

Synthesis of Recyclable Tire Additives via Equilibrium Ring Opening Metathesis Polymerization

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ABSTRACT. Linear *trans*-polypentenamers are highly desired materials among the synthetic tire additives due to their comparable physical properties to natural rubber. *Trans*-polypentenamer can be prepared by equilibrium ring-opening metathesis polymerization (ROMP) using well-defined ruthenium catalyst systems. This unique feature of the equilibrium polymerization reaction opens a way for the synthesis of durable, environmentally benign elastomers where polymers including synthetic tire additives can be synthesized and readily recycled using the same transition metal catalyst system.

The addition of silica fillers significantly improves the physical properties of the composite materials in comparison to the use of polymeric material. It is also known that the structural effects and the polymer-filler surface interaction are of prime importance. Herein, we report on the synthesis of silica filler compatible recyclable polypentenamer co-polymers *via* equilibrium ROMP of cyclopentene **1** and 4-(triethoxy)siloxy cyclopentene **11**. It has been demonstrated that polypentenamer tire additive can be synthesized *via* equilibrium ROMP affording polymers with high yields (> 80%) at 0 °C and can be readily depolymerized at 40 °C and/or under diluted condition using the same metathesis catalyst systems. Furthermore, the polypentenamer can also be synthesized in neat at room temperature and at very low (10^5) monomer/catalyst ratio. This methodology is based on the synthesis of polyolefins utilizing ruthenium based metathesis catalyst *via* equilibrium ROMP of cyclopentenes and their silylated derivatives.

INTRODUCTION

Synthetic rubbers such as polypentenamers are highly relevant materials due to their exceptional physical and mechanical properties.¹ Polypentenamer elastomers, especially their functionalized derivatives are of great industrial interest. In particular *trans*-polypentenamer is a remarkable polymer that has similar physical properties to natural rubber.² Tires are usually composed from different rubber compounds, such as carbon black and/or silica, clay and different chemicals and minerals. They also contain steel and textile to improve the mechanical and physical properties.³ Typically 45 – 47% of a tire is composed of polymeric materials and 22% is made from carbon black and/or precipitated silica. The remaining 30% is steel and fabric, fillers and accelerators.⁴ The beneficial properties of silica and carbon black fillers as reinforcing agents in elastomers are well-known.⁵ It is well documented that the structural effects and the polymer-filler surface interaction are of significant importance.⁶ Moreover, it has also been reported that the increased number of grafted chains on the silica surface significantly increases the composite's elongation at break.⁷ Tire engineers around the world are working hard to develop new generation of high performance tire composites. Nevertheless the tire recyclability has been and is still being an important challenge. One alternative for overcoming this environmental related issue is the use of *trans*-polypentenamer, which is readily obtained by equilibrium ring-opening polymerization of cyclopentene.⁸ Our previous and ongoing studies have demonstrated that ruthenium metathesis catalysts (Figure 1) used for ring opening metathesis polymerization (ROMP)^{8d-f} of cyclopentene results in a cyclopentene-polypentenamer equilibrium mixture, whereby the monomer-polymer ratio can be fine-tuned by changing the reaction temperature.⁹

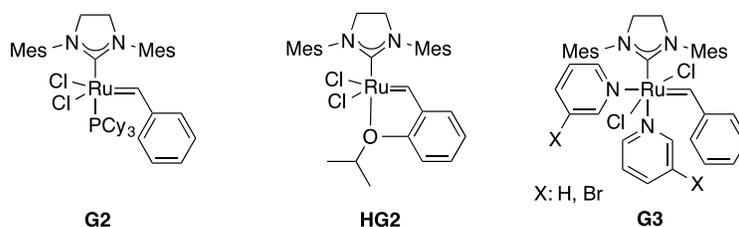


Figure 1. Ru metathesis catalysts used for cyclopentene and functionalized cyclopentene ring-opening metathesis polymerization.

