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Synthesis of narrow-distribution polycyclopentene using a ruthenium ring-opening metathesis initiator

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Abstract

Polycyclopentene was synthesized by ring-opening metathesis polymerization (ROMP) at room temperature, using a ruthenium-based initiator in the presence of tricyclohexylphosphine, which acts as a polymerization regulator by shifting the metal–ligand binding equilibrium. A kinetic model was developed for the monomer conversion and polymer molecular weight as a function of time, monomer concentration, and monomer-to-initiator and phosphine-to-initiator ratios, and was fit to experimental data to extract a single rate parameter. By eliminating impurities which act as chain-transfer agents, and optimizing reaction conditions to minimize secondary metathesis, polycyclopentenes of controllable molecular weight ($M_n = 6–40$ kg/mol) and narrow distributions (PDI $\approx$ 1.15) can be routinely obtained, which could be hydrogenated to perfectly linear polyethylenes. This work extends existing ROMP methods for the synthesis of precursors to narrow-distribution polyethylene, which have employed tungsten or molybdenum catalysts, to a commercially available, robust ruthenium initiator.

Keywords: Ring-opening metathesis polymerization; Polycyclopentene; Chain transfer

1. Introduction

Because of its prevalence as a commodity polymer and the simplicity of its structure, polyethylene (PE) is often used as a model crystalline polymer. As a result, synthetic routes to well-defined PE and PE-containing block copolymers have long been of interest. Only recently have catalysts been developed which can polymerize ethylene in a living fashion [1–3], and the range of monomers for which these catalysts are effective remains limited. An alternative to the direct polymerization of ethylene monomer is to synthesize an unsaturated precursor polymer which is subsequently hydrogenated to PE. As an example, anionic polymerization of butadiene in hydrocarbon solvent yields, upon hydrogenation, a linear PE with 20 ethyl branches per 1000 backbone carbons. These ''linear low-density polyethylenes'' have often been used as components of model crystalline block copolymers, but the ethyl branches ultimately limit the crystal thickness and crystallinity [4–7].

Alternately, ring-opening metathesis polymerization (ROMP) of unsubstituted cycloolefins followed by hydrogenation can yield perfectly linear PE with no short or long branches. Several ROMP routes to PE precursors have been developed, though each has its drawbacks. Wu et al. produced a near-monodisperse polymer from cyclobutene [8,9], but the commercial unavailability of both the monomer and the tungsten catalyst (2,6-diisopropylphenylimidoneopentylidenetungsten(VI) bis(*tert*-butoxide)) have prevented widespread adoption of this approach. An alternate method, developed by Dounis et al., employs the same tungsten catalyst, but uses readily-available cyclopentene monomer [10]. However, this reaction must be conducted at low temperatures (−45 °C) and results in a polymer with a higher polydispersity. Trzaska et al. [11] polymerized cyclopentene at room temperature using a molybdenum catalyst (2,6-diisopropylphenylimidoneophenylidenemolybdenum(VI) bis(*tert*-butoxide)), in the presence of reversibly-binding trimethylphosphine, to produce

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a narrow-distribution polymer. However, even this method is not ideal in that the catalyst is quite sensitive to oxygen and moisture, and has limited tolerance to functional groups which one might wish to incorporate through comonomers.

In recent years, catalyst development for "living" ROMP has focused on ruthenium-based initiators, which are more selective for olefins, and are therefore more tolerant to functionality in the reaction system [12–14], expanding the range of monomers which can be employed. We thus sought to extend the prior work on ROMP of cyclopentene, using W or Mo catalysts, to a commercially-available "Grubbs' first-generation" Ru catalyst. Though Ru-centered initiators have been reported to polymerize monocyclic olefins, the polymers which resulted had polydispersities greater than 1.3 [15–20] or only low molecular weights [21].

By adding tricyclohexylphosphine as a polymerization regulator [21], we are able to achieve narrow distributions over a wide range of molecular weights, ultimately limited at the upper end by acyclic metathesis with polycyclopentene, as with other catalysts [22]. A simple kinetic model was developed for the reaction, which permits the synthesis of polymers of predetermined molecular weight and known monomer conversions.

