3492 *Macromolecules* **1995,** *28,* 3492−3494

Living Ring-Opening Metathesis Polymerizations of 3,4-Difunctional Cyclobutenes

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Received December 21, 1994
Revised Manuscript Received March 7, 1995

Ring-opening metathesis polymerization (ROMP) has always held interest due to the ability to generate unsaturated polymers. The development of well-defined alkylidene compounds that are both tolerant of a wide variety of functional groups and provide a living initiator for polymerization of strained olefins has spawned further growth in this field.[1] We have been interested in ROMP of 3,4-disubstituted cyclobutenes that yield polymers with a very high density of pendant functionalities but are based on the common 1,4-polybutadiene backbone. Functional groups such as esters, carboxylates, ethers and imides have all been successfully incorporated. The generation of very polar homopolymers, block copolymers, and mixtures is demonstrated in this work.

A wide variety of highly functionalized cyclobutenes, attractive for the synthesis of polymers via ROMP, were synthesized from the anhydride **1**,[2] which was made from the photochemical cycloaddition of acetylene and maleic anhydride. From **1** we have synthesized the diethyl ester **2**,[3] dimethyl ester **3**,[4] dibenzyl ester **4**, benzyl imide **5**, dimethyl ether **6**, dibenzyl ether **7**, and the bicyclic tetrahydrofuran **8** (Figure 1). Initial studies showed that all of these cyclobutenes polymerized under the appropriate conditions using the Schrock alkylidene complexes **I**−**III**[5,6] as initiators (Figure 1) to form highly functionalized polymers, possessing structures analogous to substituted 1,4-polybutadiene. With the lone exception of **1**, polymerizations of these monomers were quantitative regardless of the monomer/initiator ratio, and the samples of poly-**2**−poly-**8** synthesized were monodisperse with narrow molecular weight distributions (MWD).[7] The polydispersity index (PDI) ranged from 1.04 to 1.1, which indicates living polymerizations in all cases.[8,9] Further proof of the living behavior of the polymerization of **2** is discussed below.

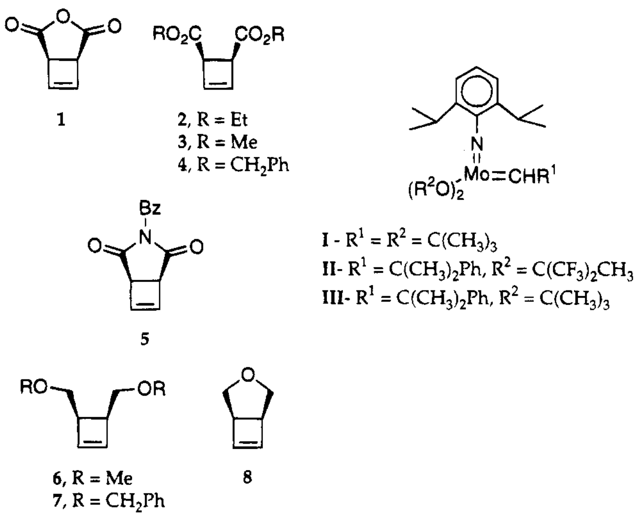

Figure 1. Structures of cyclobutene monomers and alkylidene initiators.

