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Rapid Controlled Synthesis of Large Polymers by Frontal Ring-Opening Metathesis Polymerization

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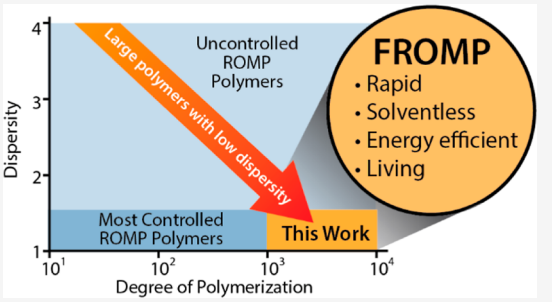
ABSTRACT: Tunable molecular weight and well-defined polydispersity are the hallmarks of a controlled polymerization. This process relies on vanishingly small termination rates, minimal chain transfer, and initiation rates faster than propagation rates. Ring-opening metathesis polymerization (ROMP) is a well-known controlled polymerization based on the opening of strained cyclic olefins. The exothermic nature of ROMP allows rapid conversion of neat monomers to polymers through frontal ROMP (FROMP). Unlike traditional ROMP, FROMP uses the exothermic heat from the opening of strained cyclic olefins to thermally activate the initiator that sustains the propagation of a cascading reaction front. Although the reaction mechanisms for ROMP and FROMP are the same, the reaction conditions differ greatly, especially in the temperature and monomer concentration. The ability to control the polymerization under FROMP conditions has yet to be investigated, as well as its potential in the synthesis of well-defined polymers without the use of solvents and with minimal energy input. Here, we show that FROMP rapidly transforms monomers into polymers of high-molecular weight (M_n) with good fidelity and low dispersity (Đ). Specifically, the synthesis of polymers with M_n up to 700 kg/mol and Đ of 1.5 was achieved with a rapid, solvent-free, and oxygen-tolerant frontal polymerization technique. Further control of the polymerization was possible with the addition of a phosphite ligand that lowered the Đ to 1.2. We anticipate that controlled FROMP will become a valuable macromolecular synthetic tool due to its reliability, speed, scalability, and simplicity.



INTRODUCTION

Ring-opening metathesis polymerization (**ROMP**) is widely used in the synthesis of well-defined structures.[1] The origins of ROMP go back to 1950s, but it was not until 1986 that ROMP was shown to have characteristics of a controlled living polymerization.[2] As with other controlled polymerizations, ROMP depends on a higher initiation rate compared to the propagation rate and on the absence of both chain transfer and termination reactions.[3] Controlled ROMP has been used for the synthesis of a variety of macromolecular architectures including block copolymers, dendrimers, cyclic polymers, bottlebrushes, and others.[4] Fundamental research has focused on tuning initiators, monomers, and reaction conditions to make low dispersity polymers in short times and under ambient conditions.[5] However, access to linear polymers with degree of polymerizations (**DPs**) higher than 1000 and low dispersity (***Đ***) remains a challenge, as seen in Figure 1. The synthesis of high polymers with low Đ via ROMP are mostly performed under an inert atmosphere with reaction times that can exceed several hours (depending on the catalyst).[6,7]

Frontal polymerization (**FP**) is a technique whereby a locally applied stimulus causes local initiation of an exothermic polymerization reaction. In frontal ring-opening metathesis polymerization (**FROMP**), the heat released from a strained cyclic monomer diffuses away from the site of initiation to bring about the thermally activated reaction at nearby locations and subsequent polymerization causes more monomer conversion. A reaction front ensues and the process continues until all monomers are converted to polymers.[8] Following the 2001 publication by Mariani et al.,[9] we used FROMP of dicyclopentadiene (**DCPD**) and 1,5-cyclooctadiene in the manufacturing of composites, gradient materials, foams, and resins for damage repair.[10−12] In such systems, Grubbs second-generation catalyst (**G2**) is used as an initiator instead of the more active Grubbs third-generation catalyst (**G3**) because FROMP requires minimal activity of the initiator at room temperature to avoid spontaneous polymerization. FP has mainly been used in the development of materials for diverse applications, though its use as a controlled polymerization technique has not yet been explored.[13]

