ACS Catalysis

Research Article

pubs.acs.org/acscatalysis

Phase Transfer Activation of Fluorous Analogs of Grubbs' Second-Generation Catalyst: Ring-Opening Metathesis Polymerization

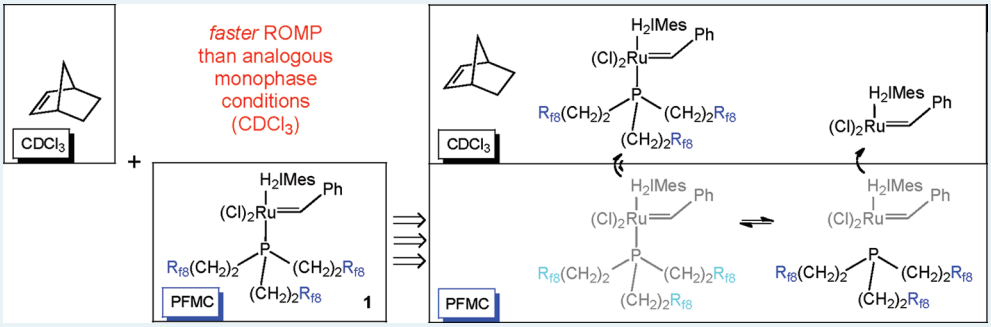
Robert Tuba,[†] Rosenildo Corrêa da Costa,[§] Hassan S. Bazzi,*[,†] and John A. Gladysz*[,‡]

[†]Department of Chemistry, Texas A&M University at Qatar, P.O. Box 23874, Doha, Qatar

[‡]Department of Chemistry, Texas A&M University, P.O. Box 30012, College Station, Texas 77842-3012, United States

[§]Institut für Organische Chemie and Interdisciplinary Center for Molecular Materials, Friedrich-Alexander-Universität Erlangen-Nürnberg, Henkestraße 42, 91054 Erlangen, Germany

Supporting Information



ABSTRACT: Grubbs' second-generation alkene metathesis catalyst and the fluorous analog $(H_2IMes)((R_{f8}(CH_2)_2)_3P)(Cl)_2Ru(=CHPh)$ (**1**; H_2IMes/R_{f8} = 1,3-dimesityl-4,5-dihydroimidazol-2-ylidene/$(CF_2)_7CF_3$) catalyze ring-opening metathesis polymerizations of norbornene at essentially identical rates ($CDCl_3$, RT). However, dramatic accelerations can be observed with **1** in the presence of the fluorous solvent perfluoro(methylcyclohexane) (PFMC). The fluorous phosphine $(R_{f8}(CH_2)_2)_3P$ must first dissociate from **1** to generate the 14-valence-electron intermediate that begins the catalytic cycle and should be scavenged by the PFMC phase (PFMC/toluene partition coefficient >99.7:<0.3). This would allow alkenes to more effectively compete for active catalyst. However, faster rates are seen only when **1** (partition coefficient 39.6:60.4) is added as a PFMC solution or a PFMC/$CDCl_3$ biphase mixture, as opposed to $CDCl_3$ solution, and possible additional contributing factors are analyzed. Analogous effects are observed with a 7-oxanorbornene-based *N*-butylsuccinimide. The molecular weights, polydispersities, glass transition temperatures, and cis/trans C=C linkage ratios of the polynorbornene produced under monophasic and biphasic conditions are compared and are usually similar.

KEYWORDS: *ROMP, fluorous, biphase catalysis, phase transfer, Grubbs' catalyst, polynorbornene*

INTRODUCTION

Phase labeled or "tagged" ligands are commonly employed to impart affinity to a metal complex or catalyst for a given phase.[1] There is a vast literature concerning hydrophilic[2] and fluorophilic (fluorous)[3] ligands, and, in particular, phosphines.[4−6] Catalysts that feature hydrophilic or fluorous phosphines are often amenable to recycling using aqueous or fluorous phases.

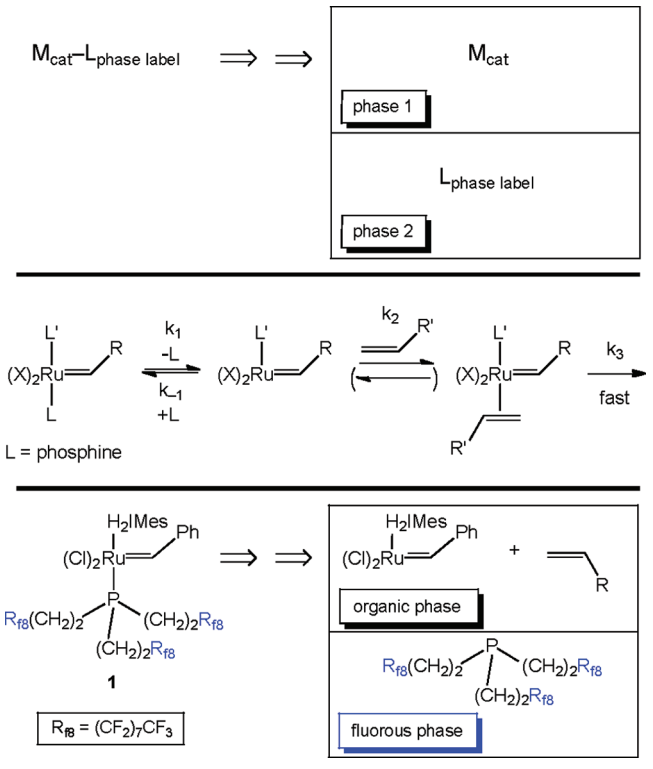
However, ligands bearing labels for phases that are *orthogonal* to the reaction medium also have potential applications. There are many catalyst precursors from which a ligand must initially dissociate before the catalytic cycle can be entered. The reverse reaction often retards the overall rate. Thus, if the ligand could be efficiently scavenged, faster reactions would occur. Most scavenging strategies involve some type of chemical trapping;[7] however, phase transfer into an orthogonal phase should also be possible, as sketched in Scheme 1 (top). The most obvious approach is to engineer the catalyst precursor containing the phase-labeled ligand to be predominantly soluble in one phase and the phase-labeled ligand to be predominantly soluble in an orthogonal phase. Such a protocol can be termed "*phase transfer activation*".

Grubbs' first- and second-generation alkene metathesis catalysts, which have been extensively studied mechanistically,[8,9] provide excellent testing grounds for this strategy. As shown in Scheme 1 (middle), a phosphine must first dissociate, giving a 14-valence-electron intermediate, to initiate the catalytic cycle.[8,9] It is well-known that the reverse (k_{-1}) reassociation step can compete with the subsequent alkene binding step (k_2), slowing the observed rate.

