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Alkyl Phosphite Inhibitors for Frontal Ring-Opening Metathesis Polymerization Greatly Increase Pot Life

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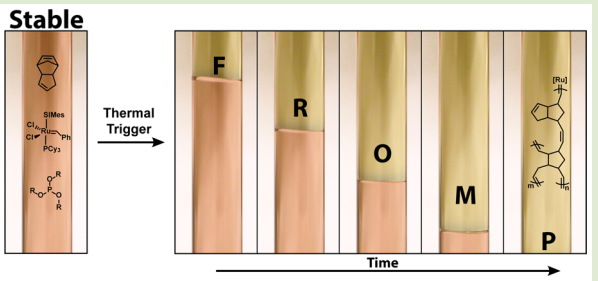
Supporting Information

ABSTRACT: Frontal ring-opening metathesis polymerization (FROMP) has potential for use in rapid fabrication of structural polymers. However, the high activity of the ruthenium catalyst used for FROMP has limited the working time to <1 h. We report the use of alkyl phosphites as inhibitors for Grubbs' type catalysts to substantially extend working time. Subtle changes in alkyl phosphite structure are shown to impact both pot life and frontal velocity. Specifically, by varying phosphite structure and concentration, we are able to control pot life between 0.25 and 30 h while still allowing FROMP to proceed at velocities between 1 and 8 cm/min to yield fully cured thermoset polymers. These results are of interest for conventional ROMP synthesis and may open the way to new FROMP-based manufacturing possibilities.



Autocatalytic reactions are widely used as a means of amplifying subtle physical or chemical stimuli to engender substantial change in material structure or function.[1] Frontal polymerizations (FPs) are a useful class of autocatalytic reaction that rapidly transform monomer to polymer upon a small thermal stimulus. This stimulus activates latent initiator to begin an exothermic polymerization reaction, which thermally activates further latent initiator and ultimately produces a propagating reaction wave that quickly polymerizes available monomer. The speed and energy efficiency of FP lends itself to applications in the synthesis of functionally gradient materials, nanocomposites, hydrogels, and sensory materials.[2−8] One of the principal limitations of frontal polymerization chemistry is the pot life of the system. The pot life of a FP reaction is the point at which FP will no longer occur due to decomposition or reaction of the reagents. Since thermal initiation and subsequent polymerization occur even at room temperature according to Arrhenius kinetics, the amount of available initiator or monomer will eventually be depleted, making it impossible to sustain the propagating front. This spontaneous bulk polymerization is particularly problematic in frontal ring-opening metathesis polymerization (FROMP), where a highly reactive monomer such as dicyclopentadiene (DCPD) is polymerized with a ruthenium Grubbs'-type catalyst in the presence of an inhibitor. Previous examples of FROMP have used known ROMP inhibitors to extend the working time while enabling FROMP to occur upon thermal activation. In the first demonstration of FROMP, Mariani et al. used triphenylphosphine as the inhibitor of first generation Grubbs' catalyst in DCPD, affording a pot life of only about 1 min at room temperature.[9] For FROMP to occur, the solution had to be flash-frozen and the reaction performed on the solid monomer, which would be nonideal for processing large components. More recently, the more strongly coordinating 4-dimethylaminopyridine (DMAP) was used to extend the pot life to nearly 30 min.[10] However, when DMAP was used with the more reactive *exo*-dicyclopentadiene monomer, the pot life was reduced to about 10 min.[11] Limonene, which forms a less active intermediate complex, was also used to retard the metathesis reaction, extending the pot life to nearly an hour, but reducing the stiffness of the resulting polymer.

A longer pot life is desirable for processing purposes, whereby the liquid monomer solution needs to persist for >1 h. Maintaining sustainable frontal polymerization activity is also important in order to avoid incomplete reaction resulting in materials of poor mechanical integrity. Previously explored inhibitors such as DMAP and triphenylphosphine reduced catalytic activity toward moderately strained olefins at low concentration and room temperature. The environment in a FROMP reaction is substantially more reactive. The catalyst is dissolved in a 7.4 M solution of highly strained olefin that reaches about 200 °C at the front. As such, FROMP inhibitors may need to bind to ruthenium with a much higher affinity than those explored so far to engender an extended pot life.

Recently, Cazin et al. have shown that replacing Cy_3P with an alkyl phosphite ligand in a ruthenium-benzylidene or ruthenium-indenylidine Grubbs-type complex suppresses reactivity toward strained olefins such as DCPD at room

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temperature, while maintaining efficient reactivity at high temperatures.[12−16] These authors did not, however, investigate the utility of alkyl phosphites in FROMP. Herein, we demonstrate that alkyl phosphites do serve a useful purpose as inhibitors for Grubbs' second generation catalyst (GC2) in FROMP, thereby increasing pot life by up to 140×, while still allowing frontal polymerization at relatively high frontal velocities (Figure 1).

