ACS Macro Letters

Letter

pubs.acs.org/macroletters

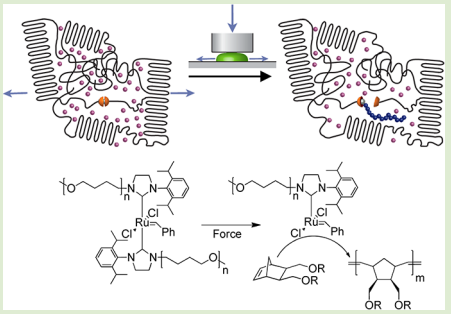
# Mechanocatalytic Polymerization and Cross-Linking in a Polymeric Matrix

Robert T. M. Jakobs, Shuang Ma, and Rint P. Sijbesma*

Laboratory of Macromolecular and Organic Chemistry and Institute for Complex Molecular Systems, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

Supporting Information

**ABSTRACT:** A latent olefin metathesis catalyst, bearing two polymeric NHC ligands, was embedded in a semicrystalline polymer matrix containing cyclic olefins. The catalyst was activated by straining the solid material under compression, resulting in polymerization and cross-linking reactions of the monomers in situ. Catalyst activation in the solid state may be employed in new self-healing materials.




Mechanochemistry uses mechanical force to activate chemical bonds[1,2] and is an alternative to thermal, (photo)chemical, and electrical activation.[3] To promote specific mechanochemical reactions, a functionality with a weak bond (a mechanophore[4]) may be incorporated into a polymer chain that acts as a handle for the macroscopic force.[5] Polymer mechanochemistry has predominantly been studied in solution because solution sonication is among the most effective methods to apply mechanical force to polymers.[6,7] Sonication of liquids causes high elongational strain rates produced by collapsing cavitation bubbles.[8,9] Application of ultrasound has been used to generate polymers with reactive end groups, such as cyanoacrylates,[10] trifluorovinyl ethers,[11] or azides.[12]

Although studied less than their counterparts in solution, mechanochemical reactions in bulk polymer are of strong interest because they are a direct method to transfer a mechanical stimulus into a chemical reaction, an essential feature of autonomous healing[13] in damaged polymeric materials. Schemes to use mechanochemical reactions to initiate autonomous self-healing in polymers include radical-induced cross-linking[14,15] and bond formation in extruded *gem*-dibromocyclopropanated polybutadiene.[16]

A few mechanochemical reactions were initially investigated in solution and subsequently studied in bulk.[17−21] However, these studies are limited to primary scission products. Follow-up reactions of the scission products in bulk polymer, required for self-healing, are slower than in solution due to diffusion limitations in the highly viscous polymer matrix, and their study is limited so far.

A promising concept to use mechanochemistry for self-healing of polymers is based on the generation of a (polymerization) catalyst by mechanical force. Experimental progress in this area is of recent date. In one study, it was shown that HCl is generated mechanically by elimination from *gem*-dichlorocyclopropanated indene units in a polymer upon compression of cross-linked polymethylacrylate.[22] An acid-induced color change of a pH indicator dye was found to take place in a solution prepared immediately after compression, but in situ catalytic activity was not reported.

A small number of latent catalysts have been demonstrated to be suitable for mechanical activation in solution[23−26] and are therefore interesting candidates for catalyst activation in the solid state. In these mechanocatalysts, the catalyst precursor, consisting of a transition metal complex with tightly bound ligands, is activated upon force-induced dissociation of a metal−ligand bond. One of the mechanocatalysts we have developed[23,26] is a latent metathesis catalyst **1a** with two tightly bound N-heterocyclic carbene (NHC) ligands on a ruthenium−alkylidene species (Scheme 1). The latent catalyst is activated upon mechanical dissociation of one of the NHC ligands to give **2a**. Complex **2a** was shown to be active in both ring-closing metathesis (RCM) and ring-opening metathesis polymerization (ROMP) upon activation of **1a** by ultrasound.