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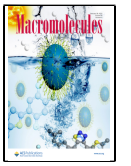

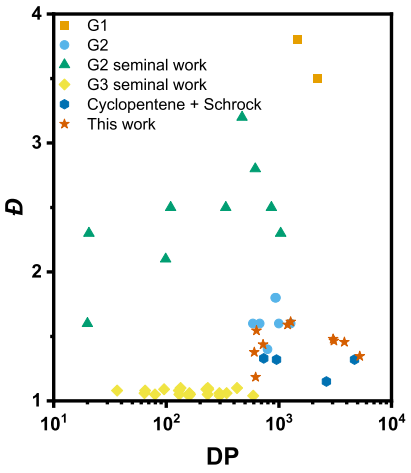

Figure 1. ROMP literature precedent for the synthesis of linear polymers. G1 (Macromolecules 2001, 44, 6637); G2 (J. Organomet. Chem. 2020, 911, 121156); G2 seminal work (Angew. Chem. Int. Ed. 2000, 39, 2903); G3 seminal work (Angew. Chem. Int. Ed. 2003, 42, 1743); and cyclopentene + Schrock (ACS Macro Lett. 2017, 6, 112).[7,14−17]

Given the high temperatures involved in FROMP (e.g., typically ∼200 ± 50 °C), one may intuitively assume that polymerization is not well controlled. However, exposure to high temperatures is short-lived and at these temperatures, the polymerization rate is exceedingly fast. We hypothesized that despite the high temperatures, FROMP is a controlled polymerization process. This hypothesis assumes that the initiation and propagation rates remain significantly larger than the rates of both initiator deactivation and cross metathesis. Most ROMP kinetic studies are based on investigations that are at temperatures much lower than those encountered in FROMP. ROMP kinetic investigations are also performed in dilute solutions with an inert atmosphere rather than neat monomers exposed to air.[18] We were thus intrigued to systematically investigate the FROMP reaction to probe whether it is useful as a simple controlled polymerization technique.

In this work, we discovered that not only is FROMP a controlled polymerization process, but it is also capable of producing high-molecular-weight polymers (up to 700 kg/mol) with dispersity as low as 1.2 in less than 45 s under air. Additionally, a detailed study of the reaction showed that the ruthenium initiator does not decompose significantly, enabling chain extension after the FROMP reaction has completed. To the best of our knowledge, this is the first demonstration of a controlled polymerization utilizing FP and introduces FROMP as a tool for the synthesis of well-defined polymers.

RESULTS AND DISCUSSION

We selected exo-dihydro dicyclopentadiene (**DCPD-H_2**) for the study of controlled FROMP. DCPD-H_2 produces linear polymers, which are characterizable using solution techniques like nuclear magnetic resonance spectroscopy (**NMR**) and size exclusion chromatography (**SEC**). DCPD-H_2 is a liquid at room temperature and has a higher boiling point than other liquid norbornene-type monomers (88−90 °C at 40 Torr).[19] Finally, DCPD-H_2 is an analogue of DCPD, making it suitable for investigating the microstructure of DCPD cross-linked polymers.

We synthesized DCPD-H_2 using a slightly modified methodology reported by Goetz and Boydston.[20] The monomer was prepared by bromination of the norbornene alkene using HBr, followed by a hydrogenation of the cyclopentene alkene with Pd/C. Finally, the norbornene alkene was retrieved by elimination using KOH/EtOH. Following this procedure, we synthesized 140 g of DCPD-H_2 with an overall yield of 69.7%.

Initially, we compared the polymerization of DCPD-H_2 using four methods. Solution ROMP, solution ROMP with the addition of tributyl phosphite [$P(^nOBu)_3$], neat ROMP, and FROMP. The reactions were run with G2 and G3 for one solution ROMP, targeting a polymer molecular weight of 100 kg/mol. We evaluated the control of each polymerization by determining the average molecular weight (M_n) and dispersity ($Đ$) of the obtained polymers (Figure 2).

