Chapter 6

Ring-Opening Metathesis Polymerization of Functionalized-Low-Strain Monomers with Ruthenium-Based Catalysts

6.1 Abstract

A detailed study of the ring-opening metathesis polymerization of low-strain monomers with ruthenium catalysts is reported. The effects of monomer concentration, reaction temperature, and catalyst dependence are described for unsubstituted cycloolefins. The ROMP of low-strain olefins with polar substituents is also examined with ruthenium olefin metathesis catalysts and a predictive model for ROMP feasibility is proposed.

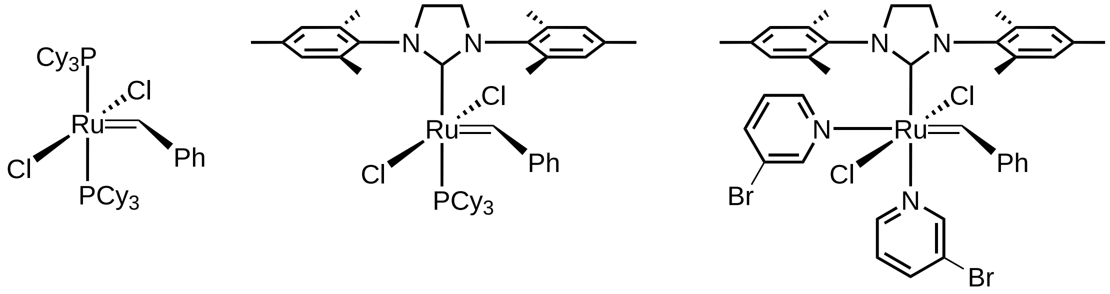
6.2 Introduction

Functionalized linear polymers represent an important class of materials. Several methods have been established to prepare functionalized polymers such as ionic and free radical polymerization of vinyl monomers, group transfer polymerization (GTP), and, more recently, ring-opening metathesis polymerization (ROMP).[1–3] ROMP is an attractive method to synthesize functional polymers as it is robust, produces absolutely linear material, and is amenable to forming various copolymers of controlled architecture.[4, 5] Substituted cyclobutenes and cyclooctenes have been used extensively to prepare linear polymers with a wide range of functionality.[6, 7] With these monomers it is difficult (or in the case of mono-substitution, impossible) to control the regioregularity of functionalities along the polymer backbone. Symmetrically substituted 5- and 7-membered ring monomers provide access to a range of regioregular polymers. Few examples, however, are reported in the literature.[8–11] The low ring strains inherent to 5-, 6-, and 7-membered cycloalkenes[12] make them more challenging substrates for ROMP.

The driving force behind the ROMP of cyclic olefins is the release of strain energy,[2] encompassed by the enthalpic term, ΔH, in the equation below.

$$\Delta G = \Delta H - T\Delta S$$

Monomer concentration and reaction temperature are intimately associated with thermodynamics of ROMP. For every cyclic olefin monomer, there exists a critical monomer concentration below which no polymerization will occur at a given temperature. Performing the ROMP at low temperatures can mitigate the entropic loss inherent to all polymerizations and drive the reaction to high molecular weight polymer. Lower reaction temperatures, however, require catalysts with higher activities. As a result, ROMP of low-strain monomers has traditionally been performed with highly active early transition metal catalysts.[2, 9] Unfortunately, these catalysts are not tolerant of many polar functionalities. It is well established that ruthenium-based olefin metathesis catalysts, such as **1**, demonstrate significantly more tolerance towards polar functionality.[13, 14] It was recently demonstrated that catalyst **2** was capable of performing the ROMP of cyclopentene at 25 °C.[15] We now report that ruthenium catalysts **1**, **2**, and **3** (Figure 6.1) are all capable of polymerizing low-strain cycloolefins, so that the ROMP of 5- and 7-membered cycloalkenes with polar substituents can now be realized.



1 **2** **3**

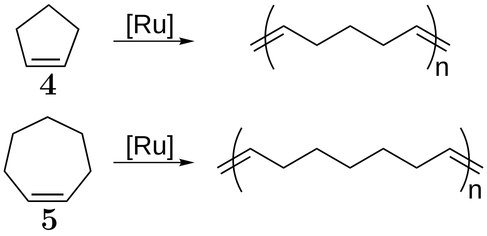
Figure 6.1: Ruthenium olefin metathesis catlaysts.

