers. Both show limited or no solubility in standard organic solvents such as THF and CHCl$_3$. Poly-**4** is soluble in DMSO and methanol at all molecular weights synthesized and insoluble in neutral water but soluble in basic water as the polycarboxylate anion. Poly-**6** is soluble in DMSO at moderate molecular weights (<250 repeat units) and shows very poor solubility at high molecular weights. Oligomeric samples of poly-**6** are soluble in chloroform/methanol mixtures as well as DMSO. The materials also show a strong binding to solvents used for precipitation, with traces still seen in the ^{1}H NMR spectrum of samples that have been under high vacuum for several days. This could indicate adhesion potential for these materials.

The removal of the benzyl side chains from block copolymers between **5** and **1** or **2** results in interesting materials combining a polar aprotic and polar protic functionality. The presence of the ethyl ester side groups on portions of the polymeric side chain does not appear to affect or participate in the deprotection chemistry of the benzyl moieties at all. Ethyl esters generally require both higher temperatures and longer times to react; under the conditions utilized in this study (room temperature, 1 day or less reaction times), no reaction between the ethyl ester side chains and TMSI was observed. As expected, the presence of the ethyl ester polymer greatly increases the solubility of materials in convenient organic solvents, particularly polar organic solvents with 5−10% methanol added. The added alchohol presumably acts as a hydrogen bond donor/acceptor and breaks up any intermolecular hydrogen bond networks. We are currently investigating the solid phase and solution phase structures of these materials.

Conclusion

In conclusion we have developed a route into the living synthesis of substituted polybutadienes bearing acidic and alcoholic side chains via a protection/deprotection route. This allows the synthesis of materials that are not directly available from the polymerization of the appropriate monomer via existing initiator systems. Polymers based on a perfectly repeating 1,4-polybutadiene backbone with benzyl ester or benzyl ether side chains were synthesized. The conversion of these materials into carboxylic acid- and primary alcohol-substituted 1,4-polybutadienes was achieved. *Cis*/*trans* ratios of the backbone olefins were dependent on the choice of initiator; values from 70% *trans* to 92% *cis* were observed. This work demonstrates the utility of well-defined metathesis initiators in the synthesis of controlled-architecture macromolecules with useful pendant functionality.

Experimental Section

General. All reactions and polymerizations using molybdenum compounds were conducted under inert gas (nitrogen or argon) atmosphere using standard Schlenk techniques. Drybox manipulations were carried out at ambient temperature under a nitrogen atmosphere in a Vacuum Atmospheres HE-533 Dri Lab with attached HE-493 Dri Train or m-Braun LabMaster 100 inert atmosphere laboratory. Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification. Initiators **I** and **II** were prepared according to literature,[8,20] or **I** was purchased from Strem Chemicals, Inc. and recrystallized from hexane before use. Solvents were dried and distilled according to standard procedures.[41] Monomers were rendered air- and water-free by twice freeze-drying from anhydrous benzene and stored at −35 °C inside a drybox prior to polymerization. Melting points (Pyrex capillary) were measured on a Mel-Temp apparatus and are uncorrected. ^{1}H NMR spectra were determined at 200, 400, or 500 MHz using Bruker AM and AMX FT spectrometers. ^{13}C{^{1}H} NMR spectra were measured at 75, 100 or 125 MHz on Bruker MSL and AMX spectrometers. Unless otherwise specified, all ^{1}H NMR spectra were acquired in CDCl$_3$ using a Bruker AM-200 spectrometer, and all ^{13}C{^{1}H} NMR spectra were acquired in CDCl$_3$ using a Bruker MSL-300 spectrometer operating at 75 MHz. Chemical shifts are referenced to a residual solvent proton (or carbon) resonance. Infrared spectra were acquired on a Perkin-Elmer FT-1600 series spectrometer; wavenumbers in cm^{-1} are reported for medium and strong peaks. Molecular weights were measured via gel permeation chromatography using a HP 1050 pump and Wyatt Technologies Optilab 903 RI detector. The stationary phase consisted of 500, 10^3, 10^4, 10^5, and 10^6 Å UltraStyragel columns (Pacific Column Co.); THF was used as the mobile phase. Molecular weights are relative to narrow molecular weight polystyrene standards (PolySciences, Inc.). Thermal analyses were performed using DuPont TA 2000/TGA 2950 and Perkin Elmer PE7700/DSC7 instruments using a nitrogen purge and heating rates of 10 °C/min. Elemental analyses were performed by the Microanalytical Laboratories of the University of California, Berkeley, and the University of Massachusetts, Amherst.