Here, we describe mechanical activation of latent metathesis catalyst **1a** in the solid state and subsequent in situ catalysis of polymerization and cross-linking reactions. Upon straining a sample in compression, **2a** is generated and catalyzes the polymerization of a monofunctional monomer or cross-linking of a bifunctional monomer which is homogenously dispersed throughout the material.

To generate catalyst **2a**, macroscopic forces need to be transferred to the metal−ligand bonds via physical cross-links with sufficiently long lifetimes. The semicrystallinity (24−80% crystalline)[27] of poly(tetrahydrofuran) (pTHF), used in **1a**,

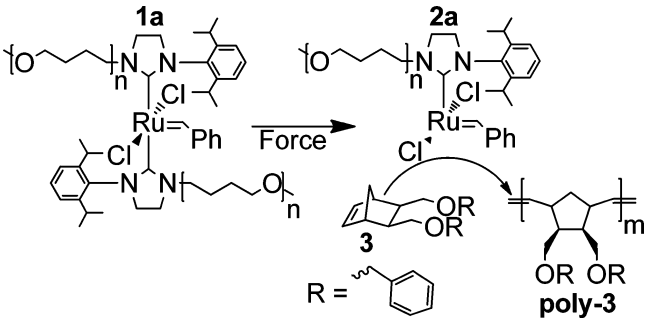
**Received:** April 22, 2013
**Accepted:** June 19, 2013
**Published:** June 24, 2013

ACS Publications © 2013 American Chemical Society



dx.doi.org/10.1021/mz400201c | *ACS Macro Lett.* 2013, 2, 613−616

**Scheme 1. Chemical Structure of Catalyst 1a ($\bar{n} \approx 240$) and Its Mechanical Activation to Form 2a, Active in Ring-Opening Polymerization of 3 to poly-3**




opens opportunities for physical cross-linking through the crystallites. However, **1a** ($M_n$ = 34 kDa) is brittle, and to obtain ductile materials, methoxy end-capped, high molecular weight pTHF ($M_n$ = 170 kDa, PDI = 1.3) was used as a matrix. Both the matrix and catalyst **1a** have a melting point of 40−44 °C in differential scanning calorimetry (DSC) with an estimated degree of crystallinity of 46% and 54%, respectively (Supporting Information). The similarities in chemical structures, melting point, and degree of crystallinity make cocrystallization of the matrix and **1a** highly plausible (Figure 1).

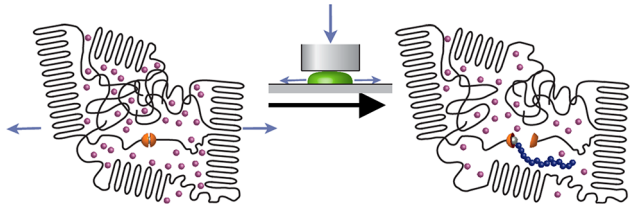


**Figure 1.** Schematic representation of activation of catalyst **1a** in the semicrystalline matrix by compressive force and subsequent polymerization of monomer **3**.

Samples for mechanically induced polymerization were prepared from the pTHF matrix (74% w/w) with 15% of **1a** and 11% w/w of norbornene monomer **3**, functionalized to reduce volatility and increase UV detectability. The presence of **3** decreases the degree of crystallinity from 46% to 32%. The Young's modulus and yield stress in compression tests decrease from 28 and 6 MPa, respectively, for the pure pTHF matrix, to 16 and 3 MPa, respectively, for the pTHF matrix containing 13% of **3** (see Supporting Information). To prepare the blend, the components were dissolved in THF; subsequent evaporation of the solvent under reduced pressure resulted in optically homogeneous dispersion of all components.