2. Experimental

2.1. Materials

Cyclopentene (96%, Aldrich Chemical Co.) was dried over butyllithium, degassed by freeze–pump–thaw cycles, and vacuum transferred prior to use. Toluene was dried over sodium benzophenone ketyl, degassed by freeze–pump–thaw cycles, and vacuum transferred. 2-Pentene (99%, mixture of *cis* and *trans*, Aldrich) was dried over freshly-cut sodium, degassed by freeze–pump–thaw cycles, and vacuum transferred prior to use. Ethyl vinyl ether, tricyclohexylphosphine, and bis(tricyclohexylphosphine)benzylidene ruthenium(IV) dichloride (a Grubbs' "first-generation" Ru initiator) were used as received from Aldrich.

2.2. Instrumentation

Gel permeation chromatography (GPC) in toluene or THF was used to determine polymer molecular weights, polydispersity indices (PDIs), and reaction conversion. Conversions were based on the integral of the polymer peak in the refractive index (RI) detector traces, using a precise injection volume and knowing the initial monomer concentration in the reaction mixture. The toluene GPC system consists of a 60 cm Polymer Laboratories PLgel Mixed-C column, a Waters 590 HPLC pump, and a Knauer differential refractometer detector. The THF GPC system consists of 2×30 cm Polymer Laboratories PLgel Mixed-C columns, a Waters 515 HPLC pump, and a Waters 410 differential refractometer. The columns were calibrated with narrow-distribution polystyrenes, and the apparent (polystyrene equivalent) molecular weights were converted to the true values [23] by dividing by $R = 1.98$, measured for polycyclopentene in both toluene and THF.

2.3. Synthesis of polycyclopentene (PCP)

All synthetic processes were performed under a nitrogen atmosphere in an Innovative Technologies glove box ($\sim$0.7 ppm O_2, $\sim$0.5 ppm H_2O) at room temperature. A typical polymerization involved the addition of tricyclohexylphosphine (4 eq) and bis(tricyclohexylphosphine)benzylidene ruthenium(IV) dichloride (1 eq) to toluene, followed by the addition of cyclopentene (3000 eq, 3 M in toluene). The reaction flask was stoppered and stirred for 60 min before termination with ethyl vinyl ether (100 eq). The mixture was stirred for an additional 30 min to ensure complete termination and removed from the glove box. Precisely diluted aliquots of the reaction solution were used for GPC.

3. Results and discussion

Our method for the ring-opening metathesis polymerization (ROMP) of cyclopentene employs a "Grubbs' first-generation" ruthenium-based initiator ($Ru(=CHPh)Cl_2(PCy_3)_2$) in the presence of tricyclohexylphosphine (PCy_3) to synthesize well-defined, unbranched hydrocarbon polymers with one double bond per five backbone carbons (Fig. 1). ROMP reactions of highly ring-strained monomers, such as cyclobutene and norbornene, proceed essentially to completion, but the less-strained cyclopentene is thermodynamically less favored to polymerize and shows an equilibrium monomer concentration of 1.3 M at room temperature [11]. To ensure that the monomer concentration remains well above 1.3 M, thereby avoiding broadening of the distribution through propagation–depropagation equilibrium, these polymerizations must be limited to relatively low conversion (<20%).

The rapid propagation of typical ROMP monomers with this Ru initiator complicates the formation of narrow-distribution polymers, but Bielawski and Grubbs showed that by adding bulky phosphines, propagation could be slowed [21]. The initiator molecule contains two PCy_3 ligands, one of which reversibly dissociates from the metal center in solution to yield the active ROMP site [24]. By adding excess phosphine to the solution, the binding equilibrium between Ru and phosphine ligand is shifted towards the inactive bound state, thereby slowing propagation without significantly slowing initiation, and producing a better-controlled polymerization. Bielawski and Grubbs were able to produce well-defined polymers of

