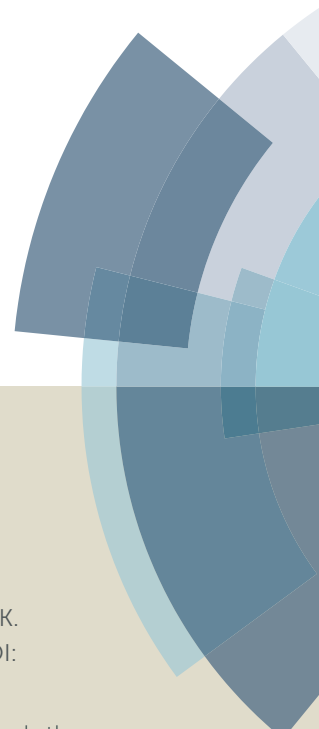


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Ring Opening Metathesis Polymerization of Cyclopentene Using a Ruthenium Catalyst Confined by a Branched Polymer Architecture

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Multi-arm polystyrene stars functionalized with Grubbs-type catalysts in their cores were synthesized and used for the ring-opening metathesis polymerization (ROMP) of cyclopentene. The spatial confinement of the catalytic sites and the nanoscale phase separation between polystyrene and the growing polypentenamer chains lead to a dramatic inhibition of the ROMP termination and chain transfer steps. Consequently, cyclopentene polymerizations proceeded fast and with a high degree of conversion even in air. The Grubbs second generation catalyst was oxidatively inactivated under the same conditions. In contrast to conventional small-molecule catalysts, the ultimate degree of conversion of cyclopentene monomer and the polydispersity of the product polypentenamer are not affected by the temperature. This indicates that spatial confinement of the catalyst resulted in a significant change in the activation parameters for the alkene metathesis ring-opening.

One of the reasons for the exquisite specificity and selectivity of enzymes is the isolation of their active sites from bulk solvent and other components of the cellular milieu. Only a few molecules of substrate, often just a single one, can approach the active site at the same time. The difference in chemical behavior between large ensembles of molecules and ultra-small sets including just a few can be dramatic.^{1,2} Such a difference is most pronounced for processes which involve competition between intermolecular and intramolecular pathways.

The principles of site isolation and confinement have been utilized in numerous chemist-designed catalytic systems.^{3,4} A variety of (meso)porous materials,^{5,6} metal-organic^{7,8} and

organic frameworks,⁹ supramolecular hosts,^{10,11} micellar assemblies,¹² and polymeric materials^{13,14} have been used to modulate reactivity and catalysis. An important class of processes which would be strongly affected by confinement of the acting catalyst or reactants are ring-closing and ring-opening reactions. For an equilibrium ring-closing/ring-opening process, confinement of the catalyst could result in an otherwise-unattainable reactivity.

Polyalkenamers, unsaturated polymers produced via ring-opening of low-strain cyclic alkenes, are highly desirable materials due to their mechanical and blending properties.¹⁵ These polymers have primarily been accessed via molybdenum- and tungsten-based ring-opening metathesis polymerization (ROMP) catalysts.^{16–20} Many of these catalytic systems are highly Lewis-acidic, require co-catalysts and activators, and lead to side reactions.²¹ Ruthenium-based catalysts are often better defined and more stable.^{21,22} However, the completely reversible nature of Ru-catalyzed polymerizations makes the reactions highly sensitive to temperature and monomer concentrations^{22,23} (the same holds true for other reversible ROMP processes).^{24,25} Ruthenium can be coerced to polymerize low-strain monomers through the judicious choice of ligands.^{26–28} In contrast to this tried and true approach, we envisioned that the spatial confinement of archetypal Grubbs-type Ru complexes²⁹ could result in impaired accessibility of the metal centers by the ROMP product. The local breaking of the monomer-polymer equilibrium shall consequently lead to a different polymerization outcome.