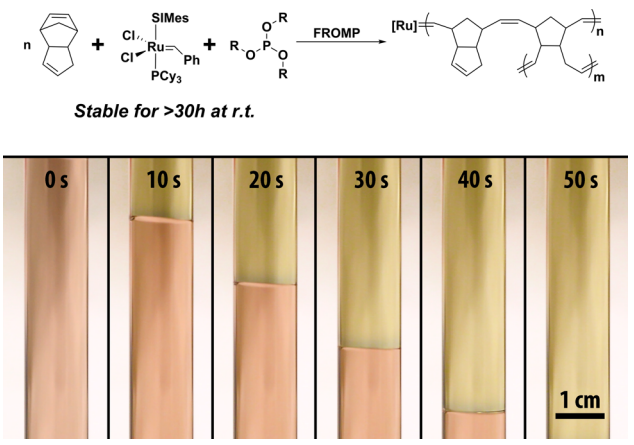


Figure 1. Scheme for phosphite-inhibited FROMP reaction. Inhibition of Grubbs' 2nd generation ruthenium catalyst (conc. = 100 ppm) by alkyl phosphites produces stable solutions with *endo*-DCPD for >30 h at r.t. that may be completely polymerized at any time via FROMP. The FROMP reaction shown here uses 0.5 equiv TBP to extend its pot life to >2 h, while maintaining a frontal velocity of ca. 7 cm/min.

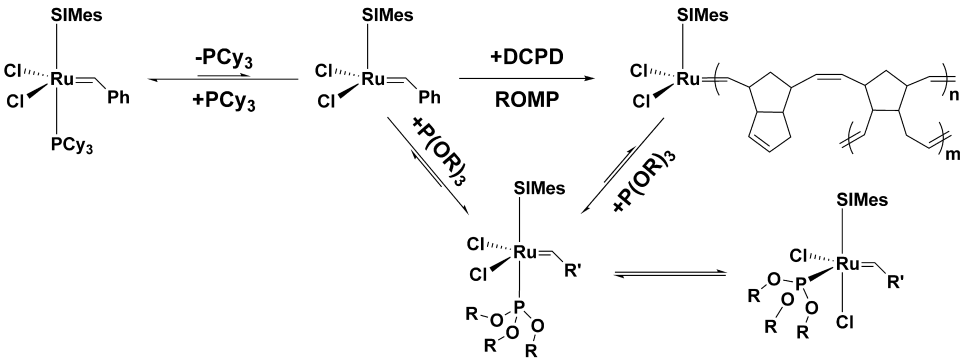
Alkyl phosphites are known to bind strongly to metal centers despite their π-acidity due to enhanced backbonding by the metal.[17] Recent work has shown that phosphites attached to metals also ligated to a N-heterocyclic carbene exhibit a synergistic bonding effect, whereby the phosphite-metal interaction is further strengthened, improving catalyst stability or effecting thermal latency.[13,16,18,19] At room temperature, the phosphite is enthalpically favored to coordinate to the metal center of the ruthenium alkylidene, which inhibits polymerization of DCPD. At high temperature, increased entropic effects favor phosphite dissociation and enable ROMP to proceed with minimal hindrance. With this in mind, we aimed to investigate the FROMP transformation using widely available GC2 in which a phosphite ligand serving as an inhibitor is added to dicyclopentadiene monomer. Since the tricyclohexylphosphine ligand may be displaced shortly after dissolution in the monomer, the dissolved phosphite will coordinate to the active catalyst and form a latent precatalyst complex in situ (Scheme 1). Using phosphite as an inhibitor of variable concentration (rather than as a stoichiometric ligand) is expected to allow for control of the pot life and FROMP reactivity.

Trimethyl phosphite (TMP), triethyl phosphite (TEP), and tributyl phosphite (TBP) were tested as inhibitors for FROMP at a range of concentrations between 0.3 and 8 equiv to explore their effects on frontal velocity and pot life. This concentration range was chosen based on two practical considerations. It was difficult to accurately measure inhibitor below 0.3 equiv, on the scale described, since the volume would be <0.1 μL in some instances. Above 8 equiv, no FP was observed, and thus it would be impossible to correlate frontal velocity to pot life in these cases. We chose to use a 100 ppm concentration of GC2 in DCPD in all experiments to evaluate the effectiveness of the inhibitors.

