Self-Inhibition of Propagating Carbenes in ROMP of 7-Oxa-bicyclo[2.2.1]hept-2-ene-5,6-dicarboxylic Acid Dendritic Diesters Initiated with Ru(=CHPh)$Cl_2(PCy_3)$(1,3-dimesityl-4,5-dihydroimidazol-2-ylidene)

Wlodzimierz Buchowicz, Marian N. Holerca, and Virgil Percec*

Roy & Diana Vagelos Laboratories, Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104-6332

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ABSTRACT: The kinetic study of the ring-opening metathesis polymerization (ROMP) of *exo,exo*-7-oxa-bicyclo[2.2.1]hept-2-ene-5,6-dicarboxylic acid diethyl ester (**2**), *exo,exo*-5,6-bis[[[3,5-bis(3,4-(dodecyl-1-oxy)-benzyloxy)]benzyloxy]carbonyl]-7-oxabicyclo [2.2.1] hept-2-ene (**3**), *exo,exo*-5,6-bis[[[3,4-bis(3,4,5-(dodecyl-1-oxy)benzyloxy)]benzyloxy] carbonyl]-7-oxabicyclo[2.2.1]hept-2-ene (**4**), and *exo,exo*-5,6-bis[[[3,4,5-tris(3,4,5-(dodecyl-1-oxy)benzyloxy)]benzyloxy]carbonyl]-7-oxa-bicyclo[2.2.1]hept-2-ene (**5**) initiated with Ru(=CHPh)$Cl_2(PCy_3)$L (L = 1,3-dimesityl-4,5-dihydroimidazol-2-ylidene) (**1**) and with the novel catalyst Ru(=CH−C_6H_4-*p*-CF_3)$Cl_2(PCy_3)$L (**1-CF_3**) revealed a competition between ROMP and a facile secondary metathesis reaction between the polymer backbone and the catalyst. Both **1** and **1-CF_3** polymerize **2** with a rate of propagation much higher than the rate of initiation and therefore yield polymers with a broad molecular weight distribution. It was demonstrated that the propagation was self-inhibited, and the extent of the secondary metathesis was decreased by increasing the size of the monodendritic side groups of the monomer. Consequently, polymers with narrow molecular weight distribution, i.e., M_w/M_n = 1.05, were obtained from monomer **5** which bears the bulkiest dendritic side groups. These results have demonstrated that, during the ROMP of **5**, backbiting and endbiting reactions are eliminated, and only the initiation, propagation, and secondary metathesis by free catalyst take place.

Introduction

Recently, a remarkable progress has been made in the development and application of single-component, well-defined alkene metathesis catalysts.[1] In our group, we have shown that the living ring-opening metathesis polymerization (ROMP) of monomers containing tapered and conical monodendritic side groups initiated with Ru(=CHPh)$Cl_2(PCy_3)_2$ is a very useful tool for the construction of polymers with complex molecular architecture.[2a−c]

The most active Ru-based metathesis catalyst reported up to date, Ru(=CHPh)$Cl_2(PCy_3)$L (L = 1,3-dimesityl-4,5-dihydroimidazol-2-ylidene) (**1**), was shown to efficiently catalyze ring-closing metathesis of α,ω-dienes, cross-metathesis involving geminal disubstituted alkenes or α,β-unsaturated carbonyl compounds, and ROMP of low-strain cyclic and bicyclic alkenes.[3] The higher catalytic activity of complex **1** as compared to that of Ru(=CHPh)$Cl_2(PCy_3)_2$ was best demonstrated with sterically hindered substrates.

This paper presents an investigation of the ROMP of 7-oxabicyclo[2.2.1]hept-2-ene derivatives[4] initiated by complex **1** and the novel complex **1-CF_3**. The monomers employed have substituents of various sizes (Scheme 1), and the influence of their bulkiness on the polymerization process was studied.

Results and Discussion

As a model compound for our studies we chose the diethyl ester **2**. Catalyst **1** polymerizes quantitatively 100 or less equivalents of monomer **2** within seconds at ambient temperature. Polymerizations of monomers **3**−**5** initiated with **1** were much slower compared to that of **2.** This is in accordance with the increasing bulkiness of their substituents (Figure 1). The plot of ln([M]$_0$/[M]) vs time for the polymerization experiments from Figure 1 does not support a living polymerization mechanism.

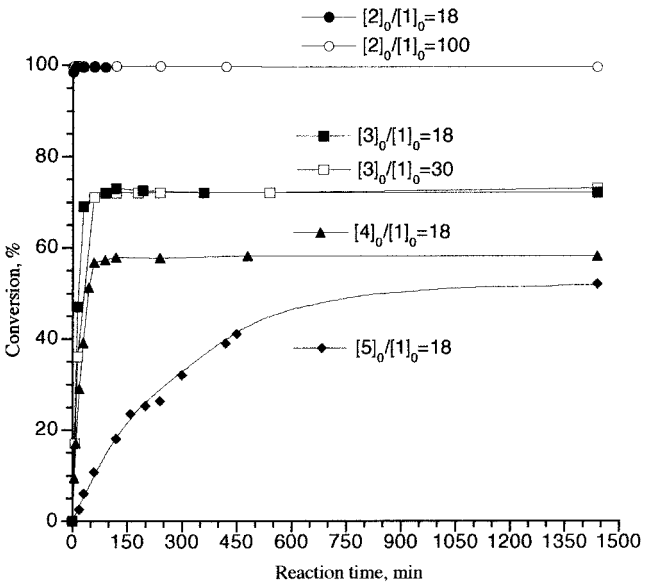

Figure 1. ROMP of monomers **2**−**5** initiated with catalyst **1**. Reaction conditions: 23 °C, $[M]_0$ = 0.06 M in CH_2Cl_2. Conversions measured by GC (monomer **2**) or GPC (monomers **3**−**5**).

Table 1 summarizes some of our results on ROMP of monomers **2**−**5** initiated with complexes **1** and **1-CF_3**. Comparing entries 3 and 4 as well as 5−8 indicates that the conversion of monomers **3**−**5** reaches a plateau. The origin of this plateau seems to be the complexation of some of the unreacted monomer into the structure of the resulted cylindrical polymer[2d,e] and not due to the limit of the catalyst lifetime and/or efficiency. Accord-