Accordingly, we have prepared analogs of Grubbs' second-generation catalyst with a series of fluorous aliphatic

Received: September 23, 2011
Revised: November 24, 2011
Published: November 29, 2011

Scheme 1. Phase Transfer Activation: General Strategy (top) and as Applied to Grubbs' Alkene Metathesis Catalysts (middle) under Organic/Fluorous Liquid/Liquid Biphase Conditions (bottom)

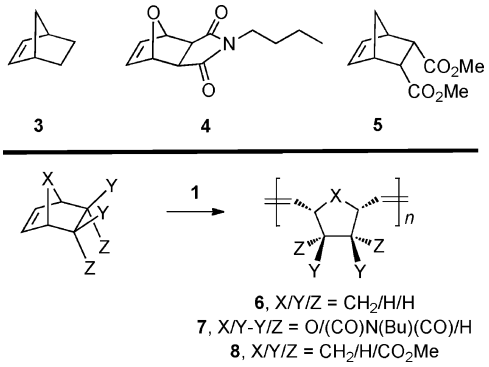


phosphines, $(H_2IMes)((CF_3(CF_2)_{n-1}(CH_2)_m)_3P)(Cl)_2Ru(=CHPh)$ (H_2IMes = 1,3-dimesityl-4,5-dihydroimidazol-2-ylidene).[10,11] The complex with n/m = 8/2 (**1**), shown in Scheme 1 (bottom), exhibits a perfluoro(methylcyclohexane)/toluene (PFMC/toluene) partition coefficient of 39.6:60.4 (25 °C), whereas the phosphine ligand $(R_{f8}(CH_2)_2)_3P$ exhibits a partition coefficient of >99.7:<0.3.[12] Only very modest amounts of unfunctionalized alkenes partition into fluorous phases, and polar alkenes are much less fluorophilic.[13] Although diffusion rates of solutes across fluorous/organic phase boundaries are not presently available, colored metal complexes with appreciable solubilities in both phases attain equilibrium within a few seconds upon shaking, as judged visually.

As expected, much faster rates of ring-closing metatheses were observed when **1** was reacted under organic/fluorous liquid/liquid biphase conditions, as opposed to organic monophasic conditions.[10,11] Rate comparisons were made between CH_2Cl_2 solutions and CH_2Cl_2/fluorous solvent mixtures that involved equal volumes of CH_2Cl_2 and charges of reactants and catalysts. Accelerations were documented with PFMC and perfluoro(2-butyltetrahydrofuran) (FC-75).

Despite this proof of principle, it was felt that this new concept would benefit from additional validation. In one approach, we have extended this chemistry to analogs of Grubbs' catalysts with water-soluble phosphines and observed analogous rate accelerations.[14] In another approach, described herein, we have extended the organic/fluorous biphase reactions of **1** to ring-opening polymerizations (ROMP) of the norbornenes shown in Scheme 2. However, in contrast to our other work, dramatic rate accelerations are found only

Scheme 2. ROMP Reactions Studied



when **1** is introduced as a PFMC solution or biphasic mixture, as opposed to a CH_2Cl_2 or $CDCl_3$ solution.

RESULTS

1. Phase Transfer Activation of ROMP. Screening reactions were conducted with **1**, Grubbs' second-generation catalyst, $(H_2IMes)(Cy_3P)(Cl)_2Ru(=CHPh)$ (**2**), and norbornene (**3**). The ROMP of norbornene by **2** has been described several times in the literature.[15−18] Polymerizations were conveniently conducted in NMR tubes at 25 °C (20 Hz spinning rate), employing $CDCl_3$ solutions that were 0.066 M in **3** (0.046 mmol in 0.700 mL) and 0.000 059−0.000 061 M (0.059−0.061 mM) in catalyst (0.10 mol %). These gave colorless solutions of polynorbornene (**6**) with low viscosities. When reactions with **2** were repeated with higher concentrations of **3** (0.22 M; 0.03 mol % catalyst loading), viscosities noticeably increased.

The rates of disappearance of **3** and appearance of **6** were monitored by ^1H NMR (Supporting Information Figure S1). In all cases, the consumption of **3** was essentially complete. In accord with previous reports, **6** exhibited both cis and trans C=C linkages. In all cases, the former was in slight excess (~58:42, 5.22/5.35 ppm), as assigned from chemical shift trends established earlier.[16,19] Additions of MeOH precipitated the white product polymers. With **2**, the average gravimetric yield of these 4−5 mg scale reactions was 70%; however, because the solids were not soluble in THF, they could not be analyzed by GPC.

Figure 1 compares the rate profiles for the fluorous and nonfluorous Grubbs catalysts **1** and **2**. There was little difference in activities (▲ vs ◆). Next, an identical reaction of **1** was conducted, but in the presence of 0.200 mL of PFMC (total volume, 0.900 mL), as sketched in Scheme 3A (top). As shown in Figure 2, the rate decreased slightly (◆ vs ▲), in contrast to the precedents described in the Introduction. Thus, a variant was investigated in which the PFMC phase was initially charged with **1** and added to a $CDCl_3$ solution of **3** (Scheme 3B, bottom). Now, a marked rate acceleration was observed, as illustrated in Figure 2 (■ vs ◆ or ▲).

This phenomenon was probed with related experiments. First, the order of addition of the phases was reversed ($CDCl_3$ solution of substrate added to the PFMC solution of **1**). As illustrated in Figure 2, the rate was unaffected (+ vs ■). In response to a reviewer suggestion, the catalyst was taken up in 50:50 v/v $CDCl_3$/PFMC (0.200 mL/0.200 mL), and a $CDCl_3$ solution of **3** was added (0.500 mL). As depicted in Figure 2, the rate appeared to be slightly faster than in the preceding two experiments (× vs +). This effect was reproducible. Possible

dx.doi.org/10.1021/cs200487j | ACS Catal. 2012, 2, 155−162

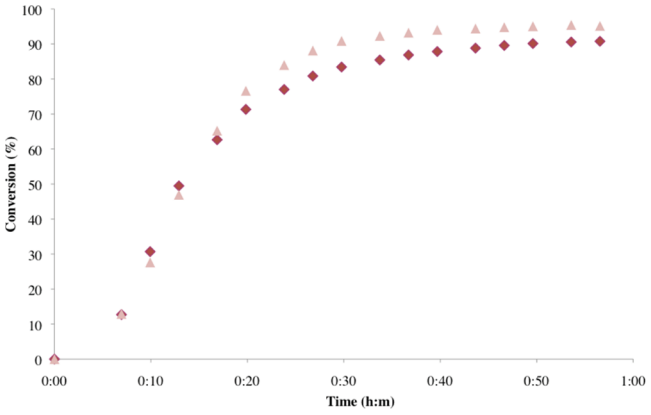


Figure 1. Rates of formation of polynorbornene in 0.700 mL of $CDCl_3$ ([**3**] = 0.0655−0.0658 M) at 25 °C with fluorous and nonfluorous catalysts: ▲ (pink), **1** (0.000 059 1 M); ◆ (red), **2** (0.000 060 6 M).