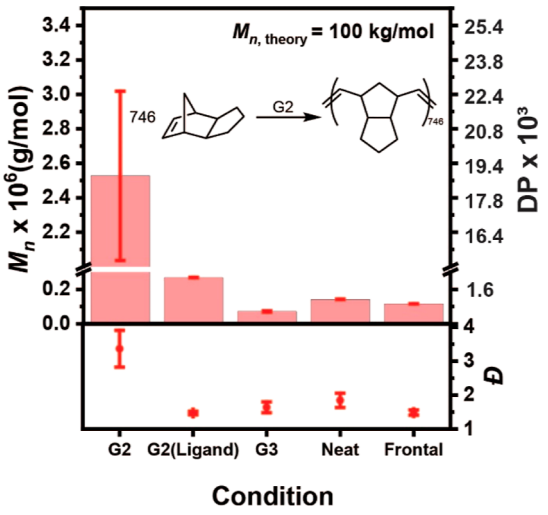

Figure 2. Average molecular weight (M_n), degree of polymerization (DP), and dispersity ($Đ$) of the DCPD-H_2 polymers targeting a M_n of 100 kg/mol. G2, G3, and G2(ligand) were done in dichloromethane (0.05 mM) under nitrogen at 20 °C for 5 min (G2 and G3) and 3.5 h [G2(ligand)]. Neat and Frontal were done solventless at 20 °C and took 6 min and 45 s for completion, respectively. Error bars in each data set were obtained from three independent experiments.

Solution ROMP (0.05 mM, CH_2Cl_2) was monitored using ^{1}H-NMR, showing complete consumption of the monomer at 5 min of reaction time (Figure S1). After isolation of the DCPD-H_2 polymer (**pDCPD-H_2**) synthesized with G2, we determined M_n = 2527 ± 491 kg/mol and $Đ$ = 3.37 ± 0.54 using SEC. The resulting polymers had a M_n 25 times larger than the targeted one (100 kg/mol) and had a broad dispersity, indicating poor control of the polymerization. This result is not surprising because solution ROMP using G2 is known to have poor initiation rates of norbornene-type monomers, which produces polymers with a higher M_n than the target and a broad $Đ$.[15]

Solution ROMP with the addition of $P(^nOBu)_3$ (a G2 ligand) was performed following the same conditions of the previous polymerization, but the reaction required 3.5 h to consume all the monomer (Figure S2). The obtained polymer have a M_n = 268 ± 13 kg/mol and $Đ$ = 1.47 ± 0.05, which corresponds to a M_n 2.7 times higher than the theoretical one. We observed an improvement in the polymerization control, likely due to the increase of the k_i/k_p ratio, which has been

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observed previously.[21] Additionally, we performed the same solution polymerization with G3, obtaining polymers with a M_n = 71.5 ± 3.6 kg/mol and $Đ$ = 1.64 ± 0.16, after 5 min of reaction, which shows a better control of the polymerization compared with the experiments done with G2 and G2/P(^{n}OBu)$_3$. However, the requirements of solvents and (in some cases) poor initiation rates limit the practicality of solution polymerizations.

Neat (solventless) ROMP was done by stirring DCPD-H$_2$ with G2 at room temperature until polymerization was completed, typically taking about 6 min. During this time the liquid gelled, followed by a spontaneous transformation into a solid with a concomitant increase of temperature (Figure S3). Using this protocol, we obtain polymers with M_n = 142 ± 13 kg/mol and $Đ$ = 1.85 ± 0.2. We speculate that the control of the polymerization exceeds that of the G2 solution ROMP experiments due to the spike in temperature, which in turn increases the initiation rate. Nonetheless, M_n is significantly closer to the theoretical value as compared to solution ROMP, $Đ$ is still broad due to a higher initiator degradation, which is a consequence of multiple initiation points during the reaction.

FROMP was performed by mixing DCPD-H$_2$, P(^{n}OBu)$_3$, and G2 at 20 °C, followed by a local triggering of the reaction front with a soldering iron, initiating a polymerization cascade that transforms 0.5 mL of liquid monomer into a solid polymer in 45 s (Figure 3). Polymers obtained via FROMP have M_n = 116 ± 11 kg/mol and $Đ$ = 1.31 ± 0.2, which shows that FROMP produces pDCPD-H$_2$ with a comparable M_n to that of neat ROMP, and produces polymers with the lowest $Đ$. We posit that localized and singular heating in FROMP decreases the chances of initiator degradation, which sustains a more controlled reaction than that of neat ROMP.