Mechanical deformation was performed by compressing a sample in a KBr press, using a standard 13 mm pellet die. This method has been described as an efficient way to activate polymer-functionalized mechanophores in the solid state.[20,22] Globular polymer samples of approximately 15 mg were compressed at a final compressive pressure of 0.8 GPa (calculated according to full surface area of plunger of the pellet die, as upon applying the compressive force the material fully covers this surface; see Supporting Information). The resulting true strain was calculated to be approximately −3, although after the force is released part of the strain is recovered elastically, leading to a true plastic strain of approximately −2.5.

Upon compressing the blend at 0.8 GPa for 5 min, approximately 4% conversion to **poly-3** was measured with $^1$H NMR spectroscopy on a dissolved sample (Figure 2a).

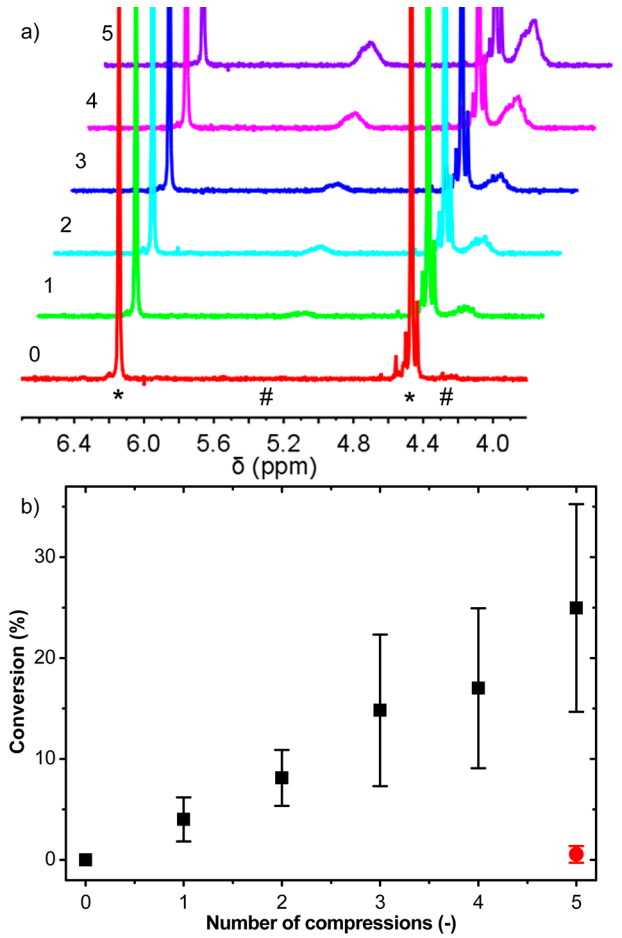



**Figure 2.** Compression of samples containing 74 wt % pTHF matrix, 15 wt % catalyst **1a**, and 11 wt % monomer **3**. Compression was performed at 0.8 GPa, applying pressure for 5 min, folding the sample in between compression cycles. (a) Typical $^1$H NMR spectra of dissolved films before and after indicated number of compressions. Signals were assigned to monomer **3** (*) or **poly-3** (#). (b) Conversion toward **poly-3** as determined by $^1$H NMR spectroscopy after indicated times of applying pressure using catalyst **1a** (black ■) or control catalyst **1b** (red ●). Points represent the average of 4−6 experiments with standard deviation indicated by bars.

When a sample was folded and compressed a second time for 5 min, conversion increased to around 8%. Upon five compression cycles, conversion increased approximately linearly to 25% (Figure 2b). The linear increase in conversion is in line with an earlier observed linear increase in mechanophore activation upon multiple compressions.[20] The reproducibility of the conversion was limited due to sample-to-sample differences as well as differences within one sample (Figure S5, Supporting Information). The use of a KBr press has been reported to give relatively large experimental errors.[20,22] The necessity to do multiple compression cycles to perform proper $^1$H NMR analysis and (local) variation in the degree of crystallinity is proposed to reduce reproducibility further. However, conversions in experiments with catalyst **1a**


dx.doi.org/10.1021/mz400201c | ACS Macro Lett. 2013, 2, 613−616

differ significantly ($p < 0.01$) from the control experiment with catalyst **1b**, having *n*-butyl groups instead of pTHF chains on the NHC ligands.[28] Using the control catalyst, no conversion (<1%, red dot in Figure 2b) of **3** was observed in $^1$H NMR spectroscopy after five compression cycles, indicating that thermal catalyst activation is negligible.