Exploiting the temperature-dependence of the equilibrium polymerization provides high yield at 0 °C for polypentenamer (> 80 %). However, increasing the reaction temperature (> 40 °C) will result in the polypentenamer/monomer equilibrium being shifted to the starting material. In theory we can postulate that polypentenamer tire additives may possibly be recyclable. Moreover, it is tentatively presumed that the polypentenamer starting material (cyclopentene, **1**) and other components associated with the tires can be recovered. Herein, we report our preliminary findings for recyclable and silica filler compatible polypentenamer tire additives.

RESULTS AND DISCUSSION

We have recently reported the synthesis of polypentenamer by equilibrium ring-opening metathesis polymerization of cyclopentene using well-defined ruthenium catalysts **G2**, **G3** and **HG2** (Figure 1). The polymerization conditions including applied reaction temperature, type of catalyst and the loading has been studied in detail and optimized. A wide range of polypentenamers with molecular weights between 30 – 150 kDa have been prepared during the study.⁹ The catalyst activity and loading was found to have a profound effect on the equilibrium time. However, as it was expected the overall monomer **1** conversion (i.e. equilibrium concentration) was influenced only by the applied reaction temperature.¹⁰ The thermodynamic parameters for the cyclopentene polymerization employing ruthenium-based complexes were calculated and found to be lower than those of achieved *via* tungsten catalyzed systems.¹¹ Recently many transition metal complexes have been developed as cyclopentene polymerization catalyst.¹² Nevertheless, ruthenium systems appear to be one of the most efficient catalysts for the equilibrium polymerization of wide range of functionalized cyclopentene species due to their higher stability and functional group tolerance

ROMP of cyclopentene at low catalyst loading in toluene. Following our previous studies and in order to widen the scope of such polymers, we decided to investigate the ROMP of cyclopentene at low catalyst loading. First, we studied the ruthenium complex **G2** catalyzed cyclopentene polymerizations at room temperature ($[\text{monomer}]/[\text{catalyst}] = 10^4$) in toluene. The molecular weight (M_w) and molecular mass dispersities (\mathcal{D}) of the polymer were determined as function of reaction time. It was found that within one hour the monomer-polymer equilibrium was achieved, while extended reaction time resulted in polymers with broader \mathcal{D} values and lower molecular weights (Table 1). The molecular weight of the polymer synthesized at room

temperature ($t_r = 1\text{h}$) was determined by GPC to be 129 kDa (D : 1.64). This value is significantly higher than the reported values in the literature, where a higher catalyst loading was used (69.6 and 31.8 kDa synthesized at 20 and 30 °C (D : 1.96 and 2.07, respectively)); $[\text{monomer}]/[\text{catalyst}] = 10^{2.6} \approx 437$.⁹ Lower molecular weights and higher D values were observed when the reaction time was extended from one to sixteen hours ($t_r = 2\text{h} - M_W$: 106 kDa, D : 1.77; $t_r = 4\text{h} - M_W$: 94.0, D : 1.82). This can be explained by the undesired cross-metathesis reaction of the formed, high molecular weight polymer due to the catalyst's relatively fast propagation and slow initiation rate, which is often observed for ROMP reactions using **G2**.¹³ Comparison of polymers obtained by the ROMP of cyclopentene **1** and its siloxy functionalized derivative **11** showed afforded polymers with lower molecular weight and higher polydispersity ($t_r = 2\text{h} - M_W$: 39.10 kDa, D : 2.05) with reasonable isolated yield (Table 1).

Table 1. M_W and molecular mass dispersity (D) values of polypentenamers derived from cyclopentene **1** isolated at different reaction times using catalyst **G2**.

Entry	Reaction time (h)	M_W (kDa) $\cdot 10^2$	D	Isolated yield (mg/%*)
1	1	1.29	1.64	140.1/83
2	2	1.06	1.77	160.0/94
3	4	0.94	1.82	136.4/80
4	8	0.78	1.83	140.9/83
5	16	0.76	1.84	163.0/96
6 ^[a]	2	0.39	2.05	260.0/88

[**G2**]= 0.225 mM, [**1**]= 2.17 M, toluene, room temperature. [^a] Results for monomer **11**;

*Theoretical yield (at 45% cyclopentene equilibrium concentration, 25 °C):⁹ 169.6 mg (the polymers were isolated by precipitation in MeOH except entry 6, see ESI.).