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Scheme 1

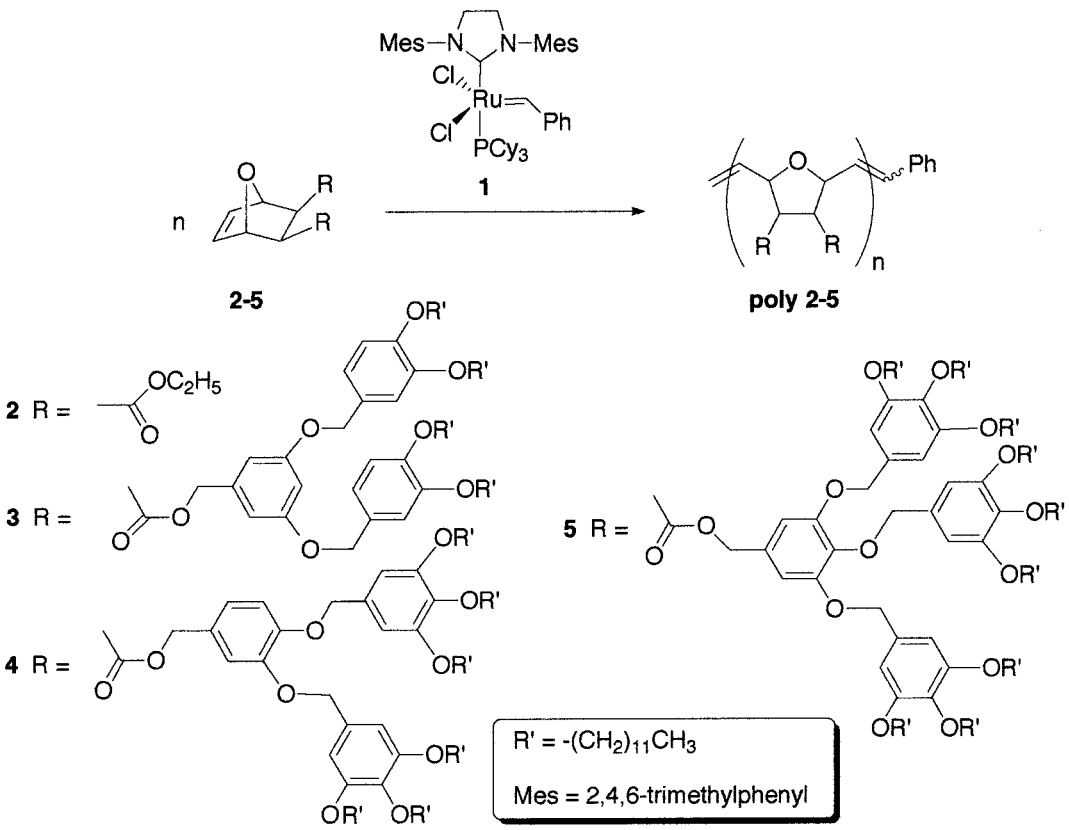


Table 1. ROMP of Monomers 2−5 Initiated with Complexes 1 or 1-CF_3[a]

entry	monomer	initiator	$[M]_0/[I]_0$	time	M_n[b]	M_w/M_n[b]	conv (%)[c]
1	**2**	**1**	100	2 min	160 000	1.4	>99
				24 h	38 000	1.8	>99
2	**2**	**1-CF_3**	100	5 min	220 000	1.7	>99
				24 h	92 000	2.7	>99
3	**3**	**1**	30	15 min	88 000	1.5	36
				48 h	57 000	1.7	70
4	**3**	**1**	18	15 min	61 000	1.4	47
				24 h	42 000	1.7	72
5	**4**	**1**	18	20 min	31 000	1.2	29
				24 h	25 000	1.3	58
6	**4**	**1**	28	24 h	36 000	1.4	56
7	**4**	**1**	37	24 h	35 000	1.5	56
8	**4**	**1**	112	24 h	120 000	2.2	57
9	**5**	**1**	18	5 h	21 000	1.05	32
				24 h	21 000	1.05	52
10	**5**	**1-CF_3**	18	12 h	15 000	1.03	43
				36 h	15 000	1.03	47

[a] Reaction conditions: $[M]_0 = 0.06$ M in CH_2Cl_2, 23 °C. [b] Determined by GPC in THF and reported relative to polystyrene standards. [c] Measured by GC for monomer **2** or by GPC for monomers **3**−**5**.

ingly, adding a fresh amount of the catalyst to a reaction mixture after 24 h increased the conversion only slightly.

Typical GPC traces illustrating changes in the polymer molecular weight with reaction time are shown for monomers **2** and **5** in Figures 2 and 3, respectively.

In ROMP of monomer **2** with $[\mathbf{2}]_0/[\mathbf{1}]_0 = 100$ (Figure 2), an initial product with $M_n = 160\,000$ was detected after 2 min while the monomer conversion was >99% (Table 1, entry 1). As the reaction was studied beyond this point, the M_n of this polymer decreased to 38 000 in 24 h. The molecular weight distribution (M_w/M_n) of the polymer formed within 2 min was 1.4, and then it increased to 2.5 due to the intermediate bimodal distribution and subsequently decreased to 1.8 after 24 h (Figure 2).

With monomer **3**, broadening of the polymer peak and formation of a shoulder was observed (Table 1, entries 3 and 4). ROMP of monomer **4** yielded at conversion below 10% mainly a polymer with $M_n = 200\,000$. However, at 30% conversion only a product with $M_n = 31\,000$ and $M_w/M_n = 1.2$ was observed (Table 1, entry 5). At 58% conversion the main product was a polymer with $M_n = 25\,000$ and $M_w/M_n = 1.3$. However, a small amount of the high molecular weight polymer was also present. Therefore, ROMP of monomers **2**, **3**, and **4** initiated with **1** and **1-CF_3** yields polymers whose molecular weight decreases and molecular weight distribution increases with conversion. This is evidence for a nonliving chain polymerization accompanied by backbiting and other secondary metathesis reactions.

In the case of monomer **5** (Figure 3), an initial product ($M_n = 32\,000$) was formed slowly and was completely converted into the secondary product with $M_n = 21\,000$ (Table 1, entry 9). This polymer is stable under the

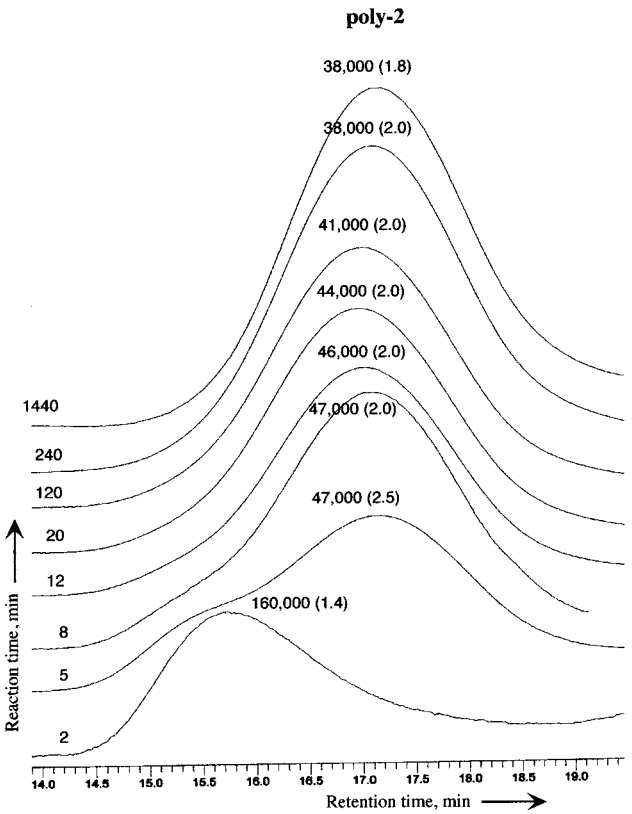


Figure 2. GPC chromatograms of ROMP of monomer **2** initiated with complex **1**. M_n and M_w/M_n (in parentheses) are shown for each chromatogram. Reaction conditions: $[\mathbf{2}]_0/[\mathbf{1}]_0 = 100$, $[\mathbf{2}]_0 = 0.06$ M, CH_2Cl_2, 23 °C.