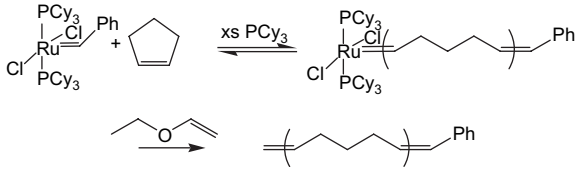

Fig. 1. Synthesis of polycyclopentene using a "Grubbs' first-generation" ruthenium-based initiator in the presence of excess tricyclohexylphosphine, terminated with ethyl vinyl ether.

exo-norbornene phenylimide, and even a narrow-distribution polycyclooctadiene of low molecular weight [21]. We follow a similar approach here for the polymerization of cyclopentene, but aim to build polymers of significantly higher molecular weight (>10 kg/mol). Even though the polymerization is termination-free, because the cyclopentene is only partially converted to polymer, the polymer product's chain length is not simply given by the monomer-to-initiator ratio. Instead, a kinetic model is required to predict how monomer conversion and polymer molecular weight evolve with time under different reaction conditions.

3.1. Kinetic model

The reaction kinetics for this system were modeled as first-order in both effective monomer and initiator concentrations, following the approach of Trzaska et al. for the Mo-based ROMP of cyclopentene [11]. Only a fraction f of the Ru sites is in the active (dissociated) form at any given time, slowing the rate accordingly:

$$\frac{-\mathrm{d}[\mathrm{M}]}{\mathrm{d}t} = k_1 f [\mathrm{I}]\left([\mathrm{M}] - [\mathrm{M}]_{\mathrm{eq}}\right) \tag{1}$$

where [M] is the monomer concentration, t is the time, k_1 is the propagation constant, [I] is the total initiator concentration, and $[\mathrm{M}]_{\mathrm{eq}}$ is the equilibrium monomer concentration (1.3 M at room temperature). The fraction f of active Ru is directly related to the initiator–ligand binding equilibrium constant (K_{eq}) and the concentration of added phosphine:

$$K_{\mathrm{eq}} = \frac{[\mathrm{CP}]}{[\mathrm{P}][\mathrm{C}]} \approx \frac{1}{f[\mathrm{P}]_{\mathrm{o}}} \tag{2}$$

where [CP] is the concentration of the inactive initiator:phosphine complex, [P] (= $[\mathrm{P}]_{\mathrm{o}} + f[\mathrm{I}]$) is the concentration of free phosphine (PCy_3) in solution, [C] (= f[I]) is the concentration of active initiator, and $[\mathrm{P}]_{\mathrm{o}}$ is the concentration of PCy_3 added to the reaction solution. The approximation in the second portion of Eq. (2) applies in the limit $f \ll 1$. By substituting f from Eq. (2) into Eq. (1), integrating to the polymerization time t_{p}, and calculating M_{n} (= $m_{\mathrm{o}}([\mathrm{M}]_{\mathrm{o}} - [\mathrm{M}])/[\mathrm{I}]$, where m_{o} is the monomer molecular weight), we obtain the following expression:

$$M_{\mathrm{n}} = m_{\mathrm{o}}\left(\frac{[\mathrm{M}]_{\mathrm{o}} - [\mathrm{M}]_{\mathrm{eq}}}{[\mathrm{M}]_{\mathrm{o}}}\right)\left(\frac{[\mathrm{M}]_{\mathrm{o}}}{[\mathrm{I}]}\right)\left(1 - \exp\left(\frac{-k_1}{K_{\mathrm{eq}}}\frac{[\mathrm{I}]}{[\mathrm{P}]_{\mathrm{o}}}\right)t_{\mathrm{p}}\right) \tag{3}$$

Since all polymerizations are limited to low conversion ([M] ≈ $[\mathrm{M}]_{\mathrm{o}}$) to remain well-controlled, the exponential in Eq. (3) may be expanded to terms linear in t_{p}, which allows us to more easily see the anticipated effect of each reaction parameter:

$$M_{\mathrm{n}} = m_{\mathrm{o}}\frac{k_1}{K_{\mathrm{eq}}}\left(\frac{[\mathrm{M}]_{\mathrm{o}} - [\mathrm{M}]_{\mathrm{eq}}}{[\mathrm{M}]_{\mathrm{o}}}\right)\left(\frac{[\mathrm{M}]_{\mathrm{o}}}{[\mathrm{I}]}\right)\left(\frac{[\mathrm{I}]}{[\mathrm{P}]_{\mathrm{o}}}\right)(t_{\mathrm{p}}) \tag{4}$$

To evaluate the validity of our model, each parameter group in parentheses in Eq. (4) was varied, while holding the others constant. Ideally, polymer molecular weight could be controlled by adjusting any of these parameters.