6.3 Results and Discussion

6.3.1 ROMP of Unsubstituted Monomers

The ROMP of the low-strain monomers cyclopentene (**4**) and cycloheptene (**5**) was investigated with ruthenium catalysts **1**–**3** (Scheme 6.1). Polymerization behavior of **4** and **5** was studied with respect to catalyst loading, monomer concentration, and reaction temperature. The experimental strain energy for **4** and **5** are 6.8 and

Scheme 6.1: ROMP of cyclopentene and cycloheptene with ruthenium catalysts.



6.7 kcal/mol, respectively,[12] suggesting they should behave similarly with the olefin metathesis catalysts. Indeed, this appeared to be the case with a few notable exceptions (Table 6.1).

In agreement with previous reports that utilized early transition metal catalysts, relatively high yields of polymer could be obtained for neat polymerization with the ruthenium catalysts at 25 °C.[9] Entries 1–4 in Table 6.1 illustrate that yields of 80% and greater are obtained by the neat ROMP of **4** with ruthenium catalysts **1** and **2**, however, a low yield is obtained for neat ROMP of **4** and **5** with catalyst **3**. This is due to the sparing solubility of the bromo-pyridine catalyst in neat hydrocarbon monomers. In solution studies, where catalyst solubility is not a factor, the yields of polymer are all similar as expected. This can be seen in entries 6–8 in Table 6.1 which all produce polymer in comparable yield with catalyst **3** giving the best molecular weight control. By increasing the monomer to catalyst ratio, ([M]/[cat]), the yields remain constant with a commensurate increase in the molecular weights, M_n, for ROMP of monomer **4**. In the case of monomer **5**, however, the yields drop off as the monomer to catalyst ratio increases (entries 13–15). In all cases, yields decrease with a lower monomer concentration as expected with the thermodynamic constraints discussed previously for low-strain monomer.

6.3.2 ROMP of Substituted Monomers

After successfully demonstrating that catalysts **1**–**3** could ROMP monomers **4** and **5** to high molecular weight polymer, we decided to explore derivatives of these low-strain monomers bearing polar substituents. These functionalities are incompatible

Table 6.1: Results for the ROMP of **4** and **5** with ruthenium catalysts at 25 °C.

Entry	Monomer ([M])	Catalyst	[M]/[cat]	% yield	M_n ($\times10^{-3}$) GPC[a]	PDI
1[c]	**4** (11.3)[a]	**1**	250	80	15.2	1.5
2[c]	**4** (11.3)[a]	**1**	500	92	27.1	1.6
3[c]	**4** (11.3)[a]	**1**	1000	84	75.4	1.6
4[c]	**4** (11.3)[a]	**2**	500	87	19.9	1.3
5[c]	**4** (11.3)[a]	**3**	500	38[f]	28.5	1.6
6[c]	**4** (5)[b]	**1**	500	64	22.1	1.5
7[c]	**4** (5)[b]	**2**	500	68	15.7	1.5
8[c]	**4** (5)[b]	**3**	500	67	13.3	1.3
9[c]	**4** (4)[b]	**1**	500	48	13.6	1.5
10[c]	**4** (4)[b]	**2**	500	51	38.4	1.5
11[c]	**4** (4)[b]	**3**	500	41	12.2	1.5
12[d]	**5** (8.6)[a]	**1**	250	84	23.7	1.3
13[d]	**5** (8.6)[a]	**2**	250	85	116	1.7
14[d]	**5** (8.6)[a]	**2**	500	67	160	1.7
15[d]	**5** (8.6)[a]	**2**	1000	23	191	1.6
16[d]	**5** (8.6)[a]	**3**	250	41[f]	50.2	1.6
17[d]	**5** (5)[b]	**1**	250	87	39.2	1.5
18[d]	**5** (5)[b]	**2**	250	86	53.9	1.5
19[d]	**5** (5)[b]	**3**	250	72	43.7	1.4
20[d]	**5** (2)[b]	**1**	250	64	24.8	1.6
21[d]	**5** (2)[b]	**2**	250	44	103	1.5
22[d]	**5** (2)[b]	**3**	250	64	35.6	1.4

[a]ROMP of neat monomer. [b]Polymerizations carried out in in CH_2Cl_2. [c]Polymerization time of 24 h. [d]Polymerization time of 30 min. [e]Samples run in THF; molecular weight values obtained using MALLS. [f]Low yields due to sparing solubility of **3** in neat monomers.