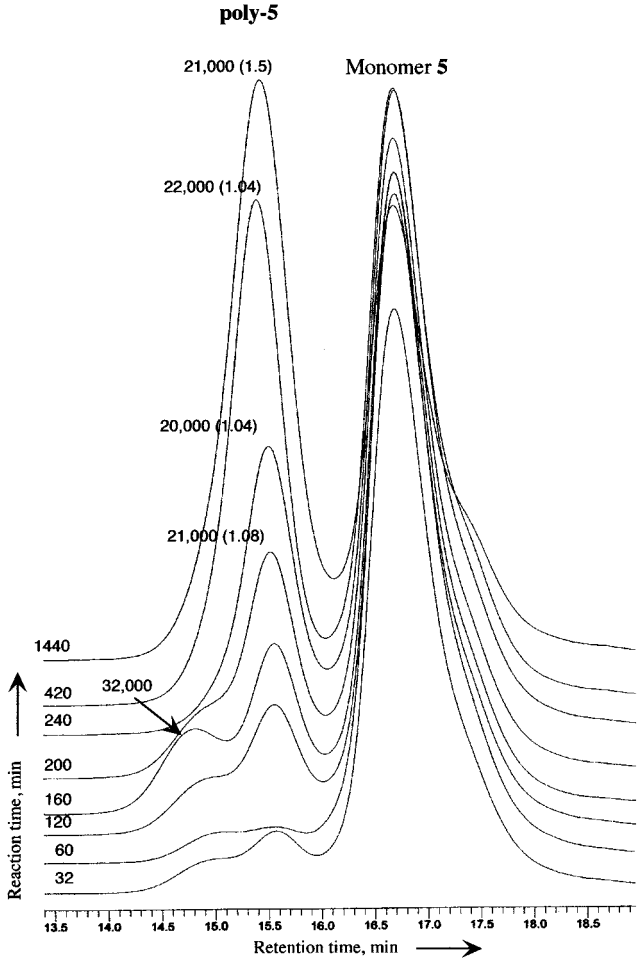


Figure 3. GPC chromatograms of ROMP of monomer **5** initiated with complex **1**. M_n and M_w/M_n (in parentheses) are shown for selected chromatograms. Reaction conditions: $[\mathbf{5}]_0/[\mathbf{1}]_0 = 18$, $[\mathbf{5}]_0 = 0.06$ M, CH_2Cl_2, 23 °C.

reaction conditions and has a very narrow molecular weight distribution $M_w/M_n = 1.05$. Therefore, during the ROMP of **5** the M_n decreases in time and M_w/M_n also decreases.

We have also studied the polymerization initiated with **1** by means of ^1H and ^{31}P NMR spectroscopy. A slow initiation by catalyst **1** is evident from reactions performed directly in an NMR sample tube. In contrast to the decrease of the apparent rate of polymerization, the consumption of the catalyst increases from monomer **2** to **4** (Figure 4, curves b−d). In a control experiment (i.e., in the absence of a monomer), we only observed a slow decomposition of complex **1** in a CD_2Cl_2 solution that followed zero-order kinetics (Figure 4, curve a). This trend is expected and can be explained as follows. The increase in the size of the side group of the monomer decreases the rate constant of both initiation and propagation. However, since the steric hindrance around the growing chain is higher than the one of the monomer, the decrease of the rate constant of initiation is lower than the decrease of the rate constant of propagation. As a consequence, the initiator efficiency increases. This is illustrated by the enhanced amount of catalyst consumed during the polymerization process (Figure 4) from monomer **2** to **5**.

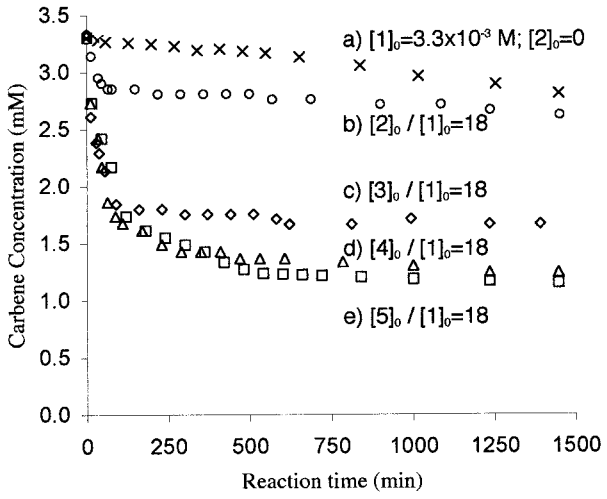
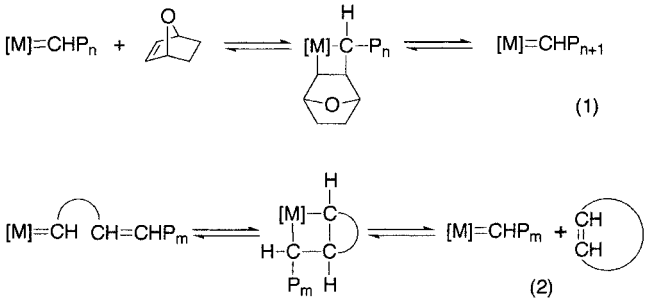


Figure 4. Decay of the complex **1** concentration with time in CD_2Cl_2 at 25 °C: (a) in the absence of a monomer; (b) $[\mathbf{2}]_0/[\mathbf{1}]_0 = 18$; (c) $[\mathbf{3}]_0/[\mathbf{1}]_0 = 18$; (d) $[\mathbf{4}]_0/[\mathbf{1}]_0 = 18$; (e) $[\mathbf{5}]_0/[\mathbf{1}]_0 = 18$.

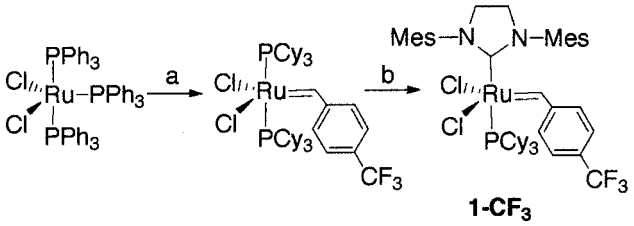
Concurrent formation of cyclic oligomers and linear polymers is a well-known phenomenon in ROMP of cyclic olefins.[1a,5−7a] It is readily explained in terms of the metal carbene mechanism as a competition between propagation (Scheme 2, eq 1) and the first-order intramolecular cyclization reaction (i.e., backbiting, Scheme 2, eq 2).

With respect to bicyclic monomers, cyclic oligomers were identified by GC and GPC in ROMP of bicyclo-[2.2.1]hept-2-ene (norbornene) using $WCl_6/Sn(CH_4)_4$ as a catalyst.[6] Recently, formation of macrocyclic compounds via an endbiting reaction was demonstrated in the polymerization of 7-*tert*-butoxybicyclo-[2.2.1]hepta-2,5-diene with $Ru(=CHPh)Cl_2(PCy_3)_2$ on the basis of NMR data.[7a] A secondary metathesis between the growing chain and the polymer double bond is also known.[7b]

Scheme 2



Scheme 3



Reagents and conditions: (a) p-$CF_3C_6H_4CHN_2$, CH_2Cl_2, -50 °C, then PCy_3 (2.2 equiv), -20 °C to rt; (b) 1,3-dimesityl-4,5-dihydroimidazolium tetrafluoroborate, ^{t}BuOK, THF, rt, then $PhCH_3$/THF, 80 °C.