Supported metathesis catalysts for ROMP have been reported before.^{30,31} Here, we describe a Grubbs-type alkene metathesis catalyst that is covalently anchored in the core of a globular star polymer. This type of catalyst support will not create a significant diffusion barrier for small molecules. However, the nanoenvironment surrounding the Ru sites is spatially hindered and has different local properties compared to the bulk solvent. The star polymer-confined catalyst is capable of efficient ROMP of an unstrained monomer, cyclopentene, under the conditions where an analogous small-molecule ruthenium complex is completely inactive.

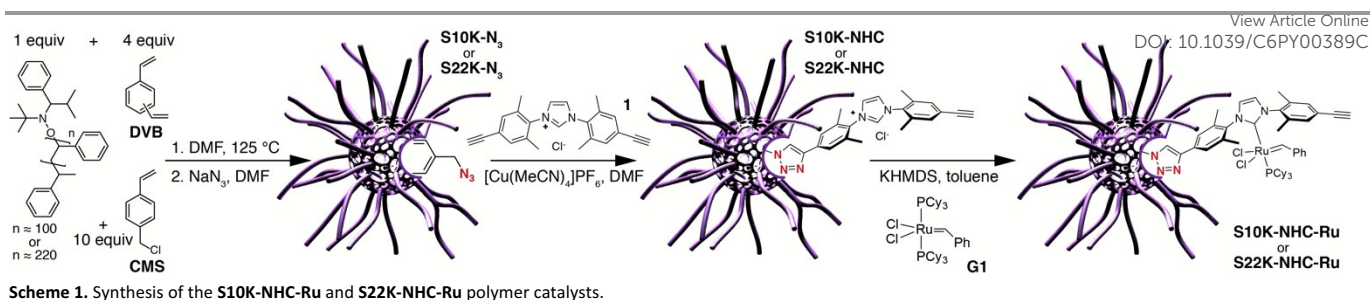
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We prepared two functional star polymer supports using a close adaptation of a previously reported arm-first strategy.^{32, 33}

Linear polystyrene macroinitiators with $M_n \sim 9.7$ kg/mol and 22 kg/mol were synthesized via nitroxide-mediated controlled radical polymerization.³⁴ The macroinitiators were used to initiate copolymerizations of divinylbenzene (DVB) and chloromethylstyrene (CMS) at a 1/4/10 macroinitiator:DVB:CMS feed ratio (Scheme 1), and the resulting Cl-functionalized star polymers **S10K-Cl** and **S22K-Cl** were purified by fractional precipitation. Static light scattering analysis established the M_w to be 313 kg/mol for **S10K-Cl**, and 270 kg/mol for **S22K-Cl**. The number of Cl groups per star as estimated by elemental analysis was ~ 160 for **S10K-Cl**, and ~ 54 for **S22K-Cl**. This suggests that the degree of polymerization of the cores of the star polymers is comparable to that of just 1-2 linear macroinitiator chains, and the number of arms per star is ~ 30 for **S10K-Cl**, and ~ 10 for **S22K-Cl**. The lower M_w and the smaller number of arms for the **S22K-Cl** star are dictated by the larger radius of gyration of the parent macroinitiator.

As the M_w of the **S10K** and **S22K** star polymers are similar, it is evident that the more voluminous core of the **S10K** polymer represents a larger fraction of its total molecular volume. Thus, its core is more flexible and not as isolated from the bulk solvent as compared to the **S22K** star. This consideration was supported by atomic force microscopy (AFM) imaging of the polymers (Figures S28 and S29, ESI). The **S22K-Cl** star polymer presented a substantially particulate morphology, with each polymer species being a distinct object on the substrate. In contrast, the **S10K-Cl** star aggregated into a network-like arrangement.