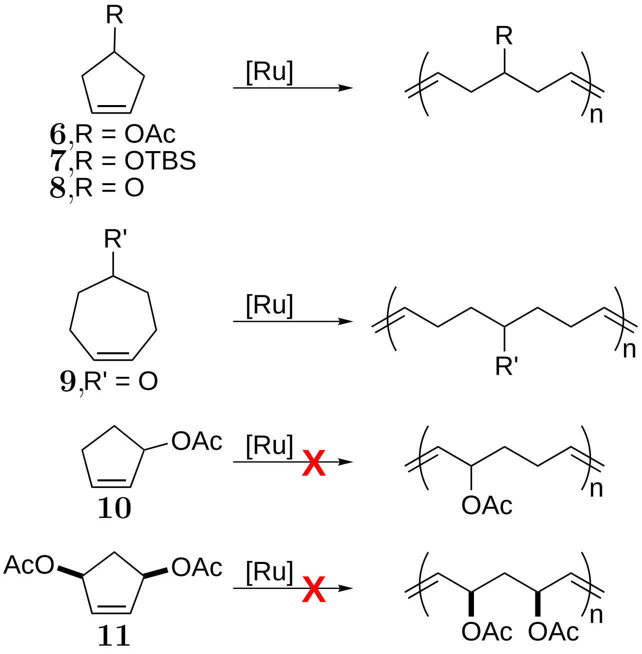
with early transition metal catalysts, but present no difficulty for the ruthenium systems.[5, 14, 15] This would allow for the direct preparation of polar functionalized linear polymers without the need for subsequent polymer modification.[4, 13] Furthermore, as we have previously demonstrated, ROMP of a symmetric monomer will ensure an absolutely regioregular polymer,[13, 16] thus providing new materials for detailed structure–property studies.

The addition of substituents to monomers **4** and **5** will certainly make the ROMP of these low-strain monomers more challenging.[2] This can be explained by the "*gem-*

dialkyl effect" whereby substituents on a ring serve to stabilize the ring-closed system relative to its linear counterpart.[17] As ROMP is a process governed by thermodynamic equilibrium, this effect results in a lower concentration of the linear polymer.

The polar monomers employed in this study, and shown in Scheme 6.2, possess ester, silyl ether, and ketone functionalities. The ROMP of monomers **6**, **7**, **8**, **9** provide a synthetic route for oxygen containing materials such as ethylene vinyl alcohol (EVOH) and ethylene carbon monoxide (E/CO) copolymers. These materials have been demonstrated to have useful properties in commercial applications.[13, 18, 19]

Scheme 6.2: ROMP of substituted low-strain monomers.



ROMP of the substituted monomers was successfully carried out neat at 25 °C with catalysts **1**–**3**, as illustrated in Table 6.2. Entries 1–6 in Table 6.2 illustrate that the ROMP of symmetric monomers **6** and **7** could be carried out in high yield and with controlled molecular weights with all three ruthenium catalysts. Moreover, no significant difference was observed in the ROMP of **6** and **7** as expected for structurally similar monomers. Monomer **8** does not undergo polymerization with catalysts **1** or **2**, indicating a low ring strain. Catalyst **3**, however, allows for the formation of **poly**(**8**) which is an insoluble material. This suggests that **poly**(**8**) is trapped through a kinetic process.[1, 20, 21] Catalyst **3** is known to initiate much faster than either **1** or **2**, and may allow for rapid polymerization of **8** to high molecular weight insoluble polymer. No conditions were found under which monomers **10** and **11** would successfully polymerize.

Table 6.2: Results for the ROMP of **6–11** with ruthenium catalysts at 25 °C.

Entry	Monomer	Catalyst	[M]/[cat]	% yield	M_n ($\times10^{-3}$) GPC[e]	PDI
1[c]	**6**	**1**	500	75	36.9	1.4
2[c]	**6**	**2**	500	66	28.9	1.3
3[c]	**6**	**3**	500	65	28.0	1.5
4[c]	**7**	**1**	150	72	18.7	1.7
5[c]	**7**	**2**	150	66	17.0	1.3
6[c]	**7**	**3**	150	71	16.6	1.3
7[c]	**8**	**1**	250	0	—	—
8[c]	**8**	**2**	250	0	—	—
9[c]	**8**	**3**	250	24	—	—
10[c]	**8**	**3**	500	63	5.6	1.8
11[d]	**10**	**1**	500	0	—	—
12[d]	**10**	**2**	500	0	—	—
13[d]	**10**	**3**	500	0	—	—
14[d]	**11**	**3**	250	0	—	—

[a]ROMP of neat monomer. [b]Polymerizations carried out in in CH_2Cl_2. [c]Polymerization time of 24 h. [d]Polymerization time of 30 min. [e]Samples run in THF; molecular weight values obtained using MALLS. [f]Low yields due to sparing solubility of **3** in neat monomers.