Polymers with dendritic side groups exhibit a rigid-rod-like cylindrical conformation since their backbone is jacketed with a dendritic coat.[2,8] Therefore, a backbiting reaction is expected to have a low probability in this case since the backbone double bonds are not accessible to the growing chain for both steric and stiffness reasons. However, an endbiting reaction would be more probable since the two chain ends of the cylindrical polymer are less sterically hindered than the double bond of the polymer backbone.

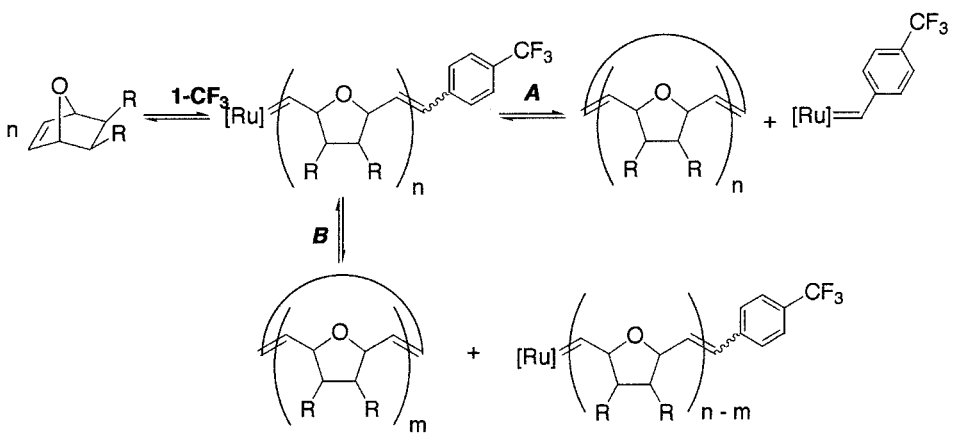
To test whether the observed secondary metathesis reaction is due to the endbiting or backbiting, a novel catalyst Ru(=CH−C_6H_4-*p*-CF_3)Cl_2(PCy_3)L (**1-CF_3**) was synthesized following the route developed for its parent compound (Scheme 3).

A macrocyclic compound formed by backbiting with the terminal (Scheme 4, path ***A***) or internal double bond (Scheme 4, path ***B***) would not contain the trifluoromethylbenzyl moiety from catalyst **1-CF_3**. If only endbiting would be responsible for the change in the polymers hydrodynamic volume and the apparent decrease in molecular weight determined by GPC, the resulting cyclic polymer would have no moiety from the **1-CF_3**. However, if backbiting occurs, cyclics free of **1-CF_3** and linear polymers containing the **1-CF_3** residue would result. ^{19}F NMR spectra of **poly-2** or **poly-5** obtained with catalyst **1-CF_3** after purification featured four broad resonances in the range from −62.5 to −63.0 ppm. Integration of these peaks vs a standard (1,1,2-trichloro-1,2,2-trifluoroethane) allowed to estimate the amount of fluorine in theses samples as corresponding to roughly 30% and 40%, respectively, of the catalyst used for these polymerizations. Therefore, taking into account the incomplete initiation by **1** (Figure 4), this finding demonstrates that most of the fluorinated moiety from the catalyst that initiated was incorporated in the final polymer. This observation unambiguously excludes the cyclization with the terminal double bond (i.e., endbiting) (Scheme 4, path ***A***) as a plausible explanation for the behavior depicted in Figures 2 and 3. The backbiting with internal double bonds (Scheme 4, path ***B***) produces a homologous series of cyclic oligomers and linear polymers, giving broad and multimodal molecular weight distribution, as shown for norbornene.[5d,6a] The monomodal, and in the case of **poly-5**, narrow molecular weight distribution, suggests that this cyclization (Scheme 4, path ***B***) does not operate in this system.[2,8] The lack of cyclization is in agreement with the stiff and sterically hindered cylindrical shape expected for these polymers. At the same time, since these polymers are stiff, attempts to determine the cis/trans configuration of their backbone double bonds by ^{13}C NMR spectroscopy were not successful since the NMR spectra exhibit broad resonances.

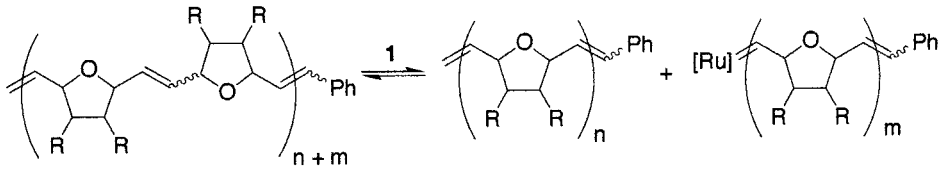
The molecular weight of polymers formed by ROMP initiated by complex **1** decreases significantly with time (Table 1, entries 1−5). This observation together with the presence of complex **1** in the polymerization mixture suggests that the secondary metathesis reaction is a statistical scission of double bonds in the polymer backbone by the free catalyst.[1a,5c,9] To gain further support for this mechanism, depolymerization experiments with samples of **poly-2** isolated after short reaction times were performed (Scheme 5). For instance, in a reaction of **poly-2** (M_n = 82 000, M_w/M_n = 2.6) with catalyst **1** a slow decrease in the polymer molecular weight and polydispersity was observed. A polymer with M_n = 68 000 and M_w/M_n = 2.2 was obtained within 24 h.

We expected that, as a consequence of the slower rate of initiation than propagation during the polymerization

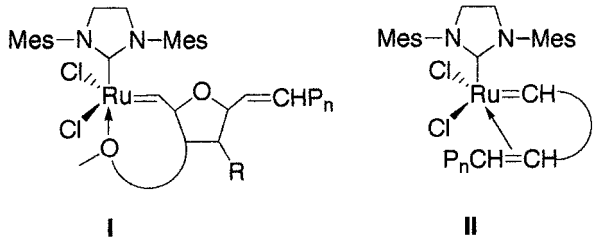
Scheme 4



Scheme 5



Scheme 6



of **2** initiated by catalyst **1**, at short reaction times only a small fraction of Ru centers would be active in the propagation step (Figure 4). This would explain, in the case of monomer **2**, the formation of polymers with M_n exceeding significantly the theoretical value, e.g., 160 000 vs 24 000. The complete conversion of monomer **2** within minutes and the slow initiation suggest that indeed the rate of propagation is larger than the rate of initiation. The broad molecular weight distribution of this initial product (Table 1, entry 1) is therefore explained as a combined result of the faster propagation than initiation and the subsequent secondary metathesis by free catalyst.

The apparent rate of polymerization significantly decreases from monomer **2** to **5** as it can be qualitatively observed in Figure 1. This effect could be attributed to a solvent and dilution effect of the dendritic side groups because it has been shown that the activity of Ru-based metathesis initiators depends markedly on the reaction medium.[10] In particular, this activity is usually lower in Et_2O and hexane than in CH_2Cl_2. Therefore, the dendritic side groups, which consist of alkyl tails and benzyl ether groups, could slow the polymerization by changing the nature of the reaction medium.