In FROMP, the pot life is limited by either rapid, exothermic polymerization or gelation of the material, after which processing is difficult. Pot lives of alkyl phosphite inhibited samples were dramatically increased even with concentrations of phosphite substantially less than 1 equiv relative to the ruthenium complex. Since it was difficult to accurately determine a specific time at which FROMP was no longer possible, we quantified the pot life as the working time of the system by measuring the time required for the mixture to reach its gel point. The gel point was determined via bulk rheology based on the crossover of shear storage and shear loss modulus. The time at which the gel point was reached in isothermal measurements (temperature = 23 °C) is defined as the pot life.

As expected, in all cases, pot life increased as inhibitor concentration increased (Figure 2). All three of the tested phosphites dramatically improved the pot life of the system. However, despite their structural similarity, the chosen alkyl phosphites inhibited polymerization to different degrees. Samples inhibited with TBP exhibited the greatest effect. Even with 0.3 equiv of TBP, the pot life was extended by 6-fold to about 1 h. With 8 equiv of TBP, the pot life was remarkably extended to over 30 h, by far the longest FROMP pot life

Scheme 1. Upon Dissociation of PCy_3, Free Phosphite Can Coordinate to Ru and Limit Further Reaction at Room Temperature[a]



[a]The formation of the latent complex may involve phosphite isomerization to the latent *cis*-form. Additionally, phosphite may coordinate to the propagating catalyst to form an analogous complex with reduced reactivity.

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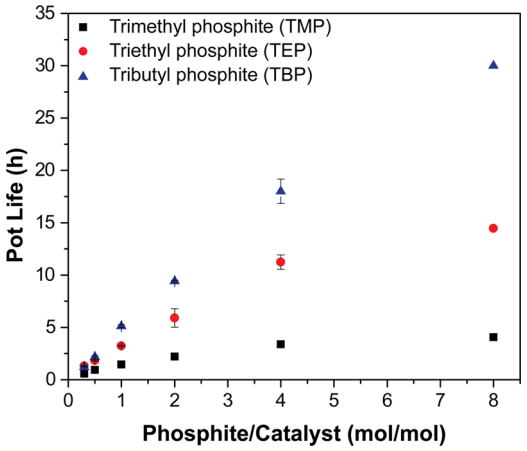

Figure 2. Effect of alkyl phosphite inhibitors on pot life of FROMP solutions (100 ppm GC2 complex). TBP exhibits the greatest pot life extension, followed by TEP, followed by TMP. Application of 8 equiv TBP to catalyst can increase pot life by >140×. Error bars are standard deviation; $N = 3$.

reported in the literature. Inhibition by TEP showed a diminished effect compared to TBP. Samples with 0.3 equiv of TEP also gelled in ca. 1 h, while with 8 equiv of TEP, samples gelled in 14 h. TMP showed the least effect, such that samples containing 0.3 equiv of TMP gelled in 35 min, while samples with 8 equiv of TMP gelled in 4 h.

Frontal velocity shows an inverse trend to pot life; greater quantities of inhibitor correspondingly reduce frontal velocity (Figure 3). However, unlike pot life, there was essentially no

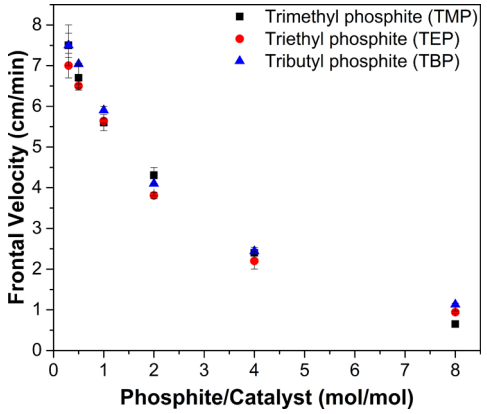

Figure 3. Effect of each alkyl phosphite on frontal velocity. While all tested phosphites slow frontal velocity, the effects are similar for all three compared to their disparate effect on in the pot life. Error bars are standard deviation; $N = 3$.

difference in the effect of the three phosphites on frontal velocity. Furthermore, the magnitude of reduction in frontal velocity is significantly smaller than the magnitude of the increase in pot life. The addition of 1 equiv of TMP, TEP, or TBP reduced the frontal velocity by only about 40%, while the pot lives of these systems were increased by 700, 1500, and 2400%, respectively. This difference in magnitude is attributable to a low concentration of inhibitor in the solution coupled to a temperature-dependent ligand−metal association constant. At room temperature, the association constant is expected to be large and the rate of polymerization (k_p) small. Thus, despite the low phosphite concentration, free phosphite readily binds to active catalyst, trapping it in a precatalytic state and minimizing spontaneous bulk polymerization. However, at high temperature, the inhibited precatalyst is activated, k_p increases, and phosphite concentration is low, meaning there is a low probability of phosphite inhibiting catalyst before DCPD is depleted.