6.3.3 Model for Low-Strain ROMP

By varying the placement and nature of the substituents, we observed a marked effect on a monomer's potential to undergo ROMP. A method to predict whether or not ROMP of a particular monomer is feasible would be very helpful for the design of new functionalized monomers. The ease of ROMP is reflected by the strain energy of each monomer.[2, 13] Therefore, a model to predict strain energy should correlate to ROMP feasibility as well.

We chose to model the strain energy of a cyclic olefin with the enthalpic terms

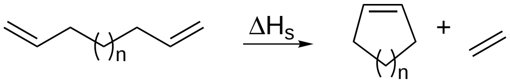


Figure 6.2: Isodesmic reaction used to calculate the strain energy released by ROMP.

of a ring-closing metathesis reaction (Figure 6.2). Our model reaction is isodesmic, having the same number and type of bonds in both reactants and products,[22] so that the change in energy is solely due to the strain inherent in the cycle form. The ring strain for the cyclic olefin is the difference in energy between the products and the reactant.

In order to validate our model, un-substituted, cyclic olefins ranging from cyclopropene to cyclooctene were calculated and compared with their experimentally determined strain energies. The calculations were carried out using DFT with a B3LYP functional and a 6-31G** basis set. As can be seen by the graph in Figure 6.3, the correlation of calculated values with experiment is quite good. Slightly larger deviations are observed for cycloheptene and cyclooctene as a result of a natural distribution of several conformers at 298 K for these larger rings that are not reflected in our calculations. We also carried out these calculations at a semi-empirical level of theory with AM1, PM3 and PM5 parameterization schemes; however, all of these resulted in poor agreement with experimental results.

Satisfied with our method, we proceeded to calculate the strain energies for the substituted monomers described above. The calculated values are shown in Table 6.3. Again, the experimental results we observe in this study appear to correlate with our model. Under our polymerization conditions, it appears that the minimal strain energy necessary for successful ROMP lies between 3.4 and 4.4 kcal/mol. The successful development of this model should allow for the evaluation of a new monomer's ability to undergo ROMP.

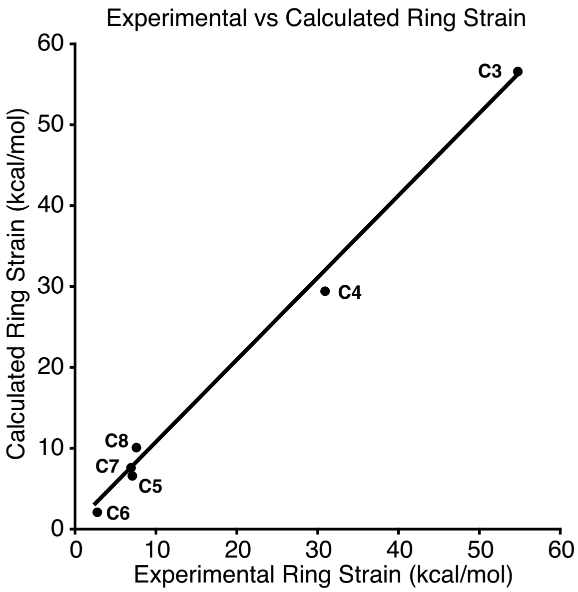


Figure 6.3: Graph depicting the correlation between calculated[12] and experimental strain energies.

Table 6.3: Calculated strain energies and "ROMP-ability" for several low-strain monomers.

Monomer	E_s(calc)[a]	ROMP[b]
5	7.84	yes
9	7.44	yes
4	6.84	yes
7	4.99	yes
6	4.47	yes
8	4.45	yes
10	3.36	no
11	2.29	no

[a] Strain energy in kcal/mol, calculated at DFT B3LYP/6-31G**. [b] Neat monomer, rt. [c] Only polymerizes with catalyst **3**.