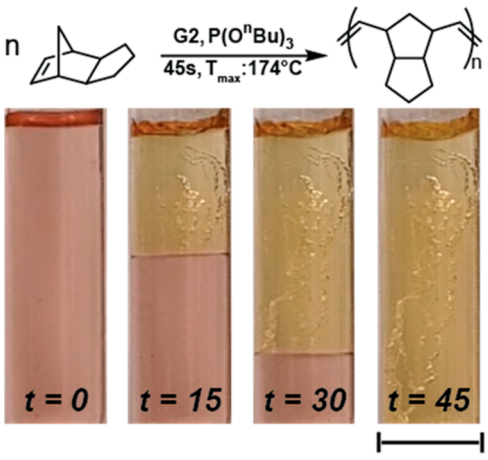

Figure 3. DCPD-H$_2$ FROMP targeting a M_n of 100 kg/mol. DCPD-H$_2$ (500.7 mg, 3.65 mmol), G2 (4.0 mg, 4.8 μmol), and P(^{n}OBu)$_3$ (1.3 μL, 4.6 μmol). Triggering of the reaction was done by direct contact of a soldering iron on the upper side of the glass. Scale bar 5 mm.

Knowing that FROMP generates well-controlled polymers, we performed several experiments to evaluate the influence of FROMP conditions on the synthesis of DCPD-H$_2$ polymers.

Initially, we investigated the effect of air on the reaction control. Following the protocol mentioned above, we purged the reactions with air, N$_2$, or vacuum for 5 min before polymerization. We observed that the reaction purged with air has a slightly higher M_n compared with the ones purged under nitrogen and vacuum; however, the difference is not statistically significant (Figure S4). The high tolerance to oxygen when initiator ligands are used during ROMP was also recently observed.[6] Moreover, we suspect the slightly higher M_n is caused by small amounts of oxygen in the monomer that can degrade the initiator during the reaction.

Next, we evaluated the M_n and $Đ$ of pDCPD-H$_2$ as a function of distance from the FROMP initiation point. We characterized samples from the top (initiation location), middle, and bottom of the polymeric monolith and observed that all locations had similar values for both M_n and $Đ$, though the error for the top site was higher (Figure S5). We attribute the increased error to an inconsistent heat transfer by the soldering iron to the monomer.

Another parameter that has a strong influence on FROMP but not necessarily on ROMP is the dimensions or shape of the reaction vessel. FROMP has been performed in diverse container sizes with differing boundary conditions, which has led to interesting morphological properties.[22] Therefore, we evaluated if a change in the container type would have an effect in the polymer by comparing the polymerization of DCPD-H$_2$ in a cylindrical container (NMR tube) with a rectangular container (glass slides separated by a 1.0 mm rubber). M_n and $Đ$ remained constant, showing that controlled polymerization of DCPD-H$_2$ is performed using different containers and boundary conditions (Figure S6).

In previous works, we have seen that the identity of the phosphite ligand used in FROMP has an effect on the length of time that the reaction remains viable for FP (storage time).[23] Therefore, we evaluated if an inhibitor ligand would also have an effect on polymer M_n and $Đ$. We tested three phosphite inhibitors: tri-*n*-butyl, tri-isopropyl, and triethyl, keeping the initiator/phosphite molar ratio constant. We observed similar M_n and $Đ$ for the three ligands, showing that under FROMP conditions the chosen phosphite has a negligible effect on the resulting polymer molecular weight (Figure S7).

As mentioned above, it is possible to store the solution of monomer, initiator, and ligand before triggering the reaction. Therefore, we also evaluated the effect of storage time on M_n and $Đ$. We delayed initiating FROMP for 0, 1, 2, and 3 h after the components were combined, seeing no change in the $Đ$ of the polymers as a function of storage time but observed a slight increase in the M_n from 94.0 kg/mol at t = 0 h up to 114.8 kg/mol at t = 3 h (Figure S8). The slight increase in the M_n could be due to the G2 precatalyst undergoing a number of changes after mixing with the monomer and inhibitor. These changes include phosphine for phosphite exchange and benzylidene for polymer chain initiation. The various species are likely to have different rates of initiation. The longer the storage time, the greater the changes. The increase in the M_n could also be due to small amounts of initiator degradation at longer times.