The Cl-functionalized star polymers were reacted with NaN_3 in DMF to produce the “clickable” **S10K-N₃** and **S22K-N₃** polymers. This substitution had no effect on the observed hydrodynamic diameter of the polymers as estimated by dynamic light scattering (DLS) (Table S2, entries 3 and 4, and Figures S20 and S22, ESI). The $-\text{N}_3$ star polymers were then coupled with an alkyne-functionalized N-heterocyclic carbene (NHC) precursor **1** using copper-catalyzed azide-alkyne cycloaddition (CuAAC) chemistry (Scheme 1).^{35, 36} Compound **1** proved to be sensitive to amine bases commonly used to mediate Cu speciation in CuAAC reactions. Thus, a base-free protocol with $[\text{Cu}(\text{MeCN})_4]\text{PF}_6$ as a Cu source was used throughout for the coupling of **1** to the polymers. The progress of the CuAAC reactions could be conveniently monitored through the disappearance of the characteristic $-\text{N}_3$ absorption band in the IR spectra of the polymers (2097 cm^{-1}).

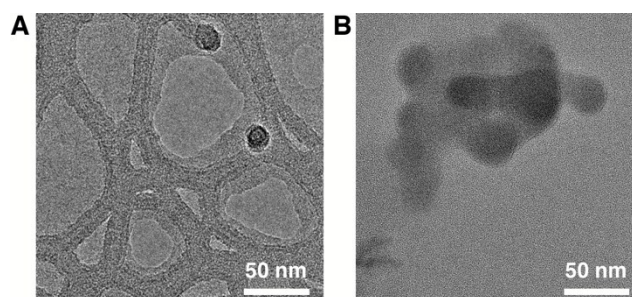


Figure 1. TEM images of (A) **S10K-NHC-Ru** and (B) **S22K-NHC-Ru**. Images obtained in dry state with no staining.

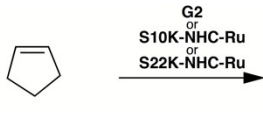
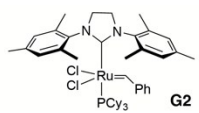
Both the **S10K-N₃** and **S22K-N₃** polymers reacted smoothly with the conversion of all the $-\text{N}_3$ groups. As NHC precursor **1** features two alkyne groups, it is possible that some of them remained unreacted. While we could not observe any discernible signals that could be attributed to alkynes in either IR or NMR spectra of the polymers, we believe this is due to the low abundance of the alkynes rather than their total absence. The presence of the small number of alkynes should not be detrimental to the subsequent experiments.

The CuAAC functionalization resulted in an increase of the apparent hydrodynamic diameters of the stars. This increase was modest for the **S22K** star (Table S2, entries 4 and 6, ESI). The analysis of intensity and volume size distributions (Figures S22 and S23, ESI) revealed that the size increase could primarily be attributed to the formation of a relatively small number of larger species, while the size of the majority population remained relatively unaffected. In contrast, the apparent hydrodynamic diameter of the **S10K** star increased dramatically after the CuAAC coupling (Table S2, entries 3 and 5, ESI). This increase was uniform across the entire population (Figures S20 and S21, ESI), suggesting a major change in the topology of the star polymer. This dramatic difference in behavior can be readily explained by the relatively lower degree of isolation of the cores of the **S10K** star as compared to the **S22K** analog. We expect that the more voluminous **S10K** cores are not as protected by the shorter linear arms, and have a higher flexibility and propensity to expand. It is important to mention that in our earlier work,³³ we did not observe a significant increase in the size of the **S10K** star after CuAAC functionalization with a more sterically-hindered, 2,6-diisopropyl analog of the NHC precursor **1**. The CuAAC protocol we used previously is different, as is the reactivity of the alkyne groups of the two NHC precursors. Thus, the two **S10K**

Table 1. ROMP reactions of cyclopentene with **G2**, **S10K-NHC-Ru** and **S22K-NHC-Ru** catalysts.