3-Oxabicyclo[3.2.0]hept-6-ene-2,4-dione[42] (3). A Schlenk tube was charged with maleic anhydride (14.9 g, 0.152 mol), acetophenone (30 mL, 0.25 mol), and ethyl acetate (240 mL). The flask was cooled in an acetone-filled quartz Dewar within the well of a Rayonet photochemical reactor (equipped with 16 300 nm fluorescent bulbs). A cooling probe from a recirculating cooler was used to maintain the bath at −40 °C. Acetylene (1 mL/min) was slowly bubbled through the solution while the solution was irradiated for 5 days. The solution was degassed with nitrogen to remove residual acetylene as the solution was slowly warmed to room temperature. The solution was concentrated to 50 mL with a rotary evaporator, filtered, concentrated again, and extracted with hexanes. Recrystallization from toluene/cyclohexane yielded colorless crystals of **3** (3.09 g, 16%): mp 88−90 °C (lit.[42] mp 92 °C); ^{1}H NMR δ 6.50 (s, 2H), 4.05 (s, 2H); ^{13}C{^{1}H} NMR δ 167.66, 139.35, 47.62.

***cis*-Cyclobutene-3,4-dicarboxylic Acid (4).** Hydrolysis of **1** (1.0 g) in 25 mL of acetone with 0.25 mL of water afforded **4** (1.2 g) as a viscous, hydroscopic solid: ^{1}H NMR δ 6.40 (s, 2H), 3.90 (s, 2H); ^{13}C{^{1}H} NMR (D_2O) δ 178.4, 139.9, 52.0; IR 3022, 2733, 2622, 1701, 1427, 1317, 1280, 1244, 1219, 1134, 991, 911, 776, 733, 588.

Alternatively, **4** can be made directly (the most useful procedure for synthesis of monomers in this study). A 250 mL Pyrex tube was charged with maleic anhydride (8 g, 0.09 mol), and xanthone (0.4 g, 2 mmol) was dissolved in ethyl acetate (180 mL). The tube was placed in a 2-propanol-filled Pyrex Dewar inside a Rayonet RPR 100 photochemical chamber (equipped with 16 350 nm bulbs). The bath was cooled to −60 °C with an external cooling probe while saturating the tube with acetylene gas. When the bath reached −60 °C, the acetylene source was disconnected and the solution was photolyzed for 8 days. The cooling bath was shut off, and the apparatus was slowly warmed up to room temperature while sparged with a nitrogen purge to remove excess acetylene. Water (50 mL) was added, and the solution stirred overnight. The organic layer was removed via rotary evaporation and the water layer filtered to remove the xanthone sensitizer. Freeze-drying of the water layer afforded crude **4** (11 g, purity estimated at 75% by ^{1}H NMR, corresponding to a true yield of 71%), which was used in further reactions without additional purification.