Besides the difference in M_n and $Đ$ between FROMP and ROMP, we were interested in understanding if there were any disparities in the overall microstructures of the final polymers for each method. Previous reports have shown that G2 has poor selectivity, i.e., norbornene-type monomer polymerization in solution with G2, which produces a polymer with similar amounts of *E* and *Z* isomers.[24] ^{1}H-NMR (CDCl$_3$) analysis of the synthesized polymers show that this is also the case for DCPD-H$_2$ ROMP in solution (Z = 51% and E = 49%). In contrast, neat ROMP and FROMP have a higher content of the *E*-isomer (Z = 39% and E = 61%) showing that reaction

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conditions also influence the polymer chain microstructures (Figure S9).

Having fully characterized different FP parameters in the synthesis of pDCPD-H_2, we turned our attention to the understanding of the polymerization control under FROMP.

Initially, we evaluated the maximum temperature of the reaction. We immersed a wire thermocouple in the reaction and monitored the temperature as a function of time, observing a maximum temperature (T_{max}) of 174 ± 14 °C (Figure S10). Although G2 might degrade due to the reaction's high temperatures, we obtained polymers with experimental M_n similar to the theoretical ones and low $Đ$, which indicates minimal initiator decomposition during FROMP. Using differential scanning calorimetry (**DSC**), we observed an exothermic peak corresponding to ROMP with an onset temperature of 55 °C (Figure S11), indicating that the polymerization begins at a temperature well below the maximum front temperature.

To better understand the FROMP temperature profile, we monitored the transformation of 0.7 mL of DCPD-H_2 into a polymer using a mold with a quartz slide, a resistor wire at 80 °C, and an infrared (IR) camera (Figure S12). We took a screenshot of the polymerization process every second until the reaction went to completion (Figure S13) and plotted the temperatures as a function of distance together with their first derivative (Figure S14). In the IR thermograms, we observed from right to left, four main regions; region 1, a pre-reaction region, which is where the liquid monomer is located; region 2, a conversion region, which is the transition from monomer to polymer; region 3, a post-curing region and finally region 4, a triggering region, characterized by a higher temperature due to the combination of the heat coming from the reaction and the initiation source (Figure 4). The polymerization begins near the observed onset temperature (55 °C) and goes until it reaches the maximum temperature/distance variation. We determined the conversion region for all the thermograms at different time points (Table S11), calculating a conversion region of 0.406 ± 0.079 mm, which is the region where the monomer is converted into a polymer. Separately, we calculated a FROMP frontal velocity (v_f) of 2.52 ± 0.13 mm/s by monitoring the reaction distance as a function of time. Based on the frontal speed of the reaction, we calculated that 160 ± 8 ms is required to consume the monomer in the conversion region (0.406 ± 0.079 mm). To determine the maximum initiator degradation in the conversion region, we performed a degradation study of the initiator at the FROMP maximum temperature (174 °C) for 10 s, indicating a first-order degradation rate of 0.118 ± 0.002 s^{-1} (Figure S15). By using the rate constant from the degradation study and the amount of time required to consume the monomer in the conversion region, we calculated that the maximum amount of decomposed initiator is 1.87% of the initial loading (see the Supporting Information), demonstrating that initiator degradation is insignificant during FROMP due to the localized rapid increase in temperature and exceedingly fast polymerization at these temperatures.

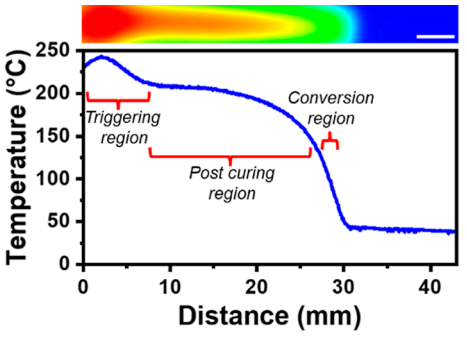

Figure 4. Top. Thermogram of the DCPD-H_2 frontal polymerization targeting a M_n of 100 kg/mol in a quartz mold. Thermogram obtained from the recording of the reaction with an infrared camera at 5 s after triggering. Scale bar 3 mm. Bottom. Temperature profile extracted from the FROMP thermogram, where we converted pixels to the distance (1 pixel = 0.057 mm).