However, it is also plausible to consider that the decrease of the rate of polymerization is due to steric reasons. The bulkiness of the substituents surrounding the Ru center in the propagating species results in a restricted access of a monomer to the growing chain end. Additionally, we suggest that this steric crowding may favor chelation of the Ru center by an oxygen atom of a dendritic side group that would also decrease the catalytic activity considerably,[11] most likely due to an intermediate represented by structure **I** in Scheme 6. Alternatively, the substituents may stabilize a conformation in which a double bond of the polymer backbone remains in the coordination sphere of the Ru atom after the metallacycle breakdown (structure **II**, Scheme 6).[12]

The overall consumption of complex **1**, which is the sum of the initiation and the reaction of **1** with the polymer backbone, increases in the order **2** < **3** < **4** ≅ **5** as shown in Figure 4. Because it is unlikely that the latter reaction (Scheme 5) becomes more efficient with increasing the size of the side groups in monomers **2**−**5**, this observation can be rationalized only in terms of the side groups having a less detrimental effect on the initiation than on the propagation step. Accordingly, we suggest that the intramolecular steric interactions of the side groups with the growing chain ends are more significant than the dilution and solvent effects induced by the constitution of these groups. As a consequence, self-inhibition of the propagating carbenes is observed. Thus, this self-inhibition could result in the rate of propagation being lowered more then the rate of initiation for monomer **5**, which allows for the secondary metathesis to occur at a rate comparable with the polymerization. The conversion of the initial **poly-5** into the secondary product before the polymer reaching a high molecular weight (Figure 3) could therefore be explained by such a mechanism.

This secondary **poly-5** exhibits exceptional stability toward further metathesis with complex **1** (Table 1, entry 9) most probably because its number of cis double bonds is very low. In line with this observation, a sample of **poly-5** does not undergo any detectable cleavage with complex **1** in a CH_2Cl_2 solution for 24 h. The secondary metathesis, i.e., the reversible cleavage and formation of the double bonds (Scheme 5), shortens the chain length and changes the polymer microstructure.[9c,13] In particular, we assume that the trans/cis ratio increases significantly with progress in these secondary reactions, in analogy with a macrocyclization catalyzed by **1**.[14] Nevertheless, as mentioned before, due to broad NMR resonances, this ratio could not be determined. Apparently, this reversible process takes place until the backbone-induced changes in supramolecular structure of **poly-5** prevent any further coordination of Ru species to the polymer double bonds. We propose that the restricted access of Ru species to the double bonds is due to a supramolecular structure that has the polymer backbone fully jacketed by a dendritic coat formed by the side groups.[2,8]

Conclusions

We have found that the polymerizations of *exo,exo*-7-oxa-bicyclo[2.2.1]hept-2-ene-5,6-dicarboxylic acid diethyl ester (**2**) catalyzed with complexes **1** or **1-CF$_3$** yielded polymers with broad molecular weight distribution ($M_w/M_n \sim 2$) due to the fast ring-opening metathesis polymerization and subsequent secondary metathesis, which was shown to occur as the statistical cleavage of the polymer backbone by the free catalyst. The reactivity and selectivity of the propagating carbenes was modified by increasing the size of the substituents in monomers **3**−**5**. This inhibiting effect of the monodendritic side groups, which is the most pronounced in the case of monomer **5**, results in the retardation of polymerization as well as limitation of the secondary reactions and allows for the isolation of polymers with very narrow molecular weight distribution ($M_w/M_n = 1.05$) from a nonliving ROMP reaction. The elucidation of this polymerization mechanism requires additional experiments that should be performed with less reactive metathesis catalysts. Nevertheless, to our knowledge this is the first example of chain nonliving polymerization that yields polymers with narrow molecular weight distribution in the presence of secondary metathesis reactions.

Experimental Section

Techniques. ^{1}H NMR (500 MHz), ^{13}C NMR (125 MHz), ^{19}F NMR (470 MHz), and ^{31}P NMR (200 MHz) spectra were recorded on a Bruker DRX 500 spectrometer at 25 °C. GPC analyses were performed with a Perkin-Elmer series 10 high-pressure liquid chromatograph equipped with an LC-100 column oven, a Nelson Analytical 900 series integrator data station, and two Perkin-Elmer PL gel columns of 5×10^2 and 1×10^4 Å. THF was used as a solvent at the oven temperature of 20 °C. Detection was by UV absorbance at 254 or 214 nm. Relative weight-average (M_w) and number-average (M_n) molecular weights were determined from a calibration plot constructed from poly(styrene) standards**.** All syntheses, unless stated otherwise, were carried out under a nitrogen atmosphere in an Innovative Technology glovebox (1−2 ppm of O_2, H_2O < 0.5 ppm) or using standard Schlenk techniques.

Materials. $RuCl_2(PPh_3)_3$ (Lancaster), PCy_3 (Strem), *p*-(trifluoromethyl)benzaldehyde (Aldrich), 1,3-dicyclohexylcarbodiimide (DCC, Aldrich), 4-(dimethylamino)pyridine (DMAP, Aldrich), and benzyltriethylammonium chloride (Aldrich) were used as received; *p*-toluenesulfonhydrazide (Aldrich) was crystallized from water, and ^{t}BuOK (Lancaster) was sublimed under high vacuum. Toluene, hexane, and THF were distilled from sodium benzophenone ketyl. CH_2Cl_2 was passed through a column with neutral Al_2O_3 and refluxed with CaH_2 for 3 days. Methanol was distilled from sodium methoxide. Ru(=CHPh)$Cl_2(PCy_3)$(L) (**1**),[3a] *exo*,*exo*-5,6-bis[[[3,5-bis(3,4-(dodecyl-1-oxy)-benzyloxy)]benzyloxy]carbonyl]-7-oxabicyclo[2.2.1]hept-2-ene (**3**),[2c] *exo*,*exo*-5,6-bis[[[3,4-bis(3,4,5-(dodecyl-1-oxy)benzyloxy)]benzyloxy]carbonyl]-7-oxa bicyclo[2.2.1]hept-2-ene (**4**),[2c] (dimethylamino)pyridinium *p*-toluenesulfonate (DPTS),[15] *exo*,*exo*-5,6-(dicarboxylic anhydride)-7-oxabicyclo[2.2.1]hept-2-ene,[2b] and 3,4,5-tris[3,4,5-tris(*n*-dodecyl-1-oxy)benzyloxy]benzyl alcohol[16] were synthesized by published methods.

Syntheses. *exo,exo*-7-Oxabicyclo[2.2.1]hept-2-ene-5,6-dicarboxylic Acid Diethyl Ester (2). Monomer **2** was prepared from *exo*,*exo*-5,6-(dicarboxylic anhydride)-7-oxabicyclo-[2.2.1]hept-2-ene, and ethanol with DCC according to a literature procedure;[2a] mp 52−54 °C.^{1}H NMR ($CDCl_3$, δ, ppm): 1.26 (t, $^3J_{HH}$ = 7.1 Hz, 3H, C*H*$_3$), 2.79 (s, 2H, OCHC*H*CO$_2$), 4.16 (m, 2H, C*H*$_2$), 5.25 (t, $^3J_{HH}$ = 0.9 Hz, 2H, OC*H*CHCO$_2$), 6.45 (t, $^3J_{HH}$ = 0.9 Hz, 2H, =C*H*). ^{13}C NMR ($CDCl_3$, δ, ppm): 14.1 (*C*H$_3$), 47.0 (*C*H$_2$CH$_3$), 61.1 (C(O)*C*H), 80.5 (C(O)CH*C*H(O)CH=), 136.7 (*C*H=*C*H), 171.4 (*C*=O). CI MS (CH_4) *m*/*z* (rel intensity): 296 ([M + C_2H_5]$^+$, 17%), 241 ([M + H]$^+$, 50%), 201 (32%), 173 (100%), 127 (45%). Anal. Calcd (%) $C_{12}H_{16}O_5$: C, 60.0; H, 6.71. Found: C, 60.0; H, 6.83.