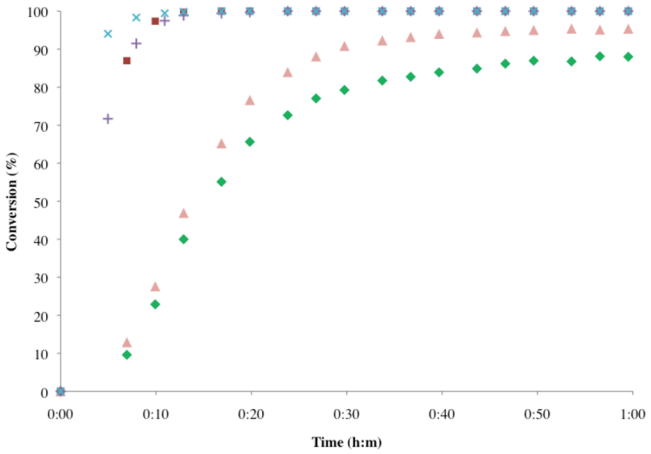


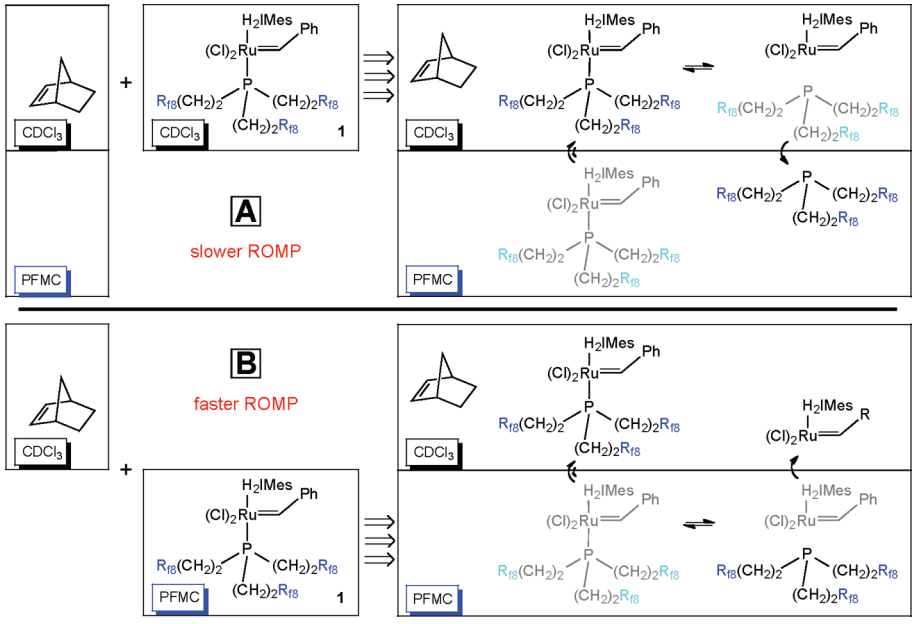
Figure 2. Rates of formation of polynorbornene in 0.700 mL of $CDCl_3$ ([**3**] = 0.0660−0.0655 M) at 25 °C with fluorous catalyst **1**: ▲ (pink), monophasic conditions with a $CDCl_3$ solution of **1** (0.000 041 4 mmol loading; 0.200 mL) added to a $CDCl_3$ solution of **3** (0.0459 mmol loading; 0.500 mL); ◆ (green), biphasic conditions with a $CDCl_3$ solution of **1** (identical loading; 0.200 mL) added to a $CDCl_3$ solution of **3** (0.0459 mmol loading; 0.500 mL) in the presence of PFMC (0.200 mL); ■ (red), biphasic conditions with a PFMC solution of **1** (0.000 045 4 mmol loading, 0.200 mL) added to a $CDCl_3$ solution of **3** (0.0462 mmol loading; 0.700 mL); + (purple), biphasic inverse addition conditions with a $CDCl_3$ solution of **3** (0.0459 mmol loading; 0.700 mL) added to a PFMC solution of **1** (0.000 041 2 mmol loading, 0.200 mL); × (blue), biphasic conditions with a $CDCl_3$/PFMC biphase mixture of **1** (0.000 041 2 mmol loading; 0.200 mL/0.200 mL) added to a $CDCl_3$ solution of **3** (0.0459 mmol loading; 0.500 mL).

rationales for all of the preceding rate trends are given in the Discussion section.

We next sought to probe the generality of the preceding trends with a second substrate, the 7-oxanorbornene-based *N*-butylsuccinimide **4** (Scheme 2).[20−24] Accordingly, rates of polymerization to **7** were analogously monitored in $CDCl_3$ (0.700 mL) using solutions that were 0.064−0.067 M in **4** and 0.000 378−0.000 388 M (0.378−388 mM) in fluorous and nonfluorous catalysts **1** and **2** (Figure 3). In this case, some differences were apparent, with **1** faster at lower conversions and **2** faster at higher conversions. Both trans and cis C=C linkages were evident, with the downfield signal in slight excess (~53.5:46.5, 6.08/5.78 ppm). Studies of related *N*-alkylsuccinimide polymers have established that the downfield signal corresponds to the trans isomer.[17] The rates were slower than with monomer **3**, as reflected by the higher catalyst loadings and lower conversions after 20−40 min.

Next, biphasic reactions were conducted with the fluorous catalyst **1**. First, a reaction identical to that in Figure 3 was carried out in the presence of PFMC (0.200 mL; total volume, 0.900 mL). As was the case with monomer **3**, there was no rate acceleration, as shown in Figure 4 (◆ vs ▲). Next, the PFMC

Scheme 3. Two Approaches to Phase Transfer Activation of ROMP with Catalyst 1[a]



[a]The bottom protocol gives dramatically faster polymerization than monophase conditions ($CDCl_3$).

dx.doi.org/10.1021/cs200487j | *ACS Catal.* 2012, 2, 155−162

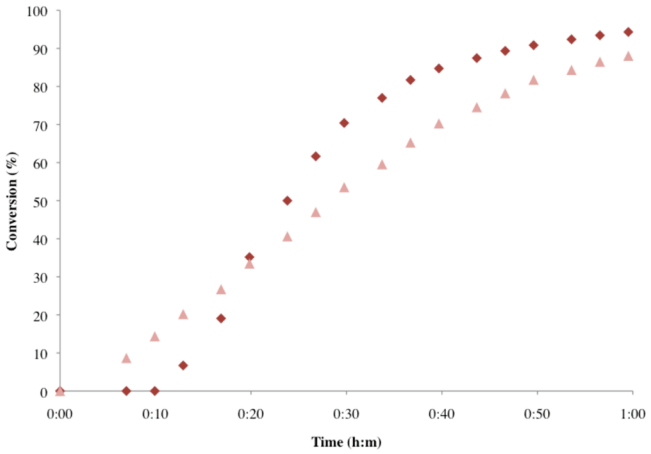


Figure 3. Rates of formation of the poly(oxanorbornene) derived from **4** in 0.700 mL of $CDCl_3$ ([**4**] = 0.0637−0.0671 M) at 25 °C with fluorous and nonfluorous catalysts: ▲ (pink), **1** (0.000 388 M); ◆ (red), **2** (0.000 379 M).