3.2. Effect of monomer concentration

In preliminary experiments, the initial monomer concentration $[\mathrm{M}]_{\mathrm{o}}$ was varied while holding $[\mathrm{M}]_{\mathrm{o}}/[\mathrm{I}] = 3000$, $t_{\mathrm{p}} = 60$ min, and $[\mathrm{P}]_{\mathrm{o}}/[\mathrm{I}] \approx 10$. From Eq. (4), we expect only slight increases in M_{n} with increases in $[\mathrm{M}]_{\mathrm{o}}$, and in fact very little difference in M_{n} or PDI was found across the three monomer concentrations attempted (3 M, 5 M and 7 M). The 5 M and 7 M solutions became very viscous during polymerization, so 3 M was chosen as the optimal value of $[\mathrm{M}]_{\mathrm{o}}$.

3.3. Effect of phosphine-to-initiator ratio

The ratio $[\mathrm{P}]_{\mathrm{o}}/[\mathrm{I}]$ was varied between 0 and 67, while keeping $[\mathrm{M}]_{\mathrm{o}}/[\mathrm{I}] = 3000$, $t_{\mathrm{p}} = 60$ min, and $[\mathrm{M}]_{\mathrm{o}} = 3$ M. Eq. (4) predicts an inverse relationship between $[\mathrm{P}]_{\mathrm{o}}/[\mathrm{I}]$ and M_{n}, which was largely borne out experimentally, as shown in the first block in Table 1. At low $[\mathrm{P}]_{\mathrm{o}}/[\mathrm{I}]$, the polymerization appears to be uncontrolled, based on the high values for M_{n} and PDI. At high $[\mathrm{P}]_{\mathrm{o}}/[\mathrm{I}]$, propagation is slowed excessively and only low conversions are achieved at $t_{\mathrm{p}} = 60$ min, resulting in a low M_{n} at $[\mathrm{P}]_{\mathrm{o}}/[\mathrm{I}] = 20$, and no polymer yield when $[\mathrm{P}]_{\mathrm{o}}/[\mathrm{I}] = 67$. Each of the intermediate values tested resulted in a fairly narrow-distribution polymer (PDI < 1.2), with M_{n} and conversion varied systematically through $[\mathrm{P}]_{\mathrm{o}}/[\mathrm{I}]$. While

Table 1
Reaction trials systematically varying parameter groups in Eq. (3)

$[\mathrm{M}]_{\mathrm{o}}$	$[\mathrm{P}]_{\mathrm{o}}/[\mathrm{I}]$[a]	$[\mathrm{M}]_{\mathrm{o}}/[\mathrm{I}]$[b]	t_{p}[c] (min)	M_{n} (g/mol)	PDI	True % conversion[d]	Apparent % conversion[e]
3	*0*	3000	60	39,600	1.61	47.4	19.4
3	*2.1*	3000	60	28,100	1.17	14.6	13.7
3	*4.0*	3000	60	19,000	1.10	8.3	9.3
3	*6.2*	3000	60	12,600	1.15	4.8	6.2
3	*8.3*	3000	60	11,000	1.16	5.3	5.4
3	*9.6*	3000	60	9500	1.13	4.1	4.6
3	*20*	3000	60	6100	1.21	2.0	3.0
3	*67*	3000	60	n/a	n/a	n/a	n/a
3	4.0	3000	*15*	4700	1.20	2.1	2.3
3	4.0	3000	*30*	9400	1.11	4.3	4.6
3	4.0	3000	*45*	14,350	1.11	6.6	7.0
3	4.0	3000	*60*	19,000	1.10	8.3	9.3
3	4.0	3000	*90*	27,600	1.15	12.9	13.5
3	4.0	3000	*120*	34,650	1.17	16.6	17.0
3	4.0	3000	*180*	44,350	1.31	24.1	21.7
3	4.0	3000	*240*	55,000	1.44	30.8	27.0
3	4.0	3000	*300*	62,950	1.56	35.5	30.9
3	4.0	3000	*360*	64,750	1.63	42.2	31.7
3	4.0	*3000*	60	19,000	1.10	8.3	13.5
3	3.9	*12,500*	60	53,800	1.40	9.6	6.3
3	3.9	*20,000*	60	57,900	1.44	5.7	4.3