***exo,exo*-5,6-Bis[[[3,4,5-tris(3,4,5-(dodecyl-1-oxy)benzyloxy)]benzyloxy]carbonyl]-7-oxabicyclo[2.2.1]hept-2-ene (5).** Monomer **5** was synthesized according to a modified literature procedure.[17] A 50 mL pear-shaped flask equipped with a Teflon-coated magnetic stirring bar was flame-dried and flushed with Ar. 3,4,5-Tris[3,4,5-tris(*n*-dodecyl-1-oxy)benzyloxy]benzyl alcohol (3.5 g, 1.68 mmol), *exo*,*exo*-5,6-(dicarboxylic anhydride)-7-oxabicyclo[2.2.1]hept-2-ene (0.139 g, 0.84 mmol), and DMAP (0.0153 g, 0.12 mmol) were dissolved under Ar in 10 mL of CH_2Cl_2. The reaction mixture was stirred for 48 h at 23 °C after which time ^{1}H NMR indicated complete alcoholysis of the anhydride. DCC (0.207 g, 1.0 mmol) and DPTS (0.053 g, 0.16 mmol) were added to the reaction mixture, and stirring was continued at 23 °C. After 24 h, the reaction mixture was filtered and the solvent was removed by rotary evaporator. The crude product was chromatographed on SiO_2 using 5:1 hexane/ethyl acetate and then precipitated into cold MeOH to yield 2.62 g (72.5%) of **5** as a white powder. Mp 36−38 °C. Purity (HPLC), 99+%; TLC (5:1 hexanes: EtOAc), R_f = 0.4. ^{1}H NMR ($CDCl_3$, δ, ppm): 0.88 (m, 54H, C*H*$_3$), 1.1−1.4 (m, 324H, (CH$_2$)$_9$), 1.85 (m, 36H, C*H*$_2$CH$_2$OPh), 2.80 (s, 2H, OCHC*H*CO$_2$), 3.7−3.9 (m, 36H, C*H*$_2$OPh), 4.8−5.1 (m, 16H, PhC*H*$_2$OCO, PhC*H*$_2$OPh), 5.19 (s, 2H, OC*H*CHCO$_2$), 6.43 (s, 2H, =C*H*), 6.58−6.63 (m, 16H, Ar*H*). ^{13}C NMR ($CDCl_3$, δ, ppm): 14.3 (*C*H$_3$), 22.9 (*C*H$_2$CH$_3$), 26.5−30.1 [(*C*H$_2$)$_8$], 32.2 (*C*H$_2$CH$_2$CH$_3$), 47.5 (OC(O)*C*H), 67.1 (Ar*C*H$_2$OCO), 69.1−69.3, 71.8 (*C*H$_2$OAr), 73.5−73.7, 75.5 (Ar*C*H$_2$OAr), 80.8 (C(O)CH*C*H(O)CH=), 106.4 (Ar*C ortho* to −CH$_2$OCO), 105.8, 108.6 (Ar*C ortho* to −OCH$_2$-CH$_2$−), 131.5 (Ar*C ipso* to −CH$_2$−OCO), 132.3 (*C*H=*C*H), 133.0, 132.3 (Ar*C ipso* to −CH$_2$−OAr), 137.9, 138.1 (Ar*C meta* to −CH$_2$OAr), 138.7 (Ar*C para* to CH$_2$OCO), 153.2, 153.3, 153.5 (Ar*C ipso* to O−CH$_2$Ar and Ar*C ipso* to −OCH$_2$CH$_2$), 171.5 (*C*=O).

The tosylhydrazone and the diazomethane solution were prepared in air.

***p*-(Trifluoromethyl)benzaldehyde Tosylhydrazone.** *p*-(Trifluoromethyl)benzaldehyde (1.14 g, 6.56 mmol) was added to a suspension of *p*-toluenesulfonhydrazide (1.37 g, 7.37 mmol) in 14 mL of absolute ethanol. The resulting solution was warmed to reflux for 15 min. Cooling to 0 °C afforded white crystals, which were filtered off and washed with cold ethanol and hexane. Yield: 1.80 g (80%). Mp 163 °C (lit. 155−157 °C).[18] ^{1}H NMR ($CDCl_3$, δ, ppm): 2.42 (s, 3H, C*H*$_3$), 7.34 (d, $^3J_{HH}$ = 8.4 Hz, 2H, Ar of $SO_2C_6H_4CH_3$), 7.61 (d, $^3J_{HH}$ = 8.4 Hz, 2H, *m*-H of $C_6H_4CF_3$), 7.70 (d, $^3J_{HH}$ = 8.2 Hz, 2H, Ar of $SO_2C_6H_4$-CH$_3$), 7.80 (s, 1H, C*H*N), 7.89 (d, $^3J_{HH}$ = 8.3 Hz, 2H, *o*-H of $C_6H_4CF_3$), 8.23 (bs, 1H, N*H*). ^{19}F NMR ($CDCl_3$, δ, ppm): −63.35 (s, CF_3).

A solution of *p*-(trifluoromethyl)phenyldiazomethane was prepared according to a general procedure described in ref 19. The tosylhydrazone (2.41 g, 7.04 mmol), benzyltriethylammonium chloride (0.30 g, 1.32 mmol), 15 mL of hexane, 5 mL of toluene, and 60 mL of 15% aqueous NaOH were placed in a flask and heated to 70 °C for 2 h with vigorous stirring. After this time the reaction mixture was poured into a separatory funnel half filled with ice. The organic layer was separated, washed with cold water, and dried over Na_2SO_4. This solution was degassed with a stream of nitrogen.

Ru(=CH−C_6H_4-*p*-CF_3)$Cl_2(PCy_3)_2$ was synthesized in a similar way as described for Ru(=CHPh)$Cl_2(PCy_3)_2$.[20] The solution of *p*-(trifluoromethyl)phenyldiazomethane described above was added to a solution of $RuCl_2(PPh_3)_3$ (2.75 g, 2.88 mmol) in 100 mL of CH_2Cl_2 at −50 °C in 10 min. The reaction mixture was warmed to −20 °C when PCy_3 (1.85 g, 6.60 mmol) was added. It was then warmed to room temperature and stirred for 1 h. CH_2Cl_2 was removed under high vacuum. MeOH (200 mL) was added to the residue to precipitate a red solid, which was filtered off and washed several times with MeOH. This crude product was redissolved in CH_2Cl_2 (5 mL), precipitated with MeOH, filtered off in air, washed repeatedly with MeOH, and dried under high vacuum.