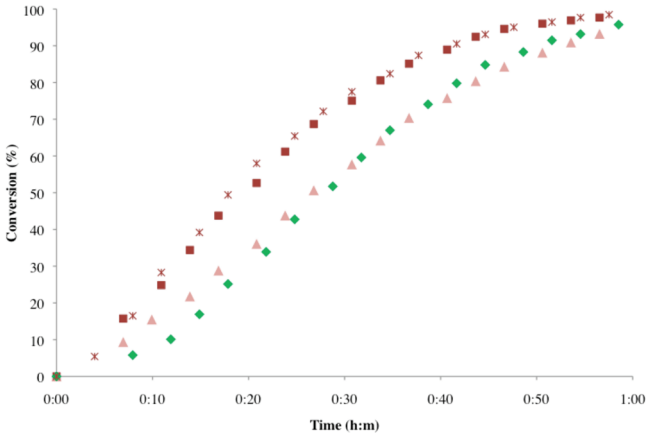


Figure 4. Rates of formation of the poly(oxanorbornene) derived from **4** in 0.700 mL of $CDCl_3$ ([**4**] = 0.0662−0.0671 M) at 25 °C with fluorous catalysts: ▲ (pink), monophasic conditions with a $CDCl_3$ solution of **1** (0.000 272 mmol loading; 0.200 mL) added to a $CDCl_3$ solution of **4** (0.0470 mmol loading; 0.500 mL); ◆ (green), biphasic conditions with a $CDCl_3$ solution of **1** (identical loading; 0.200 mL) added to a $CDCl_3$ solution of **4** (0.0470 mmol loading; 0.500 mL) in the presence of PFMC (0.200 mL); ■ and * (red), duplicate runs, biphasic conditions with a PFMC solution of **1** (0.000 271 mmol loading; 0.200 mL) added to a $CDCl_3$ solution of **4** (0.0463 mmol loading; 0.700 mL).

phase was initially charged with **1** and added to a $CDCl_3$ solution of **4**. A significant rate acceleration was again observed (■ vs ◆), although less dramatic than with **3**. All of the preceding results were repeated in duplicate or triplicate. Reproducibility was excellent, as exemplified by the additional data set in Figure 4 (* vs ■).

Larger-scale reactions were conducted in CH_2Cl_2 using higher catalyst loadings, as summarized in Table 1. The objective was to generate lower-molecular-weight polymers that would be more soluble in THF and therefore amenable to GPC analyses. Polynorbornene **6** was isolated in 99−96% yields (entries 1−3), whereas the more rubbery succinimide-containing **7** was isolated in 89−76% yields (entries 4−6). However, **6** can still be produced at acceptable rates at loadings as low as 0.0125 mol % **1**. Catalyst **1** also effected the polymerization of *endo,endo*-2,3-dicarbomethoxy-5-norbornene (**5**; Scheme 2) over the course of 16 h at 45 °C (0.49 mol % **1**; [**5**] = 0.19 M). No conversion was observed at room temperature. The molecular weight of the isolated polymer **8** was 14.5 × 10^4 g/mol (145 kDa), and the polydispersity was 1.68.

Molecular weight and polydispersity data for the polymers derived from **3** and **4** are summarized in Table 1. As shown in entries 1 and 2, the properties of **6** obtained using **1** under monophasic conditions and the biphasic conditions of Scheme 3B were similar, with molecular weights of 1.75−1.73 × 10^4 g/mol (17 kDa) and polydispersities ranging from 2.19 to 2.40. As shown in entries 4 and 5, there were much greater differences with **7** (2.86−6.84 × 10^4 g/mol and 1.84 vs 2.80). In each case, the nonfluorous catalyst **2** gave slightly lower polydispersities (entries 3 and 6).

Some preliminary experiments were conducted that bear on the above results. The monophasic polymerization of **3** by **1** (0.3 mol %) in CH_2Cl_2 (3.0 mL) was repeated, and PFMC (2.5 mL) was subsequently added. The mixture was poured into MeOH (5.0 mL) to precipitate the polynorbornene **6**. The PFMC phase was separated, and a CH_2Cl_2 solution of **3** was added. Although subsequent polymerization was slower, a 94% yield of **6** was isolated. Hence, a catalytically active fluorous ruthenium species, perhaps unreacted **1**, can partition into PFMC under biphasic workup conditions. Additional cycles were conducted as detailed elsewhere.[25] Although yields remained high, rate and other data indicated that recycling efficiencies were poor.[26] Data for the polymer obtained from the first cycle is presented in entry 7 of Table 1. Note that the higher monomer concentration and slightly lower catalyst loading afford a significantly higher polymer molecular weight and polydispersity.

DISCUSSION

The above data, including the key results in Figures 2 and 4, are consistent with the mechanism of catalyst activation sketched in Scheme 1 (bottom) and elaborated in Scheme 3. The locus of polymerization is the organic phase, with the orthogonal fluorous phase scavenging the phase labeled phosphine ligand. Such "phase transfer activation" has now also been established for organic/aqueous liquid/liquid biphase systems.[14] However, the orthogonal phase does not necessarily have to be a liquid, and liquid/solid biphase systems are under investigation.

Naturally, the active catalyst should have a very high affinity for the reaction phase, and the dissociated ligand, a very high affinity for the orthogonal phase. In Scheme 3, these are reflected by the black/gray shadings. The catalyst precursor **1** is soluble in both organic and fluorous phases but, as noted above, preferentially partitions into toluene in PFMC/toluene mixtures (partition coefficient 39.6:60.4). The equilibrium fraction in the more polar organic phases of PFMC/$CDCl_3$ and PFMC/CH_2Cl_2 mixtures is likely to be higher. In all of the above experiments, the volume of the organic phase is greater than that of the fluorous phase, which further biases the fraction of **1** in the organic phase.