6.4 Conclusions

The ROMP of cyclopentene and cycloheptene has been investigated with several ruthenium olefin metathesis catalysts. All of the catalysts employed afforded reasonable to high yields of ROMP polymer and demonstrated molecular weight control. As previously demonstrated, the polymer behavior is extremely dependent on the monomer concentration. This is consistent with the thermodynamic governance of the ROMP process. The use of functional group tolerant ruthenium catalysts has also allowed for the incorporation of polar substituents pendent from the linear polymer backbone. When symmetrically substituted 5- and 7-membered ring monomers are polymerized, the resulting materials possess an absolutely linear structure with a perfectly regioregular distribution of functionality. In order to better understand the relationship between substitution patterns and ring strain of a cyclic olefin monomer, a simple model for predicting ring strains was developed. A high degree of correlation was found between experimental and calculated data for both substituted and unsubstituted cycloolefins. This model could be generally applied as a predictive tool for rational monomer design.

6.5 Experimental Section

Materials. Toluene and CH_2Cl_2 were dried by passage through solvent purification columns.[23] $(PCy_3)_2(Cl)_2Ru{=}CHPh$ (**1**),[24] $(H_2IMes)(PCy_3)(Cl)_2Ru{=}CHPh$ (**2**),[25] $(H_2IMes)(3\text{-Br-py})_2(Cl)_2Ru{=}CHPh$ (**3**),[26] 4-acetoxycyclopentene (**6**),[27, 28] 4-*tert*-butyldimethylsilyloxycyclopentene (**7**),[28] 4-cyclohepten-1-one (**9**),[29] and 3-acetoxycyclopentene (**10**)[30] were synthesized according to literature procedures. Cyclopentene (98%) (**4**) (TCI America), 3-cyclopenten-1-one (98%) (**8**) (Astatech), cycloheptene (97%) (**5**) (Pfaltz & Bauer), and *cis*-3,5-diacetoxycyclopentene (98%) (**11**) (Fluka) were used as received.

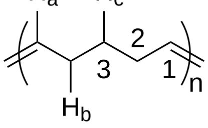
Methods and procedures. NMR spectra were recorded on either a Varian Mercury 300 (299.87 MHz for ^1H and 75.41 MHz ^{13}C) or a Varian Inova 500 (500.62 MHz for ^1H and 125.89 MHz ^{13}C). All NMR spectra were recorded in $CDCl_3$ and referenced to residual protio species. Gel permeation chromatography (GPC) was carried out in THF on two PLgel 5 μm mixed-C columns (Polymer Labs) connected in series with a DAWN EOS multiangle laser light scattering (MALLS) detector and an Optilab DSP differential refractometer (both from Wyatt Technology). No calibration standards were used, and dn/dc values were obtained for each injection assuming 100% mass elution from the columns.

Computational methodology. All calculations were performed using the hybrid DFT functional B3LYP as implemented by the Jaguar 4.0 program package.[31] A 6-31G** basis set was used for all compounds.

Polymerization procedure, neat monomer. In a typical experiment, a small vial was charged with catalyst **1** (11.1 mg, 0.0135 mmol) and a stirbar under a flow of argon. Next, monomer **4** (0.30 mL, 0.231 g, 3.39 mmol, 251 equiv) was added via syringe at room temperature and the reaction was allowed to stir. The reaction mixture gelled within 1 min. After 24 h, the polymerization was quenched with 0.1 mL ethyl vinyl ether and then dissolved in 1 mL dichloromethane. The polymer solution was then precipitated into 75 mL of MeOH at 0 °C. The polymer precipitate was washed several times with MeOH and dried under vacuo overnight; yield 0.185 g (80%).

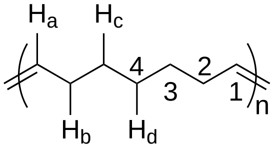
Polymerization procedure, in solution. In a typical experiment, a small vial was charged with monomer **5** (0.30 mL, 0.249 g, 2.59 mmol, 259 equiv) and a stirbar under a flow of argon. Next, 0.20 mL (0.01 mmol) of a catalyst **3** stock solution (0.05 M) was added via syringe at room temperature and the reaction was allowed to stir. The reaction mixture gelled within 1 min. After 30 min, the polymerization was quenched with 0.1 mL ethyl vinyl ether and then dissolved in 1 mL dichloromethane. The polymer solution was then precipitated into 75 mL of MeOH at 0 °C. The polymer precipitate was washed several times with MeOH and dried under vacuo overnight; yield 0.180 g (72%).