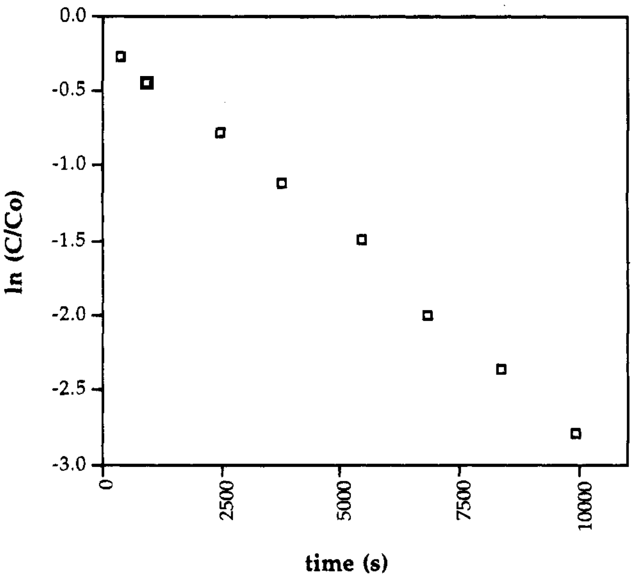

Figure 2. ^{1}H NMR solution kinetics in C_6D_6 of the polymerization of **2** at 25 °C.

The polymerization of **2**, initiated by **I**, **II**, or **III**, occurred quantitatively[10] in a wide variety of anhydrous, deoxygenated solvents. Controlled termination with benzaldehyde yielded monodisperse poly-**2**, with PDI's as low as 1.04. The Mo Schrock alkylidenes are the only initiators that polymerized **2**. Other common ROMP initiators were tried, but all failed to produce polymer in any detectable yield (via ^{1}H NMR), including the Grubbs ruthenium alkylidene, $Cl_2Ru(CHCHCPh_2)(PR_3)_2$[11] (R = cyclohexyl), as well as classical initiators based on $IrCl_3$,[12] $WCl_6/SnMe_4$[13,14] and $RuCl_3$.[15] Presumably the W analogs of the Mo initiators used would also polymerize these monomers, but since the W systems are generally much less tolerant of functionalities,[16] they were not tested. The more activated initiator **II**, with fluorinated alkoxides, also resulted in quantitative polymerizations, but higher PDI's were seen (1.2−1.4) and initial kinetic studies implied that termination processes were occurring during the polymerization. Initiators **I** and **III** (with neopentylidene and neophylidene ligands respectively) produced virtually identical samples of poly-**2**, the only spectroscopically detectable difference being the end group associated with the initiator. Polymerizations of **3** initiated by **I**−**III** were identical to **2**, with the exception of the higher solubility of poly-**2**.

The requirements for a living polymerization are the absence of chain termination and chain transfer processes.[9] To test for chain termination, a controlled kinetic study was performed on the polymerization of **2** at 25.0 °C in C_6D_6, and well-behaved second order catalysis kinetics was observed. At various initiator concentrations chosen, monomer was always consumed at a constant first-order rate until the limit of detection was reached (3−4 half-lives, ^{1}H NMR integration of the vinyl monomer resonance at 6.23 ppm vs toluene internal standard; Figure 2).

Well-behaved kinetics of this type demonstrates that a constant number of active chain ends persists over the lifetime of the polymerization. The pseudo first order rate constant was linearly dependent on the catalyst concentration, with $k_{cat} = 1.40\ (6) \times 10^{-1}\ s^{-1}\ M^{-1}$. Few absolute rate constants have been published for monomers polymerized with the Schrock initiators,

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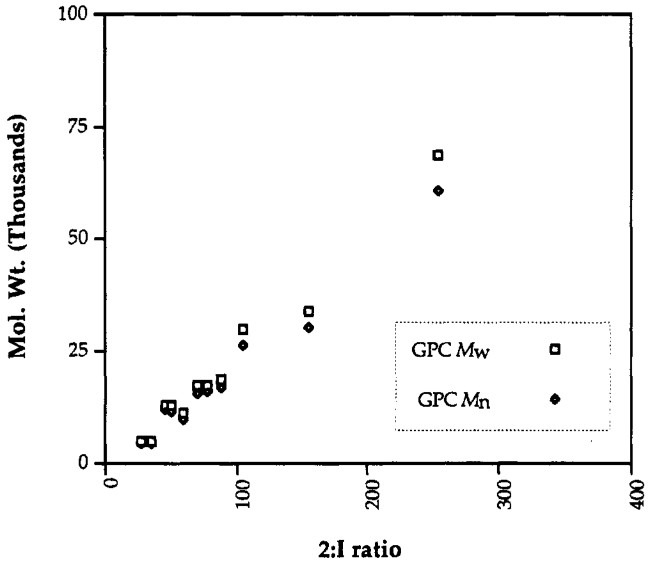