Bis(phenylmethyl) *cis*-cyclobutene-3,4-dicarboxylate (1). Following the general procedure of Hassner,[43] a 500 mL round bottom flask was charged with **4** (4.1 g, 0.029 mmol), benzyl alcohol (7.6 g, 0.070 mmol), 4-(dimethylamino)pyridine (0.20 g, 1.6 mmol), and CH_2Cl_2 (200 mL). The flask was cooled in an external ice bath, and diisopropylcarbodiimide (8.8 g, 0.070 mmol) was added dropwise. The mixture was stirred for 10 h at 0 °C. The mixture was concentrated via rotary evaporation, 50 mL of ether and 100 mL of petroleum ether were added, and the solution was filtered. The evaporated filtrate was separated in two portions on a 10 × 20 cm column of silica gel, using 20% (v/v) ethyl acetate in petroleum ether as the solvent, to yield **1** as a clear oil that slowly solidified (6.2 g, 0.019 mmol, 66%): mp 41−42 °C; ^{1}H NMR δ 7.32 (m, 10H), 6.29 (s, 2H), 4.99 (d, J = 3.0 Hz, 4H), 3.98 (s, 2H); ^{13}C{^{1}H} NMR δ 170.44, 136.71, 135.61, 128.47, 128.35, 128.19, 66.58, 48.90; IR 3065, 3033, 2953, 1728, 1498, 1455, 1378, 1326, 1262, 1161, 1110, 1025, 750, 697. Anal. Calcd for $C_{20}H_{18}O_4$: C, 74.52; H, 5.63. Found: C, 74.57; H, 5.50.

Diethyl *cis*-cyclobutene-3,4-dicarboxylate (5). Crude **4** (11 g, 0.058 mol, assuming 75% purity) was dissolved in anhydrous EtOH (100 mL). Concentrated H_2SO_4 (0.5 mL) was added, and the mixture was stirred at room temperature overnight. The mixture and washes were precooled in an ice bath before extraction; 250 mL of ether was added and the cold ether solution extracted with 100 mL of water, 2 × 100 mL of saturated $NaHCO_3$ (or until the aqueous phase was not acidic), and 100 mL of water. The organic layer was dried over $MgSO_4$ and concentrated to yield 13 g of crude **5**, which was bulb-to-bulb distilled at 55 °C/10^{-4} Torr to yield **5** as a clear oil (11 g, 0.055 mol, 95%). Analytically pure samples were obtained by separation of 5 g on a 10 × 20 cm silica gel column using 20% ethyl acetate in petroleum ether as a solvent: ^{1}H NMR (400 MHz) δ 6.25 (s, 2H), 4.13 (q, J = 7.1 Hz, 4H), 3.90 (s, 2H), 1.24 (t, J = 7.2 Hz, 6H); ^{13}C{^{1}H} NMR (100 MHz) δ 170.7, 136.7, 60.8, 49.0, 14.1. IR 2983, 2904, 1736, 1465, 1446, 1369, 1329, 1263, 1179, 1112, 1038, 764. Anal. Calcd: C, 60.59; H, 7.12. Found: C, 60.47; H, 7.07.

***cis*-3,4-Bis(hydroxymethyl)cyclobutene (6).** $LiAlH_4$ (10 g, 0.28 mol) was suspended in dry THF (350 mL) in a 500 mL round bottom flask equipped with a pressure-equalizing addition funnel. The flask was placed in an external −20 °C bath. Freshly distilled **5** (10.1 g, 0.0510 mol) in dry THF (50 mL) was added over the course of 1 h. The bath was maintained at 0 °C for 5 h and recooled to −20 °C prior to quenching; 10 mL of water was added dropwise followed by 10 mL of 4 N KOH and 30 mL of water, successively. The solution was filtered, and the salts were washed with an additional 200 mL of THF. The solution was concentrated and freeze-dried from benzene to yield 7.9 g (0.069 mmol, 76%) of crude product that was taken on without further purification, as the diol decomposed on silica gel or upon distillation attempts. ^{1}H NMR (400 MHz) δ 6.02 (s, 2H), 3.83 (m, 2H), 3.72 (t, J = 11.5 Hz, 2H), 3.23 (dd, J = 12.0, 3.9 Hz, 2H), 2.94 (br s, 2H); ^{13}C{^{1}H} NMR δ 137.2, 61.5, 47.9; IR 3329, 3045, 2914, 1720, 1574, 1435, 1289, 1058, 1026.