ROMP of cyclopentene at low catalyst loading in the absence of solvent. Herein, we studied the effect of solvent-free ROMP at low **G2** catalyst loading. Preliminary results showed that at room temperature (25 °C) the reaction was very exothermic and the reaction mixture gelled within 20 minutes ($[\text{Monomer}]/[\text{Catalyst}] = 10^4$). Actually, the reaction mixture warmed up and started to boil. Upon gelation gas bubbles were observed in the polypentenamer (Figure S1, PP-133). When the reaction was repeated at a slightly lower, thermostated reaction temperature (20 °C) (in order to avoid the mixture warming up that is caused by the exothermic reaction) longer gelation time was observed. After 15 min there was no gelation observed, the mixture solidified within 40 min. Consequently, the reaction was also carried out at 0 °C. As it was expected the polymerization took even longer (4.5h until gelation). The polymerization was also tested at considerably low catalyst loading ($[\text{Monomer}]/[\text{Catalyst}] = 10^5$). At room temperature the gelation was observed after 1h (Figure S1, PP-134). The polymerization was repeated using more active ruthenium complexes **G3** and **HG2** at 0 °C employing the same catalyst loading. However, to our surprise the reaction did not go to completion, even upon prolonged reaction time (3 days), no solidification was observed. This can only be explained by the very slow catalyst initiation rate at 0 °C and thus the very low active species concentration in the reaction mixture.

Synthesis of siloxy functionalized polypentenamers - Theoretical calculations. One possibility for enhancing and having a better affinity to the silica fillers is the introduction of siloxy functionalities onto the polymer backbone. It has tentatively been proposed that siloxy functionalized polypentenamer will result in a better silica/polypentenamer composite homogeneity. Therefore, preliminary theoretical calculations using density functional theory

(DFT) have been performed to predict the ring strain energies and bond orders of siloxy functionalized cyclopentene derivatives as potential co-polymerization agents (Figure 2 and 3).

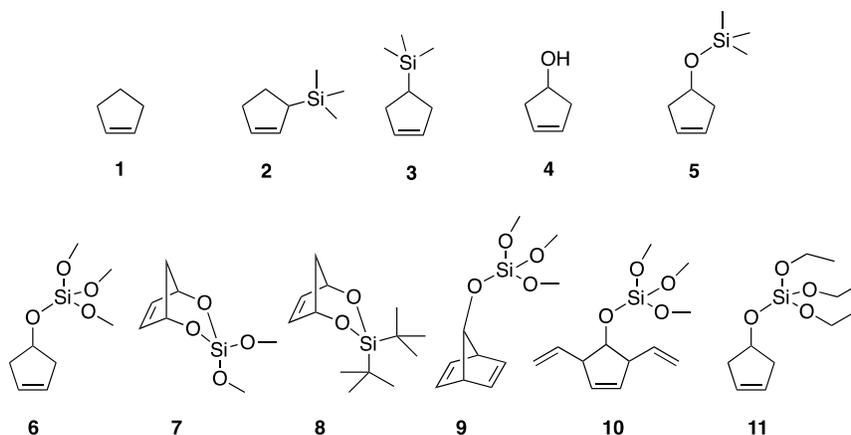


Figure 2. Cyclopentene and its functionalized derivatives used for ring strain energy calculations

The ring strain energy of a series of substituted cyclopentene species have been calculated with DFT studies performed using RB3LYP method at 6-31G (D) basis set using SPARTAN '14 version 1.1.9 software (Figure 3, Table S1).¹⁴