We propose that the initiation rate of GC2 in DCPD is actually quite small at room temperature; however, GC2 has such a low rate of termination that a small concentration of active catalyst is capable of gelling the entire solution. As shown in Scheme 1, when GC2 initiates chain growth in the presence of phosphite, it is quickly "capped" by free phosphite to produce a less active precatalyst that dissociates at high temperatures, enabling ROMP. Thus, even with less than 1 equiv inhibitor, the pot life is extended substantially by suppressing the initial concentration of active catalyst. A phosphite-catalyst complex was confirmed to slowly form in situ by ^{31}P NMR during monomer curing, supporting this mechanism (see Supporting Information). The inhibition mechanism may involve an isomerization of the phosphite complex to the *cis*-form, which is known to exhibit latency; however, we were unable to confirm the isomeric form experimentally. While the observed inhibition efficiency does correlate to the size of the alkyl group, the effect is likely unrelated to steric bulk, since TMP, TEP, and TBP all have similar cone angles (107−109°).[20] One possible explanation is that the stability of each species toward hydrolysis is quite different.[21] Imaev et al. showed the stability of phosphites toward water follows the trend $P(OMe)_3 < P(OEt)_3 < P(OPr)_3 < P(OBu)_3$. Trace water in the sample may decompose these inhibitors at different rates, leading to different inhibition efficiencies. The ultimate cause of these results will be the focus of future studies.

The resulting polymer in all samples was transparent and exhibited a high strength and stiffness typical of fully cured PDCPD. Peak temperatures observed during FP with 0.3−1 equiv phosphite were about 215 °C. Peak temperatures of FROMP with 2−4 equiv phosphite were about 200 °C, and peak temperatures of 8 equiv phosphite samples were about 175 °C. The lower temperatures seen in the 8 equiv samples are a result of substantial heat loss during the relatively slow FROMP. DSC confirmed that there was <0.2% residual reactivity in the FROMPed material from 0.3 to 4 equiv phosphite samples, while a small exotherm was observed in 8 equiv phosphite samples, indicating cure was not fully complete.

In conclusion, we have demonstrated that inexpensive and readily available alkyl phosphites improve the pot life of GC2/DCPD solutions by up to 140× while facilitating FROMP to form fully cured PDCPD. By varying phosphite concentration, pot life is easily controlled in the range of 1 to 30 h, an order of magnitude longer than previous FROMP chemistries. The high inhibition efficiency of alkyl phosphites will enable FROMP of other highly reactive monomers. This strategy is directly applicable to the polymerization of other norbornene-type monomers, enormously expanding the library of available FROMP chemistry. In addition to FROMP, we anticipate that phosphite inhibition will have applications in traditional ROMP by enabling access to slower reaction rates for highly active systems.

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■ ASSOCIATED CONTENT

Supporting Information

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FROMP experimental setup, rheology conditions, DSC conditions, and NMR analysis (PDF).

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Bissette, A. J.; Fletcher, S. P. Mechanisms of Autocatalysis. *Angew. Chem., Int. Ed.* **2013**, *52* (49), 12800−12826.

(2) Chekanov, Y. A.; Pojman, J. A. Preparation of Functionally Gradient Materials via Frontal Polymerization. *J. Appl. Polym. Sci.* **2000**, *78* (13), 2398−2404.

(3) Nuvoli, D.; Alzari, V.; Pojman, J. A.; Sanna, V.; Ruiu, A.; Sanna, D.; Malucelli, G.; Mariani, A. Synthesis and Characterization of Functionally Gradient Materials Obtained by Frontal Polymerization. *ACS Appl. Mater. Interfaces* **2015**, *7* (6), 3600−3606.

(4) Moon, R. J.; Martini, A.; Nairn, J.; Simonsen, J.; Youngblood, J. Cellulose Nanomaterials Review: Structure, Properties and Nanocomposites. *Chem. Soc. Rev.* **2011**, *40* (7), 3941.

(5) Guo, X.; Wang, C.-F.; Fang, Y.; Chen, L.; Chen, S. Fast Synthesis of Versatile Nanocrystal-Embedded Hydrogels toward the Sensing of Heavy Metal Ions and Organoamines. *J. Mater. Chem.* **2011**, *21* (4), 1124−1129.