Ru(=CH−C_6H_4-*p*-CF_3)$Cl_2(PCy_3)_2$ was isolated as a dark-purple microcrystalline solid in 75% yield. ^{1}H NMR (CD_2Cl_2, δ, ppm): 20.36 (s, 1H, Ru=CH), 8.59 (d, 2H, $^3J_{HH}$ = 8.1 Hz, *o*-H of $C_6H_4CF_3$), 7.58 (d, 2H, $^3J_{HH}$ = 8.4 Hz, *m*-H of C_6H_4-CF$_3$), 2.61, 1.72, 1.42, 1.21 (all m, 66 H, PCy_3). ^{13}C NMR (CD_2-Cl$_2$, δ, ppm): 292.0 (bs, Ru=CH), 155.0 (s, *ipso*-C of $C_6H_4CF_3$), 130.93 (s, *o*-C of $C_6H_4CF_3$), 129.44 (q, J_{CF} = 33 Hz, *p*-C of C_6H_4-CF$_3$), 126.65 (q, J_{CF} = 3.9 Hz, *m*-C of $C_6H_4CF_3$), 125.39 (q, J_{CF} = 272 Hz, CF_3), 32.56 (t, J_{CP} = 9.3 Hz, *ipso*-C of PCy_3), 30.16 (s, *m*-C of PCy_3), 28.33 (t, J_{CP} = 5.3 Hz, *o*-C of PCy_3), 27.05 (s, *p*-C of PCy_3). ^{31}P NMR (CD_2Cl_2, δ, ppm): 38.32 (s, PCy_3). ^{19}F NMR (CD_2Cl_2, δ, ppm): −63.99 (s, CF_3). Anal. Calcd (%) $C_{44}H_{71}$-$Cl_2F_3P_2Ru$: C, 59.3; H, 8.04. Found: C, 59.5; H, 8.08.

Ru(=CH−C_6H_4-p-CF_3)$Cl_2(PCy_3)$(L)(1-CF_3) was prepared by a slightly modified literature procedure.[3a] 1,3-Dimesityl-4,5-dihydroimidazolium tetrafluoroborate[3a,21] (0.294 g, 0.75 mmol) was suspended in 8 mL of freshly distilled THF. A solution of potassium *tert*-butoxide (0.0838 g, 0.75 mmol) in 15 mL of THF was added at room temperature in 30 min. A cloudy solution was formed and stirred for an additional 1 h. This ligand solution was added via a cannula to a solution of Ru(=CH−C_6H_4-*p*-CF_3)$Cl_2(PCy_3)_2$ (0.5541 g, 0.62 mmol) in 40 mL of toluene. The resulting mixture was warmed to 80 °C with stirring for 1 h when the substrate was completely consumed as shown by ^{1}H and ^{31}P NMR. The solvents were removed under high vacuum, and the product isolated by repeated crystallization from hexane. Complex **1-CF_3** was obtained as pink-brown solid in 37% yield. ^{1}H NMR (CD_2Cl_2, δ, ppm): 19.47 (s, 1H, Ru=CH), 9.1 (b, 1H, Ar of L), 7.37 (d, 2H, $^3J_{HH}$ = 8.4 Hz, *m*-H of $C_6H_4CF_3$), 7.02 (bs, 2H, *o*-H of C_6H_4-CF$_3$), 6.6 (b, 1H, Ar of L), 5.7 (b, 1H, Ar of L), 3.99 (b, 4H,

CH_2-CH_2), 2.7−0.80 (all m, 45 H, PCy_3 and *o*-CH_3 of L), 2.31 (s, 3H, *p*-CH_3 of L), 1.87 (s, 3H, *p*-CH_3 of L). ^{13}C NMR (CD_2Cl_2, δ, ppm): 291.9 (s, Ru=CH), 219.8 (d, $J_{PC} = 77$ Hz, NCN), 153.2 (s, *ipso*-C of $C_6H_4CF_3$), 139.4 (bs), 139.1 (s), 138.3 (s), 137.9 (s), 137.4 (bs), 135.6 (s), 130.4 (bs), 129.6 (bs), 128.5 (s), 128.3 (s), 128.0 (s), 126.7 (s), 125.3 (bs), 124.5 (s) (all Ar of L and $C_6H_4CF_3$), 52.92 (s, NCH_2), 51.83 (s, NCH_2), 31.95 (d, $J_{PC} = 17$ Hz), 29.65 (bs), 28.27 (d, $J_{PC} = 10$ Hz), 26.64 (s) (all PCy_3), 21.44 (s), 21.00 (s), 20.29 (s), 18.82 (bs) (all CH_3−Ar of L). ^{31}P NMR (CD_2Cl_2, δ, ppm): 31.74 (s, PCy_3). ^{19}F NMR (CD_2Cl_2, δ, ppm): −63.77 (s, CF_3). FAB MS *m*/*z* (rel intensity): 916 ($[M]^+$, 19%), 881 ($[M - Cl]^+$, 11%), 438 (100%), 356 (42%), 315 (38%), 307 ($[LH]^+$, 92%), 281 ($[HPCy_3]^+$, 95%). Anal. Calcd (%) $C_{47}H_{64}Cl_2F_3N_2PRu$: C, 61.6; H, 7.04; N, 3.05. Found: C, 60.8; H, 7.12; N, 2.78.

General Procedure for the ROMP of Monomers 2−5 Initiated with Catalyst 1 or 1-CF_3. Monomer **5** (typically, 116.5 mg, 2.70×10^{-2} mmol) and catalyst **1** (1.26 mg, 1.48×10^{-3} mmol) were weighed out in a Schlenk tube. The tube was placed in a nitrogen-filled glovebox where CH_2Cl_2 (0.50 mL) was added. The resulting solution was stirred at ambient temperature (23 °C). The conversion and molecular weight were followed by sampling the reaction mixture at suitable time intervals. The aliquots were quenched with ethyl vinyl ether and analyzed by GPC. (For monomer **2** conversion was determined by GC using biphenyl as an internal standard.) The reaction was terminated by addition of an excess of ethyl vinyl ether and stirring for 0.5 h. The polymer was purified by column chromatography on neutral Al_2O_3 (hexanes:EtOAc 10:1). Precipitation into cold methanol resulted in a white powder. ^1H NMR (CD_2Cl_2, δ, ppm): 0.88 (unresolved multiplet, 5 H), 1.27 (bs, 30 H), 1.55 (bs, 2 H) 1.65 (bs, 2 H), 3.7 (m, 1 H), 3.76 (s, 1 H), 4.7 (bs, 1 H), 6.45 (bs, 1 H).

Polymerizations in an NMR Sample Tube. Monomer **3** (81. 5 mg, 3.60×10^{-2} mmol) was weighed out in an NMR sample tube. A solution of **1** (1.7 mg, 2.0×10^{-3} mmol) and anthracene (internal standard) in 0.60 mL of CD_2Cl_2 was prepared in another NMR tube. The polymerization was started by adding the initiator solution to the monomer. The carbene peak of **1** at 19.1 ppm was integrated vs the anthracene singlet at 8.50 ppm.

Typical Depolymerization Experiments. Monomer **2** (64.1 mg, 0.267 mmol) and catalyst **1** (2.23 mg, 2.63×10^{-3} mmol) were placed in a Schlenk tube. A 4.40 mL aliquot of CH_2Cl_2 were added, and the resulting mixture was stirred for 1 min after which time an excess of ethyl vinyl ether was added (5 mL). Air was also vigorously bubbled through this mixture to ensure quenching of the catalyst. The reaction mixture was passed through a short bed of neutral Al_2O_3 to remove all colored byproducts. A 44 mg sample of **poly-2** was thus obtained. A 1.52 mg sample of **1** and 3.0 mL of CH_2Cl_2 were then added to restore the initial polymerization conditions, and the mixture was stirred at 23 °C for 24 h. The progress of the reaction was followed as described for ROMP experiments.