This study has shown that much faster polymerization rates can be realized when **1** is initially dissolved in the orthogonal phase, as sketched in Scheme 3B. Prior to analysis, it is helpful to consider factors that might account for the absence of a rate enhancement using the previously established protocol in Scheme 3A. It is well-known that ROMP reactions of norbornenes can be effected with lower loadings of Grubbs' catalysts than the ring closing metathesis reactions studied

dx.doi.org/10.1021/cs200487j | ACS Catal. 2012, 2, 155−162

Table 1. Preparative Polymerization Conditions and Polymer Properties

entry	solvent system	catalyst	monomer/polymer	reaction time (min)	[monomer] (M)	catalyst loading (mol %)	$n_{monomer}/n_{catalyst}$	polymer yield (%)	MW (g/mol)	poly dispersity	T_g (°C)[a]	T_d (°C)[b]
1	CH_2Cl_2	**1**	**3/6**	180	0.065	0.60	166	99	1.75×10^4	2.19	59	466
2	CH_2Cl_2/PFMC (14.0/4.0 mL)[c]	**1**	**3/6**	180	0.065	0.59	169	97	1.73×10^4	2.40	61	472
3	CH_2Cl_2	**2**	**3/6**	180	0.065	0.60	167	97	8.97×10^3	2.17	57	470
4	CH_2Cl_2	**1**	**4/7**	180	0.066	0.57	176	84	2.86×10^4	1.84	138	482
5	CH_2Cl_2/PFMC (5.5/1.5 mL)[c]	**1**	**4/7**	180	0.066	0.54	185	89	6.84×10^4	2.80	135	477
6	CH_2Cl_2	**2**	**4/7**	180	0.066	0.55	183	76	4.12×10^4	1.54	139	478
7	CH_2Cl_2	**1**	**3/6**	60	0.53	0.34	295	92	1.03×10^6	6.68	60	

[a]The T_g value was taken as the inflection point of the DSC trace at a heating rate of 10 °C/min under N_2. [b]Calculated on the basis of the derivative curve of the TGA trace at the maximum rate of weight loss (heating rate 10 °C/min under N_2). [c]Biphasic reaction under the conditions of Scheme 3B.

earlier,[15−18,27,28] presumably due to strain relief in the binding or propagation steps (or both). If this were to translate into a sufficiently faster k_2 step in Scheme 1 (rending k_1 rate-determining), the overall rate would no longer be impacted by the presence of the fluorous phosphine. Alternatively, the diffusion of the fluorous phosphine across the phase boundary could be slow on the time scale of polymerization.

One rationale for the effectiveness of the protocol in Scheme 3B would involve a faster aggregate rate constant for the dissociation of the fluorous phosphine $(R_{f8}(CH_2)_2)_3P$ in PFMC *and* phase transfer of the resulting active catalyst $(H_2IMes)(Cl)_2Ru(=CHPh)$ into the organic phase. Perhaps this lipophilic species is more "destabilized" when generated in the fluorous phase than the fluorous phosphine when generated in an organic phase, accelerating phase transfer. In any case, more chains would be initiated than under monophasic conditions in $CDCl_3$, leading to more rapid consumption of monomer.

The comparable rate enhancement found when **1** was added as a PFMC/$CDCl_3$ biphasic mixture would have a related origin. In this case, **1** is predominantly in the $CDCl_3$ layer, but the endergonic equilibrium yielding $(H_2IMes)(Cl)_2Ru(=CHPh)$ and the fluorous phosphine will be shifted, since some of the latter will phase-transfer into the PFMC. When this mixture contacts the monomer, proportionally more chains will be initiated, leading to more rapid consumption. Importantly, propagation is much faster than initiation when Grubbs' second-generation catalyst **2** is employed for the ROMP of norbornenes under conventional conditions.[29]

Recently, several groups have observed that the solvent hexafluorobenzene promotes ring-closing metatheses, especially for highly substituted alkenes.[30−32] The mechanistic basis for this effect is not currently understood. Perfluorinated arenes are much more polar than perfluoroalkanes, and their lipophilicities are distinctly higher than their fluorophilicities;[1,13] hence, they are not considered fluorous solvents. Nonetheless, these observations underscore the breadth of solvent effects possible with ruthenium alkene metathesis catalysts. Additional types of "fluorine effects" upon metathesis rates have been observed.[33,34]

Other groups have conducted alkene metatheses in the presence of copper species and Lewis or Brønsted acids that are believed to bind the dissociated phosphine.[35−42] In some cases, rate enhancements have been noted, but catalyst deactivation is also sometimes accelerated. Related approaches involving ruthenium metathesis catalysts with functionalized pyridine ligands have been reported.[43]

Ruthenium alkylidene catalysts that contain triphenyl phosphine ligands tend to promote the ROMP of norbornene in a controlled manner.[27,28] In contrast, those that contain more basic ligands, such as tricyclohexyl phosphine, tend to polymerize norbornene in a nonliving manner, providing high-molecular-weight polymers with broad polydispersities. Accordingly, **2** has been previously shown to give polynorbornene derivatives with broad polydispersities.[15−17] The data in Table 1 indicate that the fluorous analog **1** is similar and does not function as a living catalyst. It also gives polymers with glass transition temperatures (T_g) nearly identical to that of **2** (Table 1).

In summary, this paper has extended the concept of "phase transfer activation" to ROMP reactions that use a fluorous analog of Grubbs' second generation alkene metathesis catalyst. It has also established that rate accelerations are possible when the orthogonal, as opposed to the reaction, phase is charged with the catalyst. We anticipate that these catalyst activation strategies will be general for a wide variety of reactions, phase combinations, and phase-labeled ligands, and extensions to alkene metatheses in organic/aqueous biphase systems will be reported in the near future.[14]

EXPERIMENTAL SECTION

General. All reactions were conducted under N_2 unless noted. Chemicals were treated as follows: PFMC (Oakwood or ABCR), distilled from P_2O_5; CH_2Cl_2, distilled from CaH_2; norbornene (**3**; Aldrich), *endo*,*endo*-2,3-dicarbomethoxy-5-norbornene (**5**; Aldrich), Grubbs' second-generation catalyst (**2**; Aldrich), ethyl vinyl ether (Aldrich), $CDCl_3$ (Cambridge Isotope or Aldrich), and other solvents were used as received. The oxanorbornene succinimide **4** (Scheme 2)[44] and fluorous catalyst $(H_2IMes)((R_{f8}(CH_2)_2)_3P)(Cl)_2Ru(=CHPh)$ (**1**, $R_{f8} = (CF_2)_7CF_3$))[11] were synthesized by literature procedures.

All ^1H NMR spectra were recorded on a Bruker Avance II 400 spectrometer in $CDCl_3$ and referenced to residual internal $CHCl_3$ (δ = 7.27 ppm). IR spectra were recorded on a Perkin-Elmer Spectrum One FTIR spectrometer with a Universal ATR sampling accessory. DSC and TGA data were recorded with Perkin-Elmer Jade and Perkin-Elmer Pyris 6 instruments, respectively. GPC analyses were carried out using a Viscotek GPC Max VE 2001 instrument with a Viscotek TDA 302 triple array detector and Viscotek Org Guard column with three (in series) mixed medium columns (LT5000L) at 35 °C and a flow

dx.doi.org/10.1021/cs200487j | ACS Catal. 2012, 2, 155−162

rate of 1.0 mL/min. A 12-point universal calibration standard calibration curve was recorded.