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entry	catalyst ^a	time [h]	air/Ar	temp. [°C]	conversion [%] ^b	M _n [kDa] ^c	M _w [kDa] ^c	PDI
1	G2	0.5	Ar	20	78	33	48	1.48
2	G2	20	Ar	20	78		gel	
3	G2	0.5	air	20	0	-	-	-
4	G2	20	air	20	1	-	-	-
5	S22K-NHC-Ru	0.5	air	20	8	41	64	1.56
6	S22K-NHC-Ru	20	air	20	67	73	120	1.64
7	S22K-NHC-Ru	0.5	air	35	48	41	64	1.56
8	S22K-NHC-Ru	20	air	35	66	60	92	1.54
9	S22K-NHC-Ru	0.5	Ar	20	27	140	220	1.60
10	S22K-NHC-Ru	20	Ar	20	84	160	300	1.80
11	S10K-NHC-Ru	0.5	air	20	8	20	25	1.27
12	S10K-NHC-Ru	20	air	20	28	43	76	1.76
13	S10K-NHC-Ru	0.5	air	35	-		gel	

^a Loading was 0.028 mol % for polymer catalysts, and 0.027 mol % for **G2** based on Ru. ^b Determined by ¹H NMR. ^c Determined by SEC in CHCl₃ (calibration performed against linear polystyrene).

star polymers likely have different degrees of cross-linking with di-triazole bridges, which results in differences in their topologies and hydrodynamic diameters.

The **S10K-NHC** and **S22K-NHC** polymers were reacted with first generation Grubbs catalyst (**G1**) after the activation of NHC moieties with potassium bis(trimethylsilyl)amide in toluene. We do not expect the small number of 4-aryl-1,2,3-triazoles present to interfere with the metalation step, as these moieties are weak-binding ligands for late transition metals, not competitive with (alkyl)phosphines or NHCs.³⁷ The extent of Ru functionalization was estimated by inductively-coupled plasma optical emission spectroscopy (ICP-OES) to be 0.18 and 0.19 mmol/g for **S10K-NHC-Ru** and **S22K-NHC-Ru**, respectively. Thus, the **S10K** star incorporates 0.35 equiv. of Ru, and the **S22K** star incorporates 0.95 equiv. Ru per each equiv. of the initial -Cl moiety. We attribute the lower efficiency of functionalization for the **S10K** star polymer to the higher flexibility of its core, which allows for more extensive cross-linking. Thus, comparatively fewer NHC moieties are available to bind Ru, and it is likely the inner core of **S10K-NHC** is not as accessible as it is in **S22K-NHC**. The steric bulk of the Ru complex is clearly significant, since the metalation step resulted in a significant increase in the hydrodynamic diameters of both **S10K** and **S22K** polymers (Table S2, entries 7 and 8, ESI). This increase in size was uniform across populations (Figures S22 and S23, ESI). Transmission electron microscopy (TEM) images of **S10K-NHC-Ru** and **S22K-NHC-Ru** obtained without a contrast agent revealed dense, roughly spherical objects with diameters of ~20-25 nm (Figure 1). This is smaller than the apparent hydrodynamic diameters of the polymers estimated by DLS, or the sizes observed for the -Cl

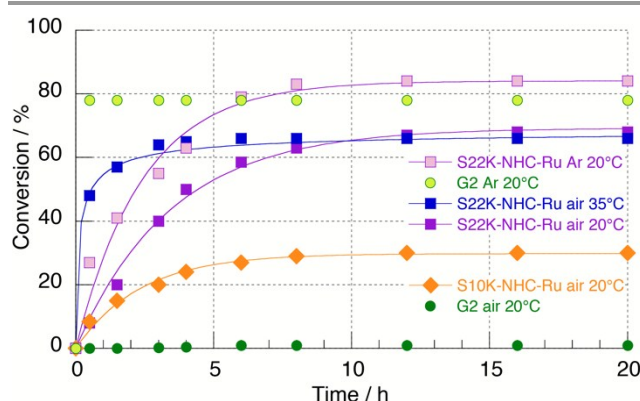


Figure 2. Conversion of cyclopentene as a function of time for different catalysts and conditions. Fit lines are included for readability only.

star polymers by AFM (Figures S28 and S29, SI). We assume the dense objects to be the ruthenium-functionalized cores of the stars. The polystyrene coronas, which spread on the substrate, lack sufficient electron density to be readily discernible by TEM. Through the entire sequence of functionalization steps, the distribution of the hydrodynamic diameters remained unimodal and narrow for both polymers, and full dispersibility was retained.