After conversion of DCPD-H_2, the reaction temperature keeps increasing due to the extra energy released from the monomer, reaching values of around 200 °C and the system stays at these high temperatures for around 2 min (Figure S16). Therefore, we evaluated if the ruthenium center survived high temperatures after FROMP by taking a ^{1}H-NMR of pDCPD-H_2 after the reaction and observed the presence of the ruthenium alkylidene end group at 19.1 ppm (Figure S17). Inspired by this result, we also performed a chain-extension experiment in solution to corroborate that the ruthenium center is still active after FROMP. We frontally polymerized DCPD-H_2 inside of a glovebox to avoid initiator decomposition caused by oxygen, obtaining a polymer with a M_n = 135 kg/mol and $Đ$ = 1.44 ($M_{n\ target}$ = 111 kg/mol). Then, we dissolved 20.0 mg of pDCPD-H_2 in tetrahydrofuran, added 19.9 mg of DCPD-H_2, and let them react for 24 h, obtaining a polymer with a M_n = 242 kg/mol and $Đ$ = 1.36 (Figure 5, $M_{n\ target}$ = 267 kg/mol). The chain extension after FROMP shows that the ruthenium center is still active and can continue adding monomers to the formed polymeric chains. Moreover, we obtained good polymerization control in the chain extension due to P(O^nBu)$_3$ that attenuates the rate of polymer propagation (k_p). The presence of the metal alkylidene and

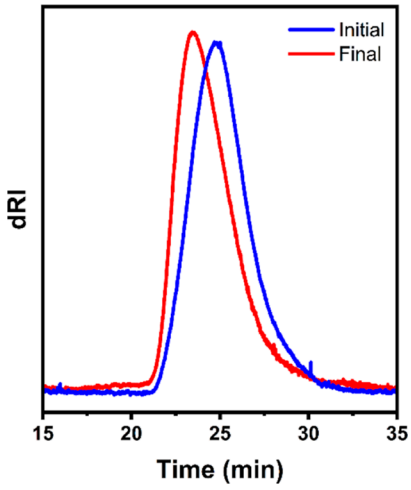

Figure 5. Chromatograms of the pDCPD-H_2 chain extension experiment. Initial polymer was obtained by FROMP in a glass mold inside of a glovebox, using quantities to obtain a 100 kg/mol polymer. Extension experiment was performed by dissolving 20.0 mg of the obtained polymer together with 19.7 mg of DCPD-H_2 in THF (4.7 mL), which aims to double the molecular weight of the polymer. The reaction was run for 24 h at 20 °C.

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chain-extension experiment demonstrate that the initiator did not completely degrade during or after FROMP.

We continued testing the ability to control DCPD-H_2 polymerization by evaluating the M_n change as a function of the monomer-to-initiator ratio (**M/I**). This experiment was performed with a minor amount of solvent, which was used to access sub-mg amounts of G2 (see the Supporting Information). M_n increased linearly with M/I, obtaining polymers up to 700 kg/mol with a $Đ$ of 1.49 ± 0.10, which demonstrates the advantage of using FROMP to synthesize linear high-molecular-weight DCPD-H_2 polymers, further supporting our hypothesis that the polymerization is indeed controlled (Figure 6). We also measured v_f of the reactions and

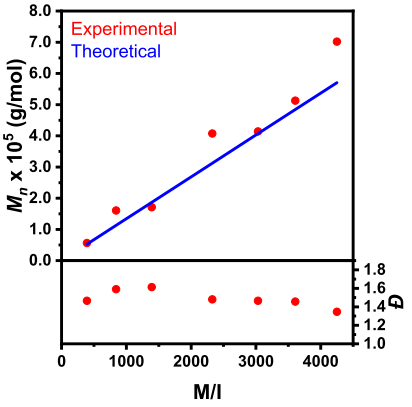

Figure 6. (A). Average molecular weight (M_n) and dispersity ($Đ$) of DCPD-H_2 polymers obtained by FROMP with a variation of the monomer to initiator ratio.

observed a decrease as a function of M/I (Figure S18), which is a consequence from the decrease of initiator at higher M/I that generates less heat per unit volume, making the monomer to polymer conversion slower. However, the reaction is hot enough to maintain DCDP-H_2 polymerization control.