Rate Studies; General Conditions (Figures 1−4). $CDCl_3$ solutions were prepared using freshly opened bottles or ampules. Rates were measured by ^1H NMR at 25.0 °C (prethermostated probe) and spin rates of 20 Hz. The first spectrum was recorded after 5−7 min, and further spectra were recorded at 3 min intervals. Conversions were calculated from the integrals of the methylene hydrogen atoms of the polymers relative to those of the monomers (no other species were detected). The initial monomer concentration was kept constant (0.064−0.067 M; 0.700 mL).

Stock solutions of catalysts were freshly prepared in a glovebox, and stock solutions of substrates were prepared in air and stored in a refrigerator. The following are representative: (1) A vial (10 mL) was charged with norbornene (**3**; 0.0432 g, 0.459 mmol) and $CDCl_3$ (7.5008 g, measured gravimetrically; 5.0005 mL) to give a 0.0918 M solution. The vial was tightly closed and stored at 4 °C. (2) A vial (10 mL) was charged with **2** (0.0213 g, 0.0251 mmol) and $CDCl_3$ (7.8804 g, measured gravimetrically; 5.2536 mL), then an aliquot (0.1555 g, 0.1037 mL) was diluted with $CDCl_3$ (3.3145 g, measured gravimetrically; 2.2097 mL) to give a 0.000 214 M solution. (3) A vial (10 mL) was charged with **1** (0.0251 g, 0.0129 mmol) and PFMC (4.8291 g, measured gravimetrically; 2.702 mL), then an aliquot (0.1904 g, 0.1065 mL) was diluted with PFMC (3.9050 g, measured gravimetrically; 2.185 mL) to give a 0.000 222 M solution. (4) A vial (10 mL) was charged with **1** (0.0246 g, 0.0127 mmol) and $CDCl_3$ (4.0833 g, measured gravimetrically; 2.722 mL), then an aliquot (0.1525 g, 0.1017 mL) was diluted with $CDCl_3$ (3.2940 g, measured gravimetrically; 2.1936 mL) to give a 0.000 207 M solution.

Experiments in Figure 1. (A) (pink ▲) A NMR tube was charged with a stock $CDCl_3$ solution of **3** (0.500 mL, 0.0918 M; 0.0459 mmol) under N_2. The tube was closed and transferred to a NMR probe (25 °C), and a reference ^1H NMR spectrum was recorded. The tube was removed, charged with a stock $CDCl_3$ solution of **1** (0.200 mL, 0.000 207 M, 0.000 041 4 mmol) by syringe, shaken, and returned to the probe, and measurements were started. Initial concentrations: [**3**] = 0.0655 M; [**1**] = 0.0000591 M). (B) (red ◆) An NMR tube was similarly charged with a stock $CDCl_3$ solution of **3** (0.500 mL, 0.0921 M; 0.0460 mmol) and a stock $CDCl_3$ solution of **2** (0.200 mL, 0.000 212 M; 0.000 042 4 mmol). Initial concentrations: [**3**] = 0.0658 M; [**2**] = 0.000 060 6 M.

Experiments in Figure 2. (A) (pink ▲) This experiment is identical to A given for Figure 1. (B) (green ◆) A NMR tube was charged with a stock $CDCl_3$ solution of **3** (0.500 mL, 0.0918 M; 0.0459 mmol) and PFMC (0.200 mL) under N_2. The tube was closed and transferred to a NMR probe (25 °C), and a reference ^1H NMR spectrum was recorded. The tube was removed, charged with a stock $CDCl_3$ solution of **1** (0.200 mL, 0.000 207 M; 0.000 041 4 mmol) by syringe, shaken, and returned to the probe, and measurements were started. Initial concentrations: [**3**] = 0.0655 M; [**1**] = 0.000 0591 M (uncorrected for partitioning). (C) (red ■) A NMR tube was charged with a stock $CDCl_3$ solution of **3** (0.700 mL, 0.0660 M; 0.0462 mmol) under N_2. The tube was closed and transferred to a NMR probe (25 °C), and a reference ^1H NMR spectrum was recorded. The tube was removed, charged with a stock PFMC solution of **1** (0.200 mL, 0.000 227 M; 0.000 045 4 mmol), shaken, and returned to the probe, and measurements were started. Initial concentrations: [**3**] = 0.0660 M; [**1**], equivalent to that in B after partitioning. (D) (purple +) A NMR tube was charged with a PFMC stock solution of **1** (0.200 mL, 0.000 206 M; 0.000 041 2 mmol) in a glovebox (order of addition reversed from C). The tube was removed, charged with a stock $CDCl_3$ solution of **3** (0.700 mL, 0.0655 M; 0.0459 mmol), shaken, and placed in an NMR probe (25 °C), and measurements were started. Initial concentrations: [**3**] = 0.0655 M; [**1**], equivalent to that in B after partitioning. (E) (blue ×) A NMR tube was charged with a stock PFMC solution of **1** (0.200 mL, 0.000 206 M; 0.000 041 2 mmol) and $CDCl_3$ (0.200 mL) in a glovebox. The mixture was shaken and kept at room temperature for 30 min. The tube was removed, charged with a stock $CDCl_3$ solution of **3** (0.500 mL, 0.0918 M; 0.0459 mmol), shaken, and placed in an NMR probe (25 °C), and measurements were started. Initial concentrations: [**3**] = 0.0655 M; [**1**], equivalent to that in B after partitioning.

Experiments in Figure 3. (A) (pink ▲) A NMR tube was charged with a stock $CDCl_3$ solution of **4** (0.500 mL, 0.0940 M; 0.0470 mmol) under N_2. The tube was closed and transferred to a NMR probe (25 °C), and a reference ^1H NMR spectrum was recorded. The tube was removed, charged with a stock $CDCl_3$ solution of **1** (0.200 mL, 0.00136 M; 0.000 272 mmol) by syringe, shaken, and returned to the probe, and measurements were started. Initial concentrations: [**4**] = 0.0671 M; [**1**] = 0.000 388 M. (B) (red ◆) A NMR tube was similarly charged with a stock $CDCl_3$ solution of **4** (0.500 mL, 0.0893 M; 0.0446 mmol) and a stock $CDCl_3$ solution of **2** (0.200 mL, 0.001 33 M; 0.000 265 mmol). Initial concentrations: [**4**] = 0.0637 M; [**2**] = 0.000 379 M.