[a] Molar ratio of added phosphine to initiator.
[b] Initial molar ratio of monomer to initiator.
[c] Reaction time.
[d] True conversion determined by GPC.
[e] Apparent conversion (X) calculated from polymer M_{n} assuming that each initiator molecule results in precisely one chain.

$[P]_o/[I]$ could thus be manipulated to control M_n, we selected a constant $[P]_o/[I] = 4$ as optimal, as this value gives control over the polymerization and still results in a satisfactory conversion and M_n in 60 min.

3.4. Effect of reaction time

The effect of reaction time t_p was analyzed by terminating aliquots taken at various times from a single reaction, with $[M]_o = 3$ M, $[P]_o/[I] = 4$, and $[M]_o/[I] = 3000$. As shown in the second block in Table 1 and in Fig. 2a, M_n monotonically increases with time, as expected. PDI, however, is minimized at intermediate times. At short times the distribution is broad but symmetric, as is typical for living polymerizations where initiation is not instantaneous. The distribution narrows with increasing t_p at first (up to 60 min), as the degree of polymerization builds, but at longer times a high molecular weight shoulder appears in the GPC trace. This shoulder (observed at less than twice M_n), visible after 90 min and more pronounced at 120 min and 180 min, is attributed to acyclic metathesis: an attack of the active catalyst site on a double bond in a polymer chain, rather than on the double bond in the monomer. Its most notable effect is the formation of a population of high molecular weight chains, a result of the two-ended propagating species [22]. Longer reaction times result in a broad molecular weight distribution, so the optimal reaction time was chosen as $t_p = 60$ min.

3.5. Effect of monomer-to-initiator ratio

As shown in the third block in Table 1, varying the monomer-to-initiator molar ratio with all other parameters held constant affects M_n drastically, as expected. Over the range $[M]_o/[I] = 3000–20{,}000$, M_n varied from 19 kg/mol to 58 kg/mol at a relatively constant conversion. For the same range of $[M]_o/[I]$, the PDI increased substantially from 1.10 to 1.44. Fig. 3a, showing the time progression of GPC traces for the $[M]_o/$