***cis*-3,4-Bis(2-oxa-3-phenylpropyl)cyclobutene (2).** Following the basic procedure of Czernecki *et al.*,[44] a 250 mL round bottom flask was charged with benzyl bromide (21.5 g, 0.126 mol) and KH (6.8 g, 0.17 mol) in THF (100 mL). An addition funnel was charged with **6** (4.82 g, 0.0423 mol) and THF (50 mL). The flask was cooled in a dry ice/acetone bath, and the solution of **6** was added dropwise over 0.5 h. The solution was stirred for 15 h, with the cooling bath allowed to warm up to room temperature slowly. Methanol (5 mL) was cautiously dripped in until no reaction with excess KH was seen. The solvent was evaporated, and 100 mL of ether was added. The ethereal solution was extracted with 2 × 100 mL of water, dried over $MgSO_4$, and concentrated to yield 10.2 g (82%) of a crude oil. The crude product was separated in two fractions on a 10 × 20 cm column of silica gel using 20% (v/v) ether in petroleum ether as a solvent to yield **2** as a colorless oil (9.5 g, 0.032 mmol, 77%): ^{1}H NMR δ 7.29 (m, 10H), 6.19 (s, 2H), 4.48 (s, 4H), 3.61 (m, 4H), 3.25 (m, 2H); ^{13}C{^{1}H} NMR δ 138.54, 138.45, 128.33, 127.71, 127.52, 73.15, 70.41, 45.50; IR 3030, 2853, 1495, 1453, 1361, 1094, 736, 697. Anal. Calcd for $C_{20}H_{22}O_2$: C, 81.60; H, 7.53. Found: C, 81.79; H, 7.72.

Typical Polymerization of Bis(phenylmethyl) *cis*-Cyclobutene-3,4-dicarboxylate (1) with I. To **I** (17.5 mg, 0.0318 mmol) in 3 mL of toluene was added solid **1** (1.0 g, 3.1 mmol, 98 equiv). The reaction mixture was stirred for 1 h and the reaction quenched with 2-naphthaldehyde (10 mg). The reaction mixture was brought out of the drybox and precipitated into methanol. The polymer was further purified by reprecipitation into methanol and hexanes (×2) and freeze-dried from benzene to yield 0.976 g (98%) of polymer as a tacky solid: ^{1}H NMR (200 MHz, $CDCl_3$) 7.20 (br, 10H, C_6H_5), 5.56 (br, 2H, C*H*=C*H*), 4.96, 4.84 (br m, 4H, C*H*$_2$Ph), 3.91 (br, 0.76H, =CH-C*H*R-*cis*), 3.32 (br, 1.24 H, =CH-C*H*R-*trans*); ^{13}C NMR (75 MHz, $CDCl_3$) 139.15, 131.69, 128.13, 127.26, 127.15, 72.67 72.48, 45.24, 44.26, 39.43, 38.97; IR 3065, 3033, 2954, 2891, 1738, 1498, 1456, 1377, 1261, 1211, 1151, 977, 910, 737, 697. Anal. Calcd for $C_{20}H_{18}O_4$: C, 74.52; H, 5.63. Found: C, 74.39; H, 5.64.

Typical Polymerization of Bis(phenylmethyl) *cis*-Cyclobutene-3,4-dicarboxylate (1) with II. As above, using **II** (2.0 mg, 0.0028 mmol) in toluene (0.3 mL) provided **1** (0.155 g, 0.481 mmol, 170 equiv): yield 0.151 g (94%); ^{1}H NMR (200 MHz, $CDCl_3$) 7.20 (br, 10H, C_6H_5), 5.56 (br, 2H, C*H*=C*H*), 4.96, 4.84 (br m, 4H, C*H*$_2$Ph), 3.82 (br, 1.82H, =CH-C*H*R-*cis*), 3.32 (br, 0.18H, =CH-C*H*R-*trans*); ^{13}C NMR (75 MHz, $CDCl_3$) 139.15, 131.69, 128.13, 127.26, 127.15, 72.67 72.48, 45.24, 44.26, 39.43, 38.97; IR 3063, 3032, 2955, 1732, 1489, 1455, 1377, 1296, 1214, 1149, 975, 735, 696. Anal. Calcd for $C_{20}H_{18}O_4$: C, 74.52; H, 5.63. Found: C, 74.20; H, 5.52.