Experiments in Figure 4. (A) (pink ▲) This experiment is identical to A given for Figure 3. (B) (green ◆) A NMR tube was charged with a stock $CDCl_3$ solution of **4** (0.500 mL, 0.0940 M; 0.0470 mmol) and PFMC (0.200 mL) under N_2. The tube was closed and transferred to a NMR probe (25 °C), and a reference ^1H NMR spectrum was recorded. The tube was removed, charged with a stock $CDCl_3$ solution of **1** (0.200 mL, 0.001 36 M; 0.000 272 mmol) by syringe, shaken, and returned to the probe, and measurements were started. Initial concentrations: [**4**] = 0.0671 M; [**1**] = 0.000 388 M (uncorrected for partitioning). (C) (red ■ and purple *) A NMR tube was charged with a stock $CDCl_3$ solution of **4** (0.700 mL, 0.0662 M; 0.0463 mmol) under N_2. The tube was closed and transferred to a NMR probe (25 °C), and a reference ^1H NMR spectrum was recorded. The tube was removed, charged with a stock PFMC solution of **1** (0.200 mL, 0.001 36 M; 0.000 271 mmol), shaken, and returned to the probe, and measurements were started. Initial concentrations: [**4**] = 0.0662 M; [**1**], equivalent to that in B after partitioning.

Preparative Polymerizations of 3. (A) (monophasic, catalyst **1**) A vial (25 mL) was charged with **1** (0.0106 g, 0.005 46 mmol) and a magnetic stir bar in a glovebox, sealed with a septum-fitted screw cap, removed from the box, and placed on a magnetic stirrer set to 500 rpm. A stock CH_2Cl_2 solution of **3** (14 mL, 0.0647 M; 0.9058 mmol) was added by syringe via the septum. After 3 h, ethyl vinyl ether (0.5 mL) was added. After 0.5 h, the solution was transferred to a Schlenk tube, and the solvent was removed by oil pump vacuum. The residue was washed with MeOH (2 × 20 mL). The pinkish MeOH solution was discarded, and the precipitate was dried under vacuum (3 h) to give polynorbornene **6** (0.0851 g, 99%). (B) (monophasic, catalyst **2**) A reaction analogous to that in A was conducted with **2** (0.0046 g, 0.005 42 mmol) and a stock CH_2Cl_2 solution of **3** (14 mL, 0.0647 M; 0.9058 mmol). An

dx.doi.org/10.1021/cs200487j | ACS Catal. 2012, 2, 155−162

identical workup gave **6** (0.0823 g, 96.5%). (C) (biphasic, catalyst **1**) A reaction analogous to that in A was conducted, with **1** (0.0104 g, 0.005 36 mmol), PFMC (4.0 mL; added in the glovebox), and a stock CH_2Cl_2 solution of **3** (14 mL, 0.0647 M; 0.9058 mmol). An identical workup gave **6** (0.0831 g, 97%).

Preparative Polymerizations of 4. (A) (monophasic, catalyst **1**) A reaction analogous to that for **3** was conducted with **1** (0.0040 g, 0.002 06 mmol) and a stock CH_2Cl_2 solution of **4** (5.5 mL, 0.0660 M; 0.363 mmol). After the addition of ethyl vinyl ether (0.5 mL), the solution was stirred for 0.5 h and poured into MeOH (18 mL). After 15 h, a white rubbery precipitate had formed. The pinkish supernatant was removed by syringe and the residue was dried by oil pump vacuum (3 h) to give **7** (Scheme 2; 0.0671 g, 84%). (B) (monophasic, catalyst **2**) A reaction analogous to that in A was conducted with **2** (0.0023 g, 0.002 71 mmol) and a stock CH_2Cl_2 solution of **4** (7.5 mL, 0.0660 M; 0.495 mmol). An identical workup gave **7** (0.0833 g, 76%). (C) (biphasic, catalyst **1**) A reaction analogous to that in A was conducted, with **1** (0.0038 g, 0.001 96 mmol). PFMC (1.5 mL; added in the glovebox), and a stock CH_2Cl_2 solution of **4** (5.5 mL, 0.0660 M; 0.363 mmol). An identical workup gave **7** (0.0717 g, 89%).

Preparative Polymerization of 5. A round-bottom flask was charged with **1** (0.0055 g, 0.002 83 mmol, 0.49 mol %) and CH_2Cl_2 (2.0 mL) and fitted with a condenser. The mixture was heated (45 °C), and a solution of **5** (0.1197 g, 0.569 mmol) in CH_2Cl_2 (1.0 mL) was added (no air exclusion; [**5**] = 0.19 M). After 16 h, the mixture was cooled, and ethyl vinyl ether (0.020 mL, 0.209 mmol, 74 equiv) was added. After 0.5 h, the mixture was poured into vigorously stirring MeOH (5.0 mL). After 0.5 h, the white precipitate was collected by filtration, washed with MeOH (15.0 mL) and dried by oil pump vacuum (4 h) to give **8** (Scheme 2; 0.0840 g, 70%).

Fluorous Catalyst Recovery. (A) A round-bottom flask was charged with **3** (0.1504 g, 1.597 mmol) and CH_2Cl_2 (3.0 mL; [**3**] = 0.53 M). Catalyst **1** (0.0105 g, 0.00541 mmol, 0.34 mol %) was added with stirring (no air exclusion). After 1 h, PFMC (2.5 mL) was added, and the mixture was stirred for a few minutes and poured into vigorously stirring MeOH (5.0 mL). The fluorous phase was separated by syringe. After 0.5 h, the precipitated **6** (0.1384 g, 92%) was collected by filtration, washed with MeOH (15.0 mL), and dried by oil pump vacuum (4 h). The pinkish fluorous phase was reused in a second cycle. (B) A solution of **3** (0.1629 g, 1.730 mmol) in CH_2Cl_2 (5.0 mL, [**3**] = 0.35 M) was added to the flask containing the pinkish fluorous phase from the previous cycle with vigorous stirring (no air exclusion). After 1 h, the mixture was poured into vigorously stirring MeOH (5.0 mL). The fluorous phase was separated by syringe. After 0.5 h, the precipitated **6** (0.1526 g, 94%) was collected by filtration, washed with MeOH (15.0 mL), and dried by oil pump vacuum (4 h). The pinkish fluorous phase was similarly reused in two subsequent cycles.[25]

■ ASSOCIATED CONTENT

Supporting Information

Representative ^{1}H NMR data for the reactions in Figures 1 and 2. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mails: (J.A.G.) gladysz@mail.chem.tamu.edu; (H.S.B.) bazzi@tamu.edu.

■ ACKNOWLEDGMENTS

We thank the Qatar National Research Fund for support (Project Number 08-607-1-108). This paper is dedicated to Dr. Christian Bruneau (Université de Rennes), a ruthenium chemist par excellence, on the occasion of his 60th birthday.