We used the Ru-functionalized star polymers, as well as the small-molecule **G2** catalyst³⁸ to initiate ROMP reactions of cyclopentene. The nature of the NHC ligands in **G2** (saturated backbone) and our star polymers (imidazolium) is different. However, both types of Ru complexes have comparable activity for the polymerization of low-strain monomers.³⁹ All the polymerizations were performed in toluene using constant Ru loading (0.028 mol %) and cyclopentene concentration

(2.52 M). The progress of the reactions was monitored by ^1H NMR. Aliquots were sampled at intervals, quenched with ethyl vinyl ether, and diluted with CDCl_3 for analysis. When the reaction was performed in an Ar-filled glovebox in a rigorously degassed solvent, we found the activity of the **G2** catalyst to be in line with previous reports. The ultimate, equilibrium-state monomer conversion of 78% was achieved before the first aliquot was collected at 30 minutes (Table 1, entry 1, and Figure 2). While there was no further change in monomer conversion, the polypentenamer formed a soft gel after several hours. When the same ROMP reaction was attempted in air in non-degassed toluene, only a trace amount of polypentenamer could be detected even after 20 h (Table 1, entries 3 and 4, and Figure 2). This finding was unexpected as the **G2** catalyst is exceptionally stable to oxidation.⁴⁰ We assume that an (alkyl)alkylidene Ru complex, the product of the ring-opening of cyclopentene with **G2**, is significantly more labile towards O_2 than the parent catalyst.

In contrast with the small-molecule catalyst **G2**, both the **S10K-NHC-Ru** and **S22K-NHC-Ru** readily catalyzed ROMP of cyclopentene even without any special precautions to exclude O_2 . Polymerizations catalyzed by the **S10K** star proceeded slower and with lower ultimate conversion of the monomer (28%) than the reactions catalyzed by the **S22K** star (67%) (Figure 2). The evolution of both reactions resulted in an increase of the M_w of the polypentenamer product (Table 1, entries 5–8). The ultimate degree of polymerization achieved in the **S10K** reaction (Table 1, entry 6) was lower than that in the **S22K** reaction (Table 1, entry 8). At the same time, the increase in PDI over time was more pronounced for the reaction catalyzed by **S10K**. Both reaction mixtures became more viscous as the polymerizations progressed, the viscosity increase being more pronounced for the **S10K** star.

These observations indicate that the star polymer environments inhibit both the inter/intramolecular chain transfers, and chain termination through irreversible oxidative deactivation of Ru catalytic sites. As the cores of the **S10K** stars are more flexible and accessible than those of **S22K** stars, the probability of intramolecular chain transfer or catalyst back-biting is higher for the **S10K-NHC-Ru** catalyst. Likewise, the probability of intermolecular chain transfers is higher for the **S10K** stars, as their cores are more permeable by external polypentenamer molecules. Thus, a higher degree of polymerization and lower PDI are attained in the **S22K**-catalyzed reactions than in **S10K**-catalyzed ones (Table 1, entries 6 and 12). For the same reason, **S22K**-catalyzed reactions reach higher monomer conversion. The ring-opening polymerization is faster when the chain transfer steps are inhibited, and is more competitive with the oxidative deactivation of Ru sites. Furthermore, it is likely that the cores of **S22K-NHC-Ru** are better isolated from ambient O_2 . The comparatively higher viscosity of the **S10K** reactions, even though these reactions result in lower degrees of polymerization and monomer conversion than the **S22K** reactions, is readily explained by the inter-star entanglement by the growing polypentenamer chains.

When the polymerization catalyzed by **S22K-NHC-Ru** was

performed at an elevated temperature of 35°C , the same ultimate monomer conversion was reached as at 20°C , but the reaction was significantly faster (Figure 2 and Table 1, entries 6 and 8). The increase in temperature resulted in an improvement in the PDI of the polypentenamer product, and only a slight decrease in ultimate degree of polymerization. For the polymerization catalyzed by the **S10K-NHC-Ru** at 35°C , we were unable to determine the degree of monomer conversion and degree of polymerization due to quick, almost instantaneous gelation. As the higher temperature makes the **S10K** polymer cores even more accessible to the growing polypentenamer chains. The double bonds on the chains form alkylidene complexes with the core-bound Ru sites, and the stars rapidly get cross-entangled and lose solubility.