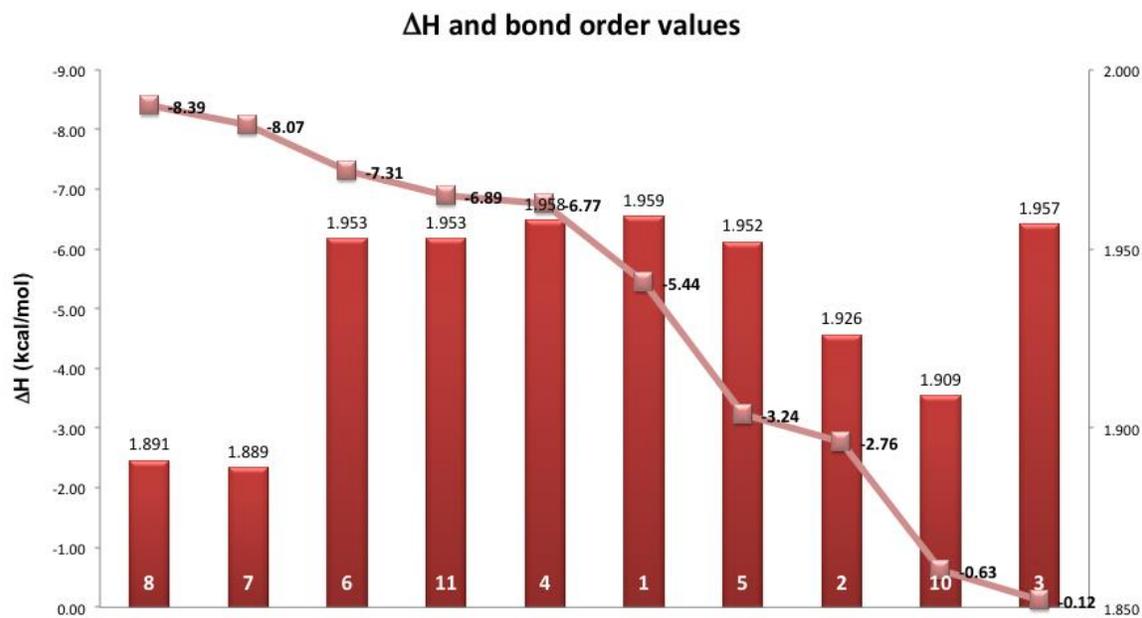


Figure 3. Ring strain energies (pink) and bond orders (red) calculated for **1 – 11** monomer (**9** = -27.36 kcal/mol)

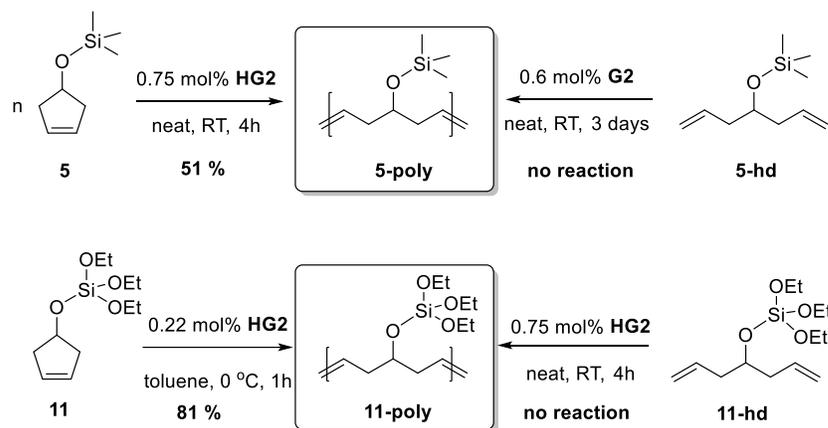
According to the DFT calculations, monomers **5**, **6**, **7** and **11** have mediocre ring strain energy (**5**: -3.24 kcal/mol; **6**: -7.31 kcal/mol; **7**: -8.07 kcal/mol; **11**: -6.89 kcal/mol), while the bond order is 1.952; 1.953, 1.889 and 1.953 respectively (Table S1 and Figure 3). Thus, the equilibrium polymerization of these compounds was expected to be feasible. As can be seen from figure 3 monomers **6** and **11** have similar ring strain energies, as one might expect due to the small difference in chain length (monomer **6** having a methoxy group in comparison to monomer **11** having an ethoxy group). The ring strain energy calculated for monomer **8** is the highest among the above depicted cyclopentene species (-8.39 kcal/mol). This is in accordance with the reported data by Scherman *et al.* explaining why compound **8** can be readily polymerized by ROMP.¹⁵ Theoretically the ROMP of **9** may take place in two steps forming a branched poly(pentenamer). However, according to the theoretical calculations the second ROMP step of monomer **9**, is most

probably not feasible due to its relatively low strain energy of the formed cyclopentene species **10**.