(6) Sanna, R.; Alzari, V.; Nuvoli, D.; Scognamillo, S.; Marceddu, S.; Mariani, A. Polymer Hydrogels of 2-Hydroxyethyl Acrylate and Acrylic Acid Obtained by Frontal Polymerization. *J. Polym. Sci., Part A: Polym. Chem.* **2012**, *50* (8), 1515−1520.

(7) Washington, R. P.; Steinbock, O. Frontal Polymerization Synthesis of Temperature-Sensitive Hydrogels. *J. Am. Chem. Soc.* **2001**, *123* (32), 7933−7934.

(8) Nagy, I. P.; Sike, L.; Pojman, J. A. Thermochromic Composite Prepared via a Propagating Polymerization Front. *J. Am. Chem. Soc.* **1995**, *117* (12), 3611−3612.

(9) Mariani, A.; Fiori, S.; Chekanov, Y.; Pojman, J. A. Frontal Ring-Opening Metathesis Polymerization of Dicyclopentadiene. *Macromolecules* **2001**, *34* (19), 6539−6541.

(10) Ruiu, A.; Sanna, D.; Alzari, V.; Nuvoli, D.; Mariani, A. Advances in the Frontal Ring Opening Metathesis Polymerization of Dicyclopentadiene. *J. Polym. Sci., Part A: Polym. Chem.* **2014**, *52*, 2776−2780.

(11) Robertson, I. D.; Pruitt, E. L.; Moore, J. S. Frontal Ring-Opening Metathesis Polymerization of Exo-Dicyclopentadiene for Low Catalyst Loadings. *ACS Macro Lett.* **2016**, *5*, 593−596.

(12) Bantreil, X.; Schmid, T. E.; Randall, R. A. M.; Slawin, A. M. Z.; Cazin, C. S. J. Mixed N-Heterocyclic Carbene/phosphite Ruthenium Complexes: Towards a New Generation of Olefin Metathesis Catalysts. *Chem. Commun.* **2010**, *46* (38), 7115−7117.

(13) Schmid, T. E.; Bantreil, X.; Citadelle, C. A.; Slawin, A. M. Z.; Cazin, C. S. J. Phosphites as Ligands in Ruthenium-Benzylidene Catalysts for Olefin Metathesis. *Chem. Commun.* **2011**, *47* (25), 7060−7062.

(14) Urbina-Blanco, C. A.; Bantreil, X.; Wappel, J.; Schmid, T. E.; Slawin, A. M. Z.; Slugovc, C.; Cazin, C. S. J. Mixed N-Heterocyclic Carbene/Phosphite Ruthenium Complexes: The Effect of a Bulkier NHC. *Organometallics* **2013**, *32* (21), 6240−6247.

(15) Bantreil, X.; Cazin, C. S. J. Phosphite Ligands in Ru-Based Olefin Metathesis Catalysts. *Monatsh. Chem.* **2015**, *146* (7), 1043−1052.

(16) Leitgeb, A.; Wappel, J.; Urbina-Blanco, C. A.; Strasser, S.; Wappl, C.; Cazin, C. S. J.; Slugovc, C. Two Commercially Available Initiators for the Retarded Ring-Opening Metathesis Polymerization of Dicyclopentadiene. *Monatsh. Chem.* **2014**, *145* (9), 1513−1517.

(17) Bedford, R. B.; Hazelwood, S. L.; Limmert, M. E. Extremely High Activity Catalysts for the Suzuki Coupling of Aryl Chlorides: Importance of Catalyst Longevity. *Chem. Commun. (Cambridge, U. K.)* **2002**, *22*, 2610−2611.

(18) Ho, C.-Y.; Jamison, T. F. Highly Selective Coupling of Alkenes and Aldehydes Catalyzed by [Ni(NHC){P(OPh)3}]: Synergy between a Strong Σ Donor and a Strong Π Acceptor. *Angew. Chem., Int. Ed.* **2007**, *46* (5), 782−785.

(19) Diebolt, O.; Jurčík, V.; Correa da Costa, R.; Braunstein, P.; Cavallo, L.; Nolan, S. P.; Slawin, A. M. Z.; Cazin, C. S. J. Mixed Phosphite/N-Heterocyclic Carbene Complexes: Synthesis, Characterization and Catalytic Studies. *Organometallics* **2010**, *29* (6), 1443−1450.

(20) Tolman, C. A. Steric Effects of Phosphorus Ligands in Organometallic Chemistry and Homogeneous Catalysis. *Chem. Rev.* **1977**, *77* (3), 313−348.

(21) Imaev, M. G.; Kazan, S. M. Hydrolysis of Complete Esters of Phosphorous acid with Pure Water. *Zh. Obshch. Khim.* **1961**, *31*, 1762−1766.

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