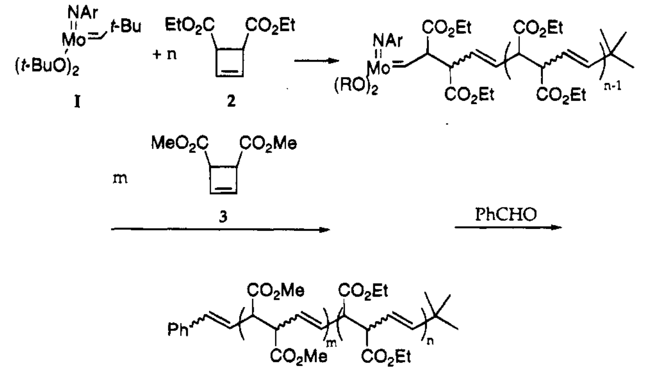
Figure 3. GPC molecular weight (relative to polystyrene) of poly-**2** vs initial **2**:**I** ratio.

but typical norbornenes are reported to polymerize much faster.[1] Even electronically deactivated norbornadienes such as 5,6-dicarbomethoxybicyclo[2.2.1]hepta-1,5-diene polymerize about 10 times faster than **2**, with $k_{\mathrm{cat}} = 2$ (1) $\mathrm{s}^{-1}\ \mathrm{M}^{-1}$ reported for that particular norbornadiene.[17] The large rate difference between ester substituted cyclobutenes and norbornenes could potentially be due to electronic effects or internal coordination of the ester on the β carbon of the polymer chain. It is certainly not due to the cyclobutene ring system itself; cyclobutene[18] and alkylcyclobutenes[19] have been reported to polymerize rapidly and uncontrollably with Mo and W alkylidene initiators, requiring the use of Ru-based catalysts and/or the addition of a strong donor ligand such as $\mathrm{PMe_3}$ to obtain living behavior. Additionally, sterically bulky dialkylcyclobutenes have been polymerized with catalysts **I**–**III**; however, no mention of rate was made.[20]

The molecular weight of poly-**2** (as determined by gel permeation chromatography relative to narrow PDI polystyrene standards) is linearly dependent on the monomer/initiator ratio chosen (Figure 3). This observation alone proves a lack of chain transfer processes.[8] Additionally, all the polymerizations were quantitative and produced monodisperse polymer with narrow MWD's. In all polymerizations where oxygen was rigorously excluded, monodisperse polymers were synthesized.[21] At the very highest **2**/initiator ratios attempted (*ca.* 600–800:1) broader PDI's were observed, but at **2**/initiator ratios below approximately 250:1, PDI's < 1.10 were routinely obtained. The synthesis of narrow PDI, monodisperse polymer at a quantitative conversion of monomer eliminates chain transfer processes,[9] and this is observed in all cases with the polymerization of **2** initiated by **II**. Hence, by the kinetic study presented above and the molecular weight data presented here, the polymerization of **2** by **I** is demonstrated to be living.

Occasionally a small shoulder to high molecular weight is observed in these Mo and W ROMP systems. As determined by both GPC elution time and GPC/sequential light scattering, this shoulder occurs at precisely twice the molecular weight of the main peak. It has been proposed that this is due to traces of dioxygen in the system,[21] and this work verifies their findings. We treated living poly-**2** with varying amounts of dried dioxygen, allowed the mixture to react for 30 min, and then quenched with an excess of benzaldehyde. The molecular weight distribution obtained from such a reaction was pronouncedly bimodal. The lower MW peak corresponded to the intended MW of living poly-**2** and the higher MW peak was exactly twice the intended MW, indicative of a bimolecular termination. The relative amounts of the 1 × MW and 2 × MW peaks were directly dependent on the amount of oxygen introduced to the system. These observations confirm the postulation made by Feast et al., that the living alkylidene end group reacts with dioxygen to form an inactive Mo oxide complex and aldehyde-terminated polymer. The just-formed aldehyde end group then quickly terminates a different living chain to form the observed 2 × MW polymer.