ROMP of (cyclopent-3-en-1-yloxy)trimethylsilane (5) and cyclopent-3-en-1-yl triethyl silicate (11) polypentenamers. Siloxy functionalized cyclopentenenes were synthesized according to standard literature procedures with modifications (see supporting information). The ROMP reactions were carried out in toluene or toluene-*d*₈ solution at 0 °C using 0.2 – 0.7 mol% **G2** or **HG2** catalyst loading.

Referring to our theoretical calculation data due to the relatively low ring strain energy of **5** higher monomer equilibrium concentration or low activity was expected for the ROMP. As the green **HG2** solution was added to the toluene solution of **5** the color of the mixture gradually turned to orange. The color change may have indicated the formation of an active catalyst species yet no formation of the polymer could be detected by ¹H NMR spectroscopy. The reaction was then repeated in neat. Following the addition of **5** to the catalyst there was no immediate gelation observed. However, the color of the mixture gradually turned from green to orange within 15 min. The mixture became viscose after 30 min and solidified after 60 min. After 3.5h reaction time the solid polymer was dissolved in CD₂Cl₂ and analyzed by ¹H NMR spectroscopy. The ¹H NMR spectrum showed a significant upshift of –CH= proton peaks. The magnitude of the chemical shifts and the shape (broad) of the peaks indicated the formation of **5-poly** (Figure S9). The polymer was isolated by precipitation using MeOH. Following the purification procedure a colorless, waxy, dense polymer was isolated in 51.2% yield. Due to the relatively low strain energy of monomer **5** (-3.24 kcal/mol) in comparison to cyclopentene (**1**; -

5.44 kcal/mol) higher monomer concentration and most probably lower temperature is needed to achieve higher monomer conversions (i.e. lower monomer equilibrium concentration).

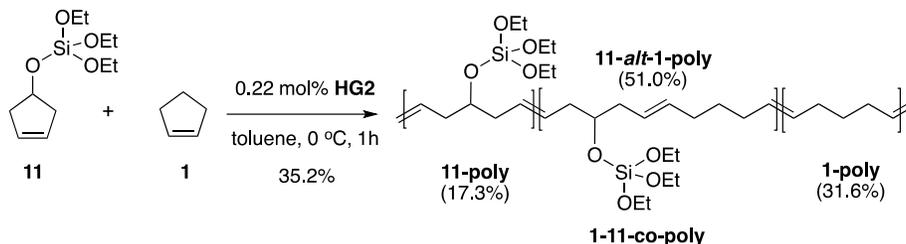


Scheme 1. Polymerization test of **5**, **11** and **5-hd**, **11-hd**

Acyclic diene metathesis (ADMET) polymerization of **5-hd** was also investigated at similar reaction condition using catalyst **G2** (Scheme 1). It was found that the polymerization is not feasible either in solution or in neat. The mixture did not form a gel and no ethylene formation was observed even at prolonged reaction times (3 days).

In general, trialkoxy silane functionalized cyclopentenes have relatively higher ring strain energies (**6**: -7.31 kcal/mol or cyclopent-3-en-1-yl triethyl silicate, **11**: -6.89 kcal/mol) than the (cyclopent-3-en-1-yloxy)trimethylsilane (**5**: -3.24 kcal/mol). It was expected that the monomers should show lower monomer equilibrium concentration in comparison to the non-functionalized cyclopentene and therefore, result in a higher activity in the ruthenium catalyzed ROMP reactions. The polymerization of monomer **11** (2.1M in toluene), afforded the desired polymer with reasonable isolated yield (81%). Interestingly, the ADMET of **11-hd** did not afford the expected polymer either. Based on our recent thermodynamic and theoretical investigations it