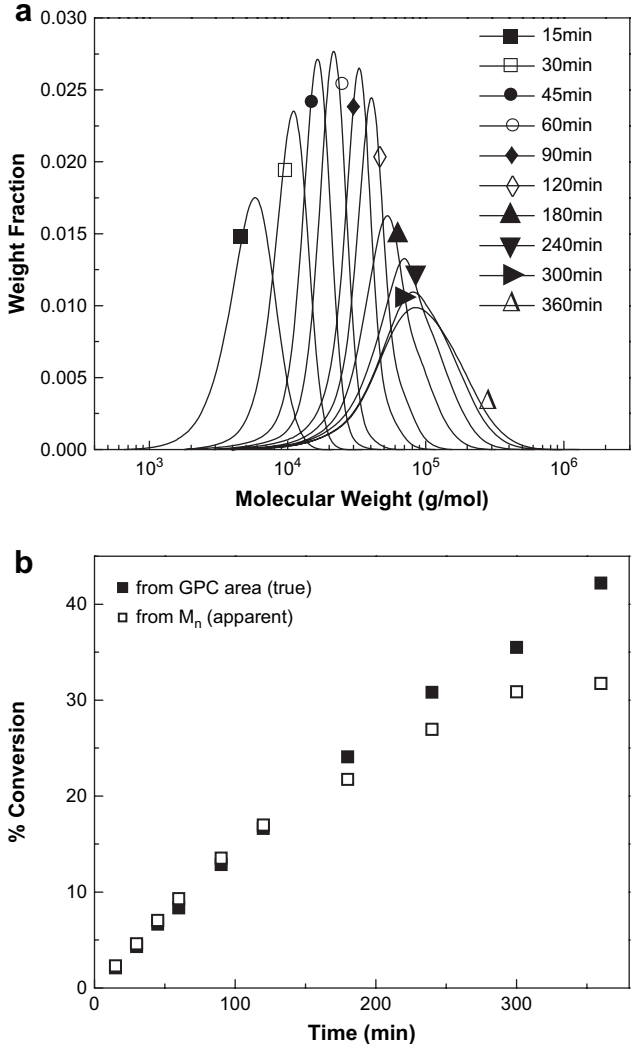

Fig. 2. (a) Molecular weight distributions of polycyclopentene at various reaction times for $[M]_o/[I] = 3000$ (second block in Table 1). (All distributions are normalized to equal area.) (b) Time evolution of true monomer conversion (filled symbols), and apparent conversion X calculated from M_n (open symbols) by assuming each initiator generates precisely one chain.

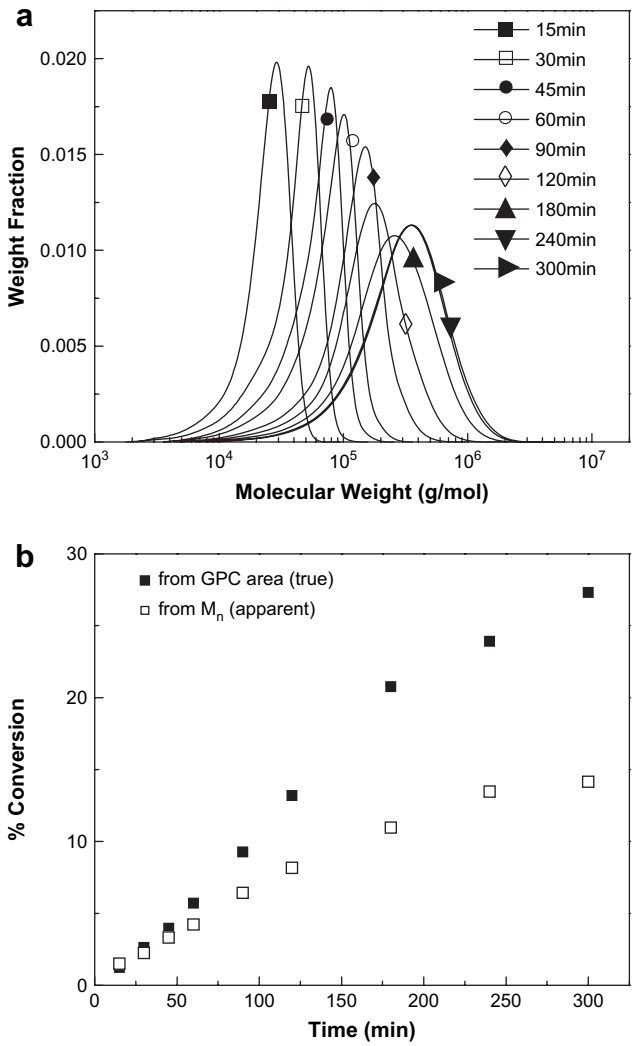

Fig. 3. (a) Molecular weight distributions of polycyclopentene at various reaction times for $[M]_o/[I] = 20{,}000$. (b) Time evolution of true monomer conversion (filled symbols), and apparent conversion X calculated from M_n (open symbols).

$[I] = 20{,}000$ samples, provides additional insight into this behavior: note the gradual slowing in the increase of peak molecular weight with time, and the virtual halt after 200 min.