For monomer **5**, the polymerization was carried out as usual for 24 h at 23 °C. **Poly-5** was isolated by column chromatography on Al_2O_3. A sample of this polymer was stirred in CH_2Cl_2 with complex **1** under conditions of the initial polymerization. No changes in M_n or M_w/M_n were detected for 24 h by GPC.

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References and Notes

(1) For recent reviews see: (a) Ivin, K. J.; Mol, J. C. *Olefin Metathesis and Metathesis Polymerization*; Academic Press: San Diego, 1997. (b) Schuster, M.; Blechert, S. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2037. (c) Grubbs, R. H.; Chang, S. *Tetrahedron* **1998**, *54*, 4413. (d) *Alkene Metathesis in Organic Synthesis*; Fürstner, A., Ed.; Springer: Berlin, 1998. (e) Fürstner, A. *Angew. Chem., Int. Ed.* **2000**, *39*, 3012. (f) Trnka, T. M.; Grubbs, R. H. *Acc. Chem. Res.* **2001**, *34*, 18.

(2) (a) Percec, V.; Schlueter, D.; Ronda, J. C.; Johansson, G.; Ungar, G.; Zhou, J. P. *Macromolecules* **1996**, *29*, 1464. (b) Percec, V.; Schlueter, D. *Macromolecules* **1997**, *30*, 5783. (c) Percec, V.; Holerca, M. N. *Biomacromolecules* **2000**, *1*, 6. (d) Percec, V.; Ahn, C.-H.; Barboiu. B. *J. Am. Chem. Soc.* **1997**, *119*, 12978. (e) Percec, V.; Ahn, C.-H.; Cho, W.-D.; Jamieson, A. M.; Kim, J.; Leman, T.; Schmidt, M.; Gerle, M.; Möller, M.; Prokhorova, S. A.; Sheiko, S. S.; Cheng, S. Z. D.; Zhang, A.; Ungar, G.; Yeardley, D. J. P. *J. Am. Chem. Soc.* **1998**, *120*, 8619.

(3) (a) Scholl, M.; Ding, S.; Woo Lee, C.; Grubbs, R. H. *Org. Lett.* **1999**, *1*, 953. (b) Chatterjee, A. K.; Grubbs, R. H. *Org. Lett.* **1999**, *1*, 1751. (c) Chatterjee, A. K.; Morgan, J. P.; Scholl, M.; Grubbs, R. H. *J. Am. Chem. Soc.* **2000**, *122*, 3783. (d) Bielawski, C. W.; Grubbs, R. H. *Angew. Chem., Int. Ed.* **2000**, *39*, 2903.

(4) (a) Novak, B. M.; Grubbs, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 960. (b) Novak, B. M.; Grubbs, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 7542.

(5) (a) Calderon, N.; Ofstead, E. A.; Judy, W. A. *J. Polym. Sci., Part A-1* **1967**, *5*, 2209. (b) Ofstead, E. A.; Calderon, N. *Makromol. Chem.* **1972**, *154*, 21. (c) Ivin, K. J. *Olefin Metathesis*; Academic Press: London, 1983. (d) Höcker, H. *Makromol. Chem., Macromol. Symp.* **1986**, *6*, 47. (e) Suter, U. W.; Höcker, H. *Makromol. Chem.* **1988**, *189*, 1603.

(6) (a) Reif, L.; Höcker, H. *Makromol. Chem., Rapid Commun.* **1981**, *2*, 183. (b) Reif, L.; Höcker, H. *Macromolecules* **1984**, *17*, 952.

(7) (a) Ivin, K. J.; Kenwright, A. M.; Khosravi, E. *Chem. Commun.* **1999**, 1209. (b) Ivin, K. J.; Kenwright, A. M.; Khosravi, E.; Hamilton, J. E. *J. Organomet. Chem.* **2000**, *606*, 37.

(8) Percec, V.; Ahn, C.-H.; Ungar, G.; Yeardley, D. J. P.; Möller, M.; Sheiko, S. *Nature (London)* **1998**, *391*, 161.

(9) (a) Hummel, K. *Pure Appl. Chem.* **1982**, *54*, 351. (b) Stelzer, F.; Graiman, Ch.; Hummel, K. *Colloid Polym. Sci.* **1982**, *260*, 829. (c) Wagener, K. B.; Puts, R. D.; Smith, D. W. *Makromol. Chem., Rapid Commun.* **1991**, *12*, 419. (d) Chung, T. C.; Chasmawala, M. *Macromolecules* **1992**, *25*, 5137. (e) Watson, M. D.; Wagener, K. B. *Am. Chem. Soc., Polym. Prepr.* **1996**, *37*, 609.

(10) (a) Nguyen, S. T.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1993**, *115*, 9858. (b) Buchowicz, W.; Mol, J. C. *J. Mol. Catal.* **1999**, *148*, 97. (c) Fürstner, A.; Thiel, O. R.; Ackermann, L.; Schanz, H.; Nolan, S. P. *J. Org. Chem.* **2000**, *65*, 2204.

(11) (a) Chang, S.; Jones, L.; Wang, C.; Henling, L. M.; Grubbs, R. H. *Organometallics* **1998**, *17*, 3460. (b) Kingsbury, J. S.; Harrity, J. P. A.; Bonitatebus, P. J.; Hoveyda, A. H. *J. Am. Chem. Soc.* **1999**, *121*, 791.

(12) (a) For a general discussion on the mechanism of alkene metathesis, see ref 1a. (b) For a detailed discussion on the mechanism and activity of closely related Ru metathesis catalysts, see: Dias, E. L.; Nguyen, S. T.; Grubbs, R. H. *J. Am. Chem. Soc.* **1997**, *119*, 3887. (c) For new insights in the mechanism of ROMP initiated by catalyst **1**, see: Sanford, M. S.; Ulman, N.; Grubbs, R. H. *J. Am. Chem. Soc.* **2001**, *123*, 749.

(13) Kumar, V. G.; Hummel, K. *J. Polym. Sci., Part A-1* **1983**, *21*, 1183.

(14) Lee, C. W.; Grubbs, R. H. *Org. Lett.* **2000**, *2*, 2145.

(15) Percec, V.; Heck, J.; Tomazos, D.; Falkenberg, F.; Blackwell, H.; Ungar, G. *J. Chem. Soc., Perkin Trans. 2* **1993**, 2381.

(16) Balagurusamy, V. S. K.; Ungar, G.; Percec, V.; Johansson, G. *J. Am. Chem. Soc.* **1997**, *119*, 1539.

(17) Percec, V.; Schlueter, D.; Ungar, G.; Cheng, S. Z. D.; Zhang, A. *Macromolecules* **1998**, *31*, 1745.

(18) Ding, W. F.-X.; Xie, J. R.-Y.; Ji, G.-Z.; Jiang, X.-K. *J. Chem. Res. Miniprint* **1998**, *7*, 1483.

(19) Wulfman, D. S.; Yausefian, S.; White, J. M. *Synth. Commun.* **1988**, *18*, 2349.

(20) Schwab, P.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1996**, *118*, 100.

(21) (a) Hutchins, R. O.; Su, W.-Y.; Sivakumar, R.; Cistone, F.; Stercho, Y. P. *J. Org. Chem.* **1983**, *48*, 3412. (b) Saba, S.; Brescia, A.-M.; Kaloustain, M. K. *Tetrahedron Lett.* **1991**, *32*, 5031.

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