Typical Polymerization of *cis*-3,4-Bis(2-oxa-3-phenylpropyl)cyclobutene (2) with I. To **I** (9.1 mg, 0.017 mmol) in 1 mL of toluene was added **2** (0.963 g, 3.26 mmol, 198 equiv) in 3 mL of toluene, dropwise. The solution was rapidly stirred for 10 min and the reaction quenched with 2-naphthaldehyde (10 mg). The reaction mixture was brought out of the drybox and precipitated into methanol. The white polymer was isolated and purified by repeated reprecipitation from methylene chloride into methanol and freeze-dried from benzene to yield 0.955 g (99%) of white polymer: ^{1}H NMR (200 MHz, $CDCl_3$) 7.19 (br, 10H, C_6H_5), 5.38 (br, 2H, $CH{=}CH$), 4.29, 4.25 (br, 4H, CH_2Ph), 3.95 (br, 4H, CH_2OCH_2Ph), 2.69 (br, 0.6H, $=$CH-C*H*R-*cis*), 2.34 (br, 1.4H, $=$CH-C*H*R-*trans*); ^{13}C NMR (75 MHz, $CDCl_3$) 138.92, 135.27, 133.07, 133.64, 132.64, 132.21, 128.13, 127.26, 127.15, 77.76, 72.65, 45.24, 44.26, 39.43, 38.97; IR 3028, 2853, 1495, 1453, 1360, 1100, 102, 734, 696. Anal. Calcd for $C_{20}H_{22}O_2$: C, 81.60; H, 7.53. Found: C, 81.36; H, 7.39.

Typical Polymerization of *cis*-3,4-Bis(2-oxa-3-phenylpropyl)cyclobutene (2) with II. As above, using **II** (2.7 mg, 0.0038 mmol) in toluene (0.3 mL) provided **2** (0.217 g, 0.738 mmol, 192 equiv): yield 0.205 g (94%) of white polymer; ^{1}H NMR (200 MHz, $CDCl_3$) 7.19 (br, 10H, C_6H_5), 5.36 (br, 2H, $CH{=}CH$), 4.25, 4.18, 4.12, 4.07 (m, 4H, CH_2Ph), 3.95 (br, 4H, CH_2OCH_2Ph), 2.72 (br, 1.84H, $=$CH-C*H*R-*cis*), 2.34 (br, 0.16H, $=$CH-C*H*R-*trans*); ^{13}C NMR (75 MHz, $CDCl_3$) 139.15, 131.69, 128.13, 127.26, 127.15, 72.67, 72.48, 45.24, 44.26, 39.43, 38.97; IR 3028, 2853, 1495, 1453, 1360, 1100, 102, 766, 734, 696. Anal. Calcd for $C_{20}H_{22}O_2$: C, 81.60; H, 7.53. Found: C, 81.45; H, 7.20.

Typical Synthesis of Poly-5-*b*-1. To a rapidly stirred solution of **I** (5.34 mg, 9.73 μmol) in toluene (1.0 mL) was added neat **5** (0.105 g, 0.530 mmol, 54.5 equiv). The solution was stirred for 20 min, and a 5% aliquot (0.05 mL) was extracted, quenched with 2 mg of 2-naphthaldehyde, and set aside. Solid **1** (0.337 g, 1.05 mmol, 114 equiv) was added to the solution of living poly-**5**, and the reaction mixture stirred for an additional hour. The reaction was quenched by addition of 10 mg of 2-naphthaldehyde dissolved in 0.1 mL of toluene. The aliquot of the first block was analyzed by ^{1}H NMR (no residual **5** observed) and GPC (M_n = 10 369, PDI of 1.06). The block copolymer was precipitated into methanol, reprecipitated from CH_2Cl_2 into methanol, and freeze-dried from benzene to yield 0.410 mg of polymer as a viscous solid (94%): M_n = 37 250; PDI of 1.12. Spectroscopically, the material exhibited a superposition of the homopolymer spectra.