To reveal the origin of this ''stalling'' of M_n at long t_p, Figs. 2b and 3b present the time course of conversion and M_n for the $[M]_o/[I] = 3000$ and 20,000 polymerizations. Here, M_n (open symbols) is expressed in the form of an apparent conversion $X \equiv M_n/(m_o*([M]_o/[I]))$; if each initiator molecule generates exactly one polymer chain, then X will be identical to the actual monomer conversion, which we also measured by GPC (filled symbols). For both polymerizations, the apparent and true conversions are identical at short times, but they deviate at longer times, starting at about 180 min for $[M]_o/[I] = 3000$ (Fig. 2b) and at only 45 min for $[M]_o/[I] = 20{,}000$ (Fig. 3b). At longer times, the apparent conversion (gauged by M_n) appears to level out, especially for the $[M]_o/[I] = 20{,}000$ polymerization, although the true conversion of monomer to polymer continues to grow essentially linearly with time.

3.6. Chain transfer

In a nominally living polymerization system, a continued increase in conversion without an increase in M_n clearly indicates the presence of a chain-transfer process, whereby each initiator can create multiple polymer chains, and the ultimate value of M_n is dictated by the chain-transfer coefficient and the concentration of the chain-transfer agent (CTA). For the $[M]_o/[I] = 20{,}000$ polymerization (Fig. 3), $M_n \approx 200$ kg/mol at long times. This value of M_n is only a little over half the value expected from the measured conversion at 300 min, indicating that there are nearly two polymer chains present per Ru. Note that the acyclic metathesis discussed above [11] cannot be the cause of this ''stalling'' in M_n; since it represents chain transfer to polymer, it does not create any additional polymer chains and thus does not affect M_n. However, such chain transfer to polymer does raise the PDI; for the $[M]_o/[I] = 20{,}000$ polymerization, PDI = 1.9 at long times, close to the limiting value of 2 expected in the limit of many chain-transfer steps per active site, even though the actual number of transfer steps per site averages slightly less than one.

We suspected that this troublesome CTA is a contaminant in the monomer supply, not removed by stirring over butyllithium and vacuum transfer, and present at levels (concentration [T]) too low to detect by ^{1}H NMR (<0.2%). Attempts at monomer purification by fractional distillation did not yield improved results, suggesting that the CTA has a boiling point similar to cyclopentene, such as acyclic C_5 olefins or dienes, which are known chain-transfer agents for Ru-initiated ROMP [25–27]. For example, Fig. 4 shows the effects of adding 2-pentene (mixture of *cis* and *trans*) to the reaction mixture; at $[T]/[I] = 200$, M_n is notably reduced, and the reduction is severe at $[T]/[I] = 2000$. From the values of M_n obtained, we determined a chain-transfer coefficient $C_T = 0.017$ for mixed 2-pentenes in cyclopentene polymerizations with this Grubbs' first-generation catalyst. The limiting value of $M_n \approx 200$ kg/mol observed in Fig. 3 corresponds to

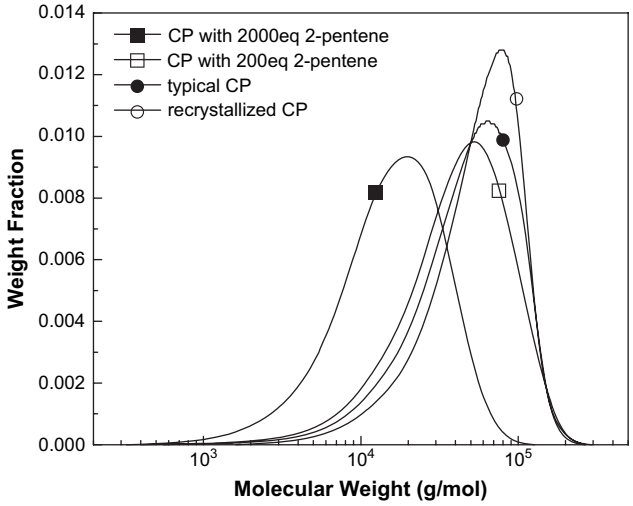

Fig. 4. Molecular weight distributions of polycyclopentene obtained with monomer feeds of varying purity; all polymerizations run at $[M]_o/[I] = 15{,}000$, $[P]_o/[I] = 4$, $t_p = 60$ min. (●) Standard purification; (□) standard + 2-pentene, $[T]/[I] = 200$; (■) standard + 2-pentene, $[T]/[I] = 2000$; (○) recrystallized prior to standard purification.