can be easily concluded that there is a correlation between the observed ring strain energies and monomer equilibrium concentration (i.e. conversion).^{9,14a} The introduction of different functionalities on the cyclopentene ring has a significant impact on the ring strain and thus the equilibrium monomer concentration in ROMP reactions. The higher the ring strain the lower the monomer equilibrium concentration that was observed. For example introducing the OSi(CH₃)₃ group **5** results in lower ring-strain energy (-3.24 kcal/mol), which as a result the reaction could only be completed in neat. On the other hand introduction of hydroxyl (OH) functionality **4**^{14a} or siloxyOSi(OC₂H₅)₃ **11** groups significantly increase the ring-strain energies (-6.77 and -6.89 kcal/mol) and thus the reactivity. Moreover, high (>80 %) conversion could be achieved even at 2.1 M toluene solution at lower temperature rang 0 – 10 °C.



Scheme 2. Random co-polymerization of **11** and **1** in toluene.

Our recent studies have shown that the equilibrium co-polymerization of **1** and **4** resulted in a polymer having randomly distributed dyads. In general, it means that the co-polymer formed contains approximately 50% alternating polymer, 25% **1** and 25% **4** homo-polymer dyads.^{14a}

The random co-polymerization of **1** with **11** has also been investigated under identical molecular ratios. It was found that the co-polymerization product contains alternating **1-alt-11-poly** (51.1%), **1-poly** (31.6%) and **11-poly** diads (17.3%), which is comparable to the composition of polymers obtained during the co-polymerization of monomers **1** and **4**.^{14a}

Depolymerization of 1-poly, 11-poly and 1-11-co-poly polypentenamers. According to the thermodynamic investigations depolymerization can be enhanced either by slightly

increasing the temperature (up to 50 °C) or by diluting the polymer solution. For example it was found that at higher dilutions (5 w/v% polymer concentration) at room temperature the isolated polypentenamer can be fully depolymerized using the **G2** complex within 4 min (Figure S15). Repeating the depolymerisation reaction of **11-poly** and **1-11-co-poly** resulted in the full monomer recovery based on *in-situ* ¹H NMR investigations (Figure S16-S17). If the depolymerization needs to be performed at higher polymer concentration then the equilibrium can be fully shifted to the depolymerization direction with increasing the temperature up to 50 °C. If we consider that the boiling point of **1** is 44 °C, then we can easily recognize that the polypentenamers can be fully depolymerized even at high concentrations and higher temperature (50 °C) and monomer **1** can easily be distilled off from the reaction mixture.

CONCLUSION

Earlier work using poorly defined catalysts demonstrated that polymers prepared from cyclopentene resulted in elastomers for tire applications that were more durable than the material used at the time. Manufacturing auto tires that would have a longer life and from starting materials that can be recycled will eliminate major disposal issues. Polypentenamers and their functionalized derivatives have great industrial interest, as these materials possess exceptional physical and mechanical properties. These materials will have a wide industrial and commercial application in areas including packaging, medicinal aid, petrochemical and tire productions.

We have reported that polypentenamer can be synthesized using very low (10^5) monomer-catalyst loading at 20 °C reaction temperature within a reasonable reaction time (3h) using well-defined ruthenium metathesis catalysts. In particular, one can postulate that 10 kg polypentenamer can be produced using only 1g of the **G2** catalyst. The recyclability of polypentenamer has been demonstrated using the same ruthenium metathesis catalyst systems at

diluted condition or slightly elevated reaction temperature. The introduction of the siloxy functionalities will result in silica filler compatible polypentenamers. Theoretical calculations have also been carried out to illustrate that siloxy functionalized polypentenamers can be formed via equilibrium polymerization. This will result in a convenient method to recycle and achieve full monomer recovery. Additional studies are ongoing to explore additional types and new recyclable polymers that are based on high performing tire additives, which will be reported in due course.

ASSOCIATED CONTENT

The Supporting Information is available free of charge on the ACS Publications website at DOI:

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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