These are striking observations, as the thermodynamic parameters previously reported²³ for the ROMP of cyclopentene with **G2** ($\Delta H = -5.6 \text{ kcal mol}^{-1}$, and $\Delta S = -18.5 \text{ cal mol}^{-1} \text{ K}^{-1}$) strongly bias the **G2**-initiated reactions towards lower conversion and degree of polymerization at higher temperatures. ROMP reactions initiated by the conventional $\text{WCl}_6/\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}_2$ system also result in higher monomer conversions and proceed significantly faster at lower temperatures.¹⁷ Thus, confinement of the **G2**-like Ru sites in the cores of **S22K** and **S10K** star polymers has largely the same impact on ROMP of cyclopentene as decreasing the temperature of the local environment around the operational catalyst.

Finally, we performed the ROMP reaction initiated by **S22K-NHC-Ru** in an Ar-filled glovebox in degassed solvent. The reaction proceeded faster than it did under aerobic conditions (Figure 2), and resulted in both higher degree of polymerization and monomer conversion (Table 1, entries 6 and 10). This was to be expected, as there can be no oxidative deactivation of Ru sites under rigorously anaerobic conditions. The PDI of polypentenamer product in the anaerobic reaction after 20 h was higher than that under aerobic conditions. This is due to irreversible deactivation of Ru sites by O_2 in the latter case, and the resultant cessation of all chain transfer reactions. These chain transfer processes are completely unchecked for the small-molecule catalyst **G2**, and prolonged reactions initiated by it formed soft, swellable gels. The ultimate monomer conversion attained with **S22K-NHC-Ru** (84%) was slightly higher than that for **G2** (Table 1, entries 10 and 2).

The fraction of *trans* bonds in polypentenamer products was determined by quantitative ^{13}C NMR. We found it to be 85% for all three catalysts in the study: the **S10K-NHC-Ru** and **S22K-NHC-Ru** star polymers and **G2** small molecule. This suggests that while the activation parameters of the cyclopentene ROMP reaction have changed due to the nanoscale effect of spatial confinement, the molecular-scale Chauvin mechanism of alkene metathesis^{41, 42} remained largely unaffected by the star polymer support and retained its intrinsic chemoselectivity.

After the polymerization of cyclopentene with **S22K-NHC-Ru** under aerobic conditions, spontaneous separation of phases occurred when the solution was kept overnight at -18°C . Viscous, transparent supernatant contained only the

polypentenamer product, while the star polymer precipitated. The supernatant was then decanted, and polypentenamer precipitated in acetone. ICP-OES analysis established that Ru content in polypentenamer obtained this way was extremely low (below the detection limit of our instrument). This is a highly desirable property for a Ru alkene metathesis catalytic system.⁴³ As no chain-terminating agent was added in this case, we attribute the release of Ru-free polypentenamer product to the oxidation of Ru sites and chain transfer.

Conclusions

In conclusion, we have synthesized star polystyrenes functionalized with Grubbs-type alkene metathesis catalysts in their cores and used them for the catalysis of ROMP of cyclopentene, a low-strain cyclic monomer. The spatial confinement of the Ru sites and the nanoscale phase separation between polystyrene and the growing polypentenamer chains led to a dramatic inhibition of key chain transfer and termination steps of ROMP. Thus, through spatial isolation, we attained new selectivity from an old catalyst.⁴⁴ The ROMP reactions with catalytic star polymers proceeded even under aerobic conditions, when the traditional Grubbs **G2** catalyst was completely deactivated. The activity of the catalytic polymers and the properties of polypentenamer products were found to be dependent on the star composition and topology. Finally, we have demonstrated easy and spontaneous separation of the nominally soluble catalyst from the ROMP reaction product. Further studies of spatially confined catalysts for entropy-challenged and entropy-limited transformations are ongoing in our laboratories.

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