Typical Synthesis of Poly-5-*b*-2. To a rapidly stirred solution of **I** (5.34 mg, 9.73 μmol) in toluene (1.0 mL) was added neat **5** (0.208 g, 1.06 mmol, 110 equiv). The solution was stirred for 20 min, and a 5% aliquot (0.05 mL) was extracted, quenched with 2 mg of 2-naphthaldehyde, and set aside. Neat **2** (0.105 g, 0.357 mmol, 38.6 equiv) was added to the solution of living poly-**5**, and the reaction mi xture stirred for an additional 10 min. The reaction was quenched by the addition of 10 mg of 2-naphthaldehyde in 0.1 mL of toluene. The aliquot of the first block was analyzed by ^{1}H NMR (no residual **5** observed) and GPC (M_n = 20 696, PDI of 1.09). The block copolymer was precipitated into methanol, reprecipitated from CH_2Cl_2 into methanol, and freeze-dried from benzene to yield 0.294 mg of polymer as a white solid (98%): M_n = 34 967; PDI of 1.09. Spectroscopically, the material exhibited a superposition of the homopolymer spectra.

Typical Conversion of Poly-1 to Poly-4. To poly-**1** (0.601 g, 3.73 mequiv of benzyl esters) in CH_2Cl_2 (6 mL) was added iodotrimethylsilane (0.820 g, 0.410 mmol, 1.1 equiv). The mixture was stirred for 36 h, 5 mL of methanol was added, and the mixture stirred for an additional 12 h. The polymer was isolated by repeated precipitations from methanol into ether and dried in vacuo for 3 days to yield 0.260 g (98%) of polymer: ^{1}H NMR (DMSO-d_6) δ 12.60 (s, 2H, CO_2H), 5.52 (s, 2H, $CH{=}CH$), 3.56 (br, 1.82H, $=$CH-C*H*R-*cis*), 3.39 (br, 0.18H, $=$CH-C*H*R-*trans*); ^{13}C{^{1}H} NMR (DMSO-d_6) δ 171.86, 170.80, 129.38, 51.96, 51.00, 45.83, 42.68; IR 3489, 3211, 2622, 1722, 1433, 1283, 1167, 972, 783.

Typical Conversion of Poly-2 to Poly-6. To poly-**2** (0.524 g, 3.56 mequiv of benzyl ethers) in CH_2Cl_2 (5 mL) was added iodotrimethylsilane (0.783 g, 3.91 mmol, 1.10 equiv). The mixture was stirred for 4 h, at which point 5 mL of methanol was added, and the mixture stirred for an additional 0.5 h. The final polymer was isolated by precipitation (3×) from DMSO to methanol. The polymer was then extracted with 30 mL of methanol for 10 h and isolated by centrifugation. This methanol extraction process was repeated three times followed by drying in vacuo for 3 days to yield 0.181 g (88.5%) of polymer: ^{1}H NMR (DMSO-d_6) δ 5.32 (br, 2H, $CH{=}CH$), 4.83 (s, 2H, -O*H*), 3.42, 3,28 (br m, 4H, -CH_2OH), 2.47 (br, 0.6H, $=$CH-C*H*R-*cis*), 2.08 (br, 1.4H, $=$CH-C*H*R-*trans*); ^{13}C{^{1}H} NMR (DMSO-d_6) δ 129.04, 128.99, 62.09, 47.89; IR 3333, 2932, 2875, 1053, 976.

Typical Synthesis of Poly-5-*b*-6. To poly-**5**-*b*-**2** (0.195 g, 41 wt % **2**, 0.54 mequiv of benzyl ethers) in CH_2Cl_2 (2 mL) was added iodotrimethylsilane (0.132 g, 0.659 mmol, 1.2 equiv). The mixture was stirred for 4 h, 5 mL of methanol was added, and the mixture stirred for an additional 0.5 h. The product was isolated by repeated precipitation from methanol into hexanes/ether (1:1, v/v) followed by precipitation into water. The polymer was then dried in vacuo for 3 days to yield 0.125 mg of polymer (85%). Spectroscopically, the material was a superposition of the homopolymer spectra.

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