■ REFERENCES

(1) Yoshida, J.-i.; Itami, K. *Chem. Rev.* **2002**, *102*, 3693.
(2) Shaughnessy, K. H. *Chem. Rev.* **2009**, *109*, 643.
(3) *Handbook of Fluorous Chemistry*; Gladysz, J. A., Curran, D. P., Horváth, I. T., Eds.; Wiley/VCH: Weinheim, 2004.
(4) Pinault, N.; Bruce, D. W. *Coord. Chem. Rev.* **2003**, *241*, 1.
(5) Snelders, D. J. M.; van Koten, G.; Gebbink, R. J. M K. *Chem.—Eur. J.* **2011**, *17*, 42.
(6) Gudmunsen., D.; Hope, E. G.; Paige, D. R.; Stuart, A. M. *J. Fluorine Chem.* **2009**, *130*, 942.
(7) Thompson, L. A. *Curr. Opin. Chem. Biol.* **2000**, *4*, 324.
(8) Sanford, M. S.; Love, J. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **2001**, *123*, 6543.
(9) Love, J. A.; Sanford, M. S.; Day, M. W.; Grubbs, R. H. *J. Am. Chem. Soc.* **2003**, *125*, 10103.
(10) Correa da Costa, R.; Gladysz, J. A. *Chem. Commun.* **2006**, 2619.
(11) Correa da Costa, R.; Gladysz, J. A. *Adv. Synth. Catal.* **2007**, *349*, 243.
(12) Alvey, L. J.; Rutherford, D.; Juliette, J. J. J.; Gladysz, J. A. *J. Org. Chem.* **1998**, *63*, 6302.
(13) Gladysz, J. A.; Emnet, C.; Rábai, J. Partition Coefficients involving Fluorous Solvents. In *Handbook of Fluorous Chemistry*; Gladysz, J. A., Curran, D. P., Horváth, I. T., Eds.; Wiley/VCH: Weinheim, 2004; pp 56−100.
(14) Xi, Z.; Bazzi, H. S.; Gladysz, J. A. *Org. Lett.* **2011**, *13*, 6188.
(15) Bielawski, C. W.; Grubbs, R. H. *Angew. Chem., Int. Ed.* **2000**, *39*, 2903. *Angew. Chem.* **2000**, *112*, 3025.
(16) Bielawski, C. W.; Benitez, D.; Morita, T.; Grubbs, R. H. *Macromolecules* **2001**, *34*, 8610.
(17) Vargas, J.; Colin, E. S.; Tlenkopatchev, M. A. *Eur. Polym. J.* **2004**, *40*, 1325 (for the generation of **6** using **2**, see the first entries in Tables 2−4 therein).
(18) See also: Buchmeiser, M. R.; Ahmad, I.; Gurram, V.; Kumar, P. S. *Macromolecules* **2011**, *44*, 4098.
(19) Interestingly, our ratios are approximately reversed from those in reference 16; see Supporting Information Figure S1.
(20) For earlier reports of ROMP polymers generated from this monomer, see refs 21−24 and Bazzi, H. S.; Bouffard, J.; Sleiman, H. F. *Macromolecules* **2003**, *36*, 7899.
(21) Metera, K. L.; Sleiman, H. *Macromolecules* **2007**, *40*, 3733.
(22) Lo, P. K.; Sleiman, H. F. *J. Am. Chem. Soc.* **2009**, *131*, 4182.
(23) Gabriel, G. J.; Maegerlein, J. A.; Nelson, C. F.; Dabkowski, J. M.; Eren, T.; Nüsslein, K.; Tew, G. N. *Chem.—Eur. J.* **2009**, *15*, 433.
(24) Sankaran, N. B.; Rys, A. Z.; Nassif, R.; Nayak, M. K.; Metera, K.; Chen, B.; Bazzi, H. S.; Sleiman, H. F. *Macromolecules* **2010**, *43*, 5530.
(25) Correa da Costa, R. doctoral thesis, Universität Erlangen-Nürnberg, 2006.
(26) Gladysz, J. A. The Experimental Assay of Catalyst Recovery: General Concepts. In *Recoverable and Recyclable Catalysts*; Benanglia, M., Ed; Wiley-Blackwell: Oxford, England, 2009; pp 1−22.
(27) Black, G.; Maher, D.; Risse, W. Living Ring-Opening Olefin Metathesis Polymerization. In *Handbook of Metathesis*; Grubbs, R. H., Ed.; Wiley/VCH: Weinheim, 2003; Vol. 3; pp 2−71; (see especially section 3.2.4.8).
(28) Bielawski, C. W.; Grubbs, R. H. *Prog. Polym. Sci.* **2007**, *32*, 1.

(29) Buchowicz, W.; Holerca, M. N.; Percec, V. *Macromolecules* **2001**, *34*, 3842.
(30) Rost, D.; Porta, M.; Gessler, S.; Blechert, S. *Tetrahedron Lett.* **2008**, *49*, 5968.
(31) Samojłowicz, C.; Bieniek, M.; Zarecki, A.; Kadyrov, R.; Grela, K. *Chem. Commun.* **2008**, 6282.
(32) Grandbois, A.; Collins, S. K. *Chem.—Eur. J.* **2008**, *14*, 9323.
(33) Ritter, T.; Day, M. W.; Grubbs, R. H. *J. Am. Chem. Soc.* **2006**, *128*, 11768.
(34) Siano, V.; D'Auria, I.; Grisi, F.; Constable, C.; Longo, P. *Cent. Eur. J. Chem.* **2011**, *9*, 605.
(35) Morgan, J. P.; Grubbs, R. H. *Org. Lett.* **2000**, *2*, 3153.
(36) Lynn, D. M.; Mohr, B.; Grubbs, R. H.; Henling, L. M.; Day, M. W. *J. Am. Chem. Soc.* **2000**, *122*, 6601.
(37) Sanford, M. S.; Henling, L. M.; Grubbs, R. H. *Organometallics* **1998**, *17*, 5384.
(38) Dias, E. L.; Nguyen, S. T.; Grubbs, R. H. *J. Am. Chem. Soc.* **1997**, *119*, 3887.
(39) Huang, J.; Schanz, H.-J.; Stevens, E. D.; Nolan, S. P. *Organometallics* **1999**, *18*, 5375.
(40) Rivard, M.; Blechert, S. *Eur. J. Org. Chem.* **2003**, 2225.
(41) See also: Garber, S. B.; Kingsbury, J. S.; Gray, B. L.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2000**, *122*, 8168.
(42) See also: Bieniek, M.; Samojłowicz, C.; Sashuk, V.; Bujok, R.; Śledź, P.; Lugan, N.; Lavigne, G.; Arlt, D.; Grela, K. *Organometallics* **2011**, *30*, 4144.
(43) Dunbar, M. A.; Balof, S. L.; Roberts, A. N.; Valente, E. J.; Schanz, H.-J. *Organometallics* **2011**, *30*, 199 and earlier work cited therein.
(44) Clevenger, R. C.; Turnbull, K. D. *Synth. Commun.* **2000**, *30*, 1379.