$C_T[T] = 1 \times 10^{-3}$ M for the unknown CTA, indicating that the unknown must be more active than 2-pentene (which would need to be present in the cyclopentene at the detectable level of 2 mol% to produce the observed effect). Though fractional distillation was ineffective, the contaminant could be removed from the cyclopentene via recrystallization, by freezing approximately half of the as-received monomer on liquid nitrogen (cyclopentene $T_m = -135$ °C) and discarding the supernatant. Fig. 4 shows that upon polymerizing this recrystallized monomer, a relatively narrow GPC peak was obtained, indicating that chain transfer has been suppressed.

By considering those polymerizations which were well-controlled and where chain transfer was negligible (PDI < 1.3), we can obtain the value of the lumped rate parameter k_1/K_{eq} at room temperature by fitting the data to Eq. (3). Fig. 5 shows this comparison, where M_n is again represented

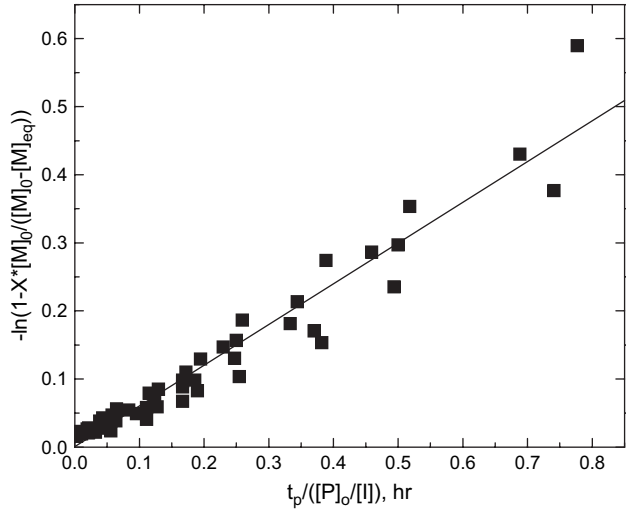

Fig. 5. Kinetic data for all well-controlled polymerizations (PDI < 1.3) plotted according to Eq. (3). Best-fit line has a slope $k_1/K_{eq} = 0.6$ h^{-1}.

through the apparent conversion X defined above. Since molecular weights were routinely measured and true conversions were not, the apparent conversions were used for this analysis; however, as demonstrated in Figs. 2b and 3b, when the polymerizations are well-controlled, these two quantities are identical. The data collapse well, with the best-fit line showing a slope of 0.6 h^{-1} (k_1/K_{eq}). This lumped rate parameter is comparable to that found by Trzaska et al. for their Mo-catalyzed ROMP of cyclopentene, 0.9 h^{-1} [11]. Though the significance of K_{eq} is slightly different in the two cases (in the Mo case, the added phosphine does not correspond to a catalyst ligand), polymerizations proceed at comparable rates with the two catalyst systems. By using this value of the rate parameter in Eq. (3), the conditions required for the synthesis of polycyclopentene of targeted M_n are easily determined. Moreover, employing this lumped rate parameter in Eq. (3) with the conditions used for polymerization of the recrystallized monomer (Fig. 4) yields $M_n = 80{,}000$ g/mol, in close agreement with the experimental $M_n = 77{,}000$ g/mol. This confirms that recrystallization was effective in removing the CTA, and that the CTA does not measurably influence the rate of polymerization.

4. Conclusions

Polycyclopentene was synthesized in a controlled manner via ROMP using a Ru-based initiator in the presence of tricyclohexylphosphine. A model was developed to describe the polymerization kinetics, which quantitatively captured the increase in M_n with increasing monomer-to-initiator ratio, increasing polymerization time, and decreasing phosphine-to-initiator ratio. At high values of M_n, chain-transfer processes became evident; chain transfer to polymer ultimately limits the molecular weights at which narrow distributions (PDI < 1.2) can be preserved, to approximately 40 kg/mol. Since the Ru catalyst is effective for the polymerization of a broad range of monomers in addition to cyclopentene, this method diversifies the range of polyethylene-containing block copolymers which can be prepared via ROMP and subsequent hydrogenation.

Acknowledgements

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