Scheme 1. Synthesis of Block Copolymers



Poly-**2** was surprisingly soluble in a wide number of organic solvents, ranging in polarity from methanol to toluene.[22] At all molecular weights synthesized, poly-**2** was a gummy solid at room temperature. Poly-**2** synthesized with **I** appears to contain approximately 55% trans double bonds, as determined by ^{1}H and ^{13}C NMR spectroscopy (double-bond geometry was determined by analogy to known polyalkenes[23]). Thermal analysis (TGA) resulted in 100% weight loss occurring at an onset of 291°C. No T_{g} was observed in the DSC from room temperature to decomposition. In contrast, the methyl ester analog, poly-**2**[24] was only soluble in chlorinated solvents and the polymer is a powdery solid at room temperature. Poly-**3** synthesized with **I** had the same virtually random distribution of cis and trans double bonds as poly-**2**, but poly-**3** synthesized with the fluorinated initiator **II** was much more stereoregular, with up to 93% cis double bonds. A reversible melt is observed in the DSC of poly-**3** (prepared with **I**), $T_{\mathrm{m}} =$ 185 °C, followed by decomposition occurring at an onset of 287 °C. It is interesting to note that the T_{m} of 1,4-polybutadiene is highly dependent on stereochemistry, with 1,4-cis melting at 2 °C and 1,4-trans melting at 145 °C.[25] Future work will address the effect of stereochemistry and/or tacticity on the T_{m} of poly-**3**.

The living behavior of the polymerization and the morphological differences between poly-**2** and poly-**3** prompted us to investigate the synthesis of block copolymers (Scheme 1). Sequential addition of monomers to a solution of **II** results in the expected block copolymer, although care must be taken to add the second monomer exactly at the correct time: too early and a tapered block copolymer will result, too late and decomposition of the living end group results in contamination by the homopolymer of the first block.

We have successfully polymerized a wide variety of cyclobutenes to form a new class of highly functionalized polymers analogous to linear 1,4-polybutadiene. In most cases, living behavior is observed, and it is also observed that the polymers are soluble and monomodal and have narrow MWD's. Poly-**2** and poly-**3** typically have a virtually random distribution of double bonds (55% trans), but with the appropriate use of initiators, more stereoregular polymers with up to 93% cis double bonds have been synthesized.

Acknowledgment. We gratefully acknowledge support of this work from the National Science Foundation Presidential Faculty Fellow Award, Alfred P. Sloan Foundation, 3M, DuPont, Exxon, Procter & Gamble, and BFGoodrich. M.G.P. acknowledges the National Science Foundation for a predoctoral fellowship.

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(3) Compound **2**: ^{1}H NMR (400 MHz, CDCl$_3$): 6.25 (s, 2 H), 4.13 (q, J = 7.1 Hz, 4 H), 3.90 (s, 2 H), 1.24 (t, J = 7.2 Hz, 6 H); ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) 170.7, 136.7, 60.8, 49.0, 14.1. Anal. Calcd: C, 60.59; H, 7.12. Found: C, 60.47; H, 7.07.

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(24) Poly-**3**: ^{1}H NMR (400 MHz CDCl$_3$) 5.75–5.45 (br, 2H), 3.95–3.20 (br m, 8H). ^{13}C{^{1}H} NMR (100 MHz CDCl$_3$) 171.2, 128.2, 52.1, 46.3. Anal. Calcd: C, 56.47; H, 5.92. Found: C, 56.70; H, 6.41.

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