As stated before, the initiation rate in controlled polymerization is imperative. Previous studies have demonstrated that controlled solution-state ROMP can be achieved by the addition of ligands that coordinate to ruthenium,[25] among them phosphites are known to form more stable ruthenium complexes compared with PCy_3-containing congeners.[26] We hypothesized that an increase in $P(O^nBu)_3$ concentration will attenuate the propagation rate, acting to increase the rate of initiation in relation to propagation to improve control over the polymerization.

We observed narrower peaks in the SEC traces by adding more $P(O^nBu)_3$ (Figure 7A), showing polymers with polydispersity values as low as 1.2. Additionally, there is no appreciable variation of the M_n as a function of the $P(O^nBu)_3$ amount, demonstrating the decrease of the polymer dispersity does not affect the targeted M_n (Figure 7B). Finally, reduction of v_f with the addition of $P(O^nBu)_3$ indicates a reduction of the activated initiator amount (Figure S19), supporting our hypothesis of the propagation rate attenuation, which leads to less disperse polymers.

CONCLUSIONS

Controlled ROMP was achieved using frontal polymerization. Specifically, FROMP of DCPD-H_2 with G2 produces polymers with lower $Đ$ and a more controlled M_n. Additionally, we demonstrated that G2 does not degrade during FROMP due to the short time the initiator stays at high temperatures. The survival of the polymer-bound initiator was further showcased with the chain extension experiment demonstrating that the initiator is still active after FROMP. We also proved the control of the polymer M_n by changing the M/I and we accessed polymers with M_n up to 700 kg/mol with low $Đ$. Finally, we made polymers with even lower $Đ$, reaching values of 1.2, by the addition of more $P(O^nBu)_3$, which attenuates the reaction propagation rate.

FROMP is a viable technique to obtain norbornene-derived polymers with good control of the M_n and $Đ$ in short periods of time, requiring no solvent, and reducing the energy input needed for polymerization.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.macromol.2c01892.

Materials, instrumentations, synthetic methods, and experimental data (PDF)

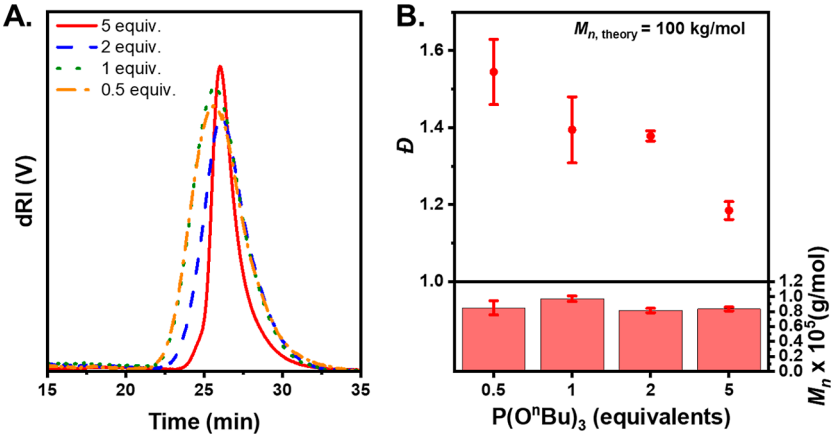

Figure 7. FROMP of DCPD-H_2 targeting a M_n of 100 kg/mol with different equivalents of $P(^nOBu)_3$ relative to G2 (A). Size exclusion Chromatograms (B). Dispersity ($Đ$) and average molecular weight (M_n).

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Author Contributions

[⊥]These authors contributed equally. The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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Notes

The authors declare no competing financial interest.

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