Polymer characterization. For **poly(4)**: ^{1}H NMR (500.62 MHz, $CDCl_3$, δ): 5.42–5.33 (m, 2H, H_a), 2.08–1.90 (m, 4H, H_b), 1.39 (quint, J = 7.5 Hz, 2H, H_c). $^{13}C\{^1H\}$ NMR (125.89 MHz, $CDCl_3$, δ): 130.45 (C1 *t*), 129.94 (C1 *c*), 32.51 (C2 *tc*), 32.37 (C2 *tt*), 30.01 (C3 *ct/tc*), 29.86 (C3 *tt*), 27.06 (C2 *ct*).



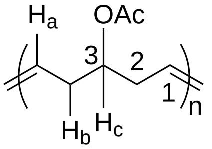
poly(4)

For **poly(5)**: ^{1}H NMR (299.87 MHz, $CDCl_3$, δ): 5.41–5.31 (m, 2H, H_a), 2.08–1.90 (m, 4H, H_b), 1.40–1.22 (m, 6H, H_c/H_d). $^{13}C\{^1H\}$ NMR (75.41 MHz, $CDCl_3$, δ): 130.53 (C1 *t*), 130.07 (C1 *c*), 32.99 (C2 *t*), 30.08 (C3 *cc*), 30.04 (C3 *ct*), 29.97 (C3 *tc*), 29.93 (C3 *tt*), 29.38 (C4 *cc*), 29.26 (C4 *ct/tc*), 29.13 (C4 *tt*), 27.60 (C2 *c*).



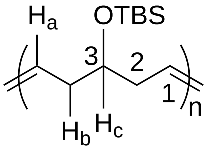
poly(5)

For **poly(6)**: ^{1}H NMR (299.87 MHz, $CDCl_3$, δ): 5.5–5.3 (br m, 2H, H_a), 4.82 (br m, 1H, H_c), 2.3–2.15 (br m, 4H, H_b), 1.99 (s, 3H, OAc). $^{13}C\{^1H\}$ NMR (75.41 MHz, $CDCl_3$, δ): 170.82 (OAc–C=O), 128.68 (C1 *t*), 127.41 (C1 *c*), 73.20 (C3), 73.04 (C3), 37.09 (C2), 31.91 (C2), 21.44 (OAc–CH_3).



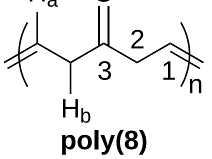
poly(6)

For **poly(7)**: ^{1}H NMR (299.82 MHz, $CDCl_3$, δ): 5.56–5.31 (br m, 2H, H_a), 3.74–3.55 (br m, 1H, H_c), 2.30–1.98 (br m, 4H, H_b), 0.88 (s, 9H, Si–*t*Bu), 0.03 (s, 6H, Si–Me_2). $^{13}C\{^1H\}$ NMR (75.40 MHz, $CDCl_3$, δ): 129.36 (C1 *t*), 127.87 (C1 *c*), 72.91 (C3), 40.81 (C2), 35.61 (C2), 26.24 (Si–C($\mathbf{C}H_3)_3$), 18.49 (Si–$\mathbf{C}(CH_3)_3$), -4.12 (Si–($\mathbf{C}H_3)_2$).



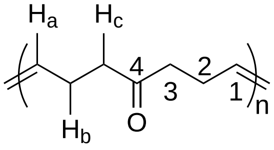
poly(7)

For **poly(8)**: **poly(8)** is an intractable solid and solution phase characterization has been unsuccessful to date.



poly(8)

For **poly(9)**:^{1}H NMR (299.82 MHz, $CDCl_3$, δ): 5.42–5.28 (m, 2H, H_a), 2.48–2.38 (m, 4H, H_c), 2.32–2.18 (m, 4H, H_b). $^{13}C\{^1H\}$ NMR (75.40 MHz, $CDCl_3$, δ): 209.92 (C4), 129.80 (C1 *t*), 129.37 (C1 *c*), 42.80 (C3 *c*), 42.76 (C3 *t*), 26.90 (C2 *t*), 21.81 (C2 *c*).



poly(9)

6.6 Acknowledgements

The authors thank Daniel P. Sanders and Professor Dennis A. Dougherty for helpful discussions. This work was supported by the National Science Foundation.

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