The formation of **poly-3** was also observed by GPC (Figure 3). Using the UV detector, the formation of a polydisperse,

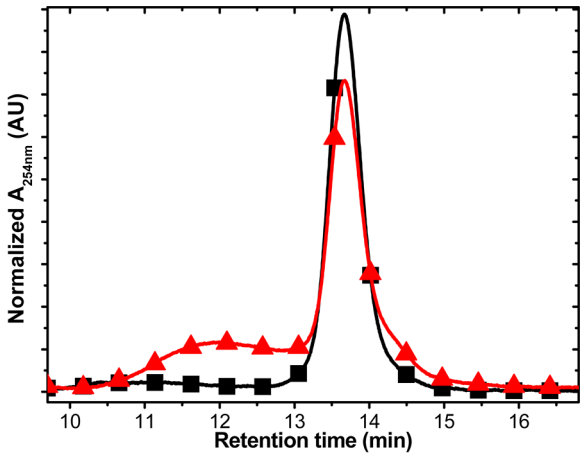



**Figure 3.** GPC trace (UV detector) of film before (black ■) and after (red ▲) five compressions by a KBr press. Normalization was performed by total peak area in RI trace.

high molecular weight polymer was observed; molecular weights as high as $1.5 \times 10^6$ g/mol were formed, while the average peak molecular weight was around $3 \times 10^5$ g/mol. The molecular weight distribution of **poly-3** could not fully be analyzed due to the overlap with the signal of **1a**.

A clear hint that the forces inside the compressed sample are indeed large enough for scission of chemical bonds can be found in the refractive index (RI) traces of the GPC. After five compressions at 0.8 GPa, the $M_n$ of the matrix pTHF decreased from 170 to 135 kDa (see Supporting Information). Furthermore, the peak ascribed to **2a** increases over multiple compressions, although overlap hampers quantification.

The moderate reproducibility impeded quantitative investigation of all parameters of interest, but the trends are clear-cut (Table 1). Applying a lower pressure of 0.08 GPa leads to significantly lower conversion, confirming the mechanical nature of activation. When the applied pressure (0.8 GPa) was released immediately and a 5 min waiting time without pressure was used between cycles, conversions were unchanged. When the sample was analyzed immediately after compression, a lower conversion was observed. Waiting for 30 min between cycles did not lead to significantly higher conversion. This indicates fast catalyst activation upon applying pressure, followed by slower polymerization toward **poly-3**, taking several minutes. The lifetime of active species **2a** has been shown to be in the order of hours.[26] Slowing of conversion after a few minutes may be explained by local monomer depletion because of slow diffusion in the solid matrix.

For self-healing applications, it is desirable to be able to initiate a cross-linking reaction with the activated catalyst. Using this approach would result in reinforcement of the material specifically at the site and time where it threatens to fail. To investigate the feasibility of the current system to yield cross-linked networks, bifunctional monomer **4** (Figure 4a) was used.

**Table 1. Influence of Applied Pressure and Waiting Time on Observed Conversion**[a,b]

| pressure (GPa) | time with constant pressure (min) | time without pressure (min) | conversion (%) #1 | #2 | #3 |
|---|---|---|---|---|---|
| 0.8 | 5 | 0 | 41 | 19 | 16 |
| 0.08 | 5 | 0 | 7 | 8 | 14 |
| 0.8 | 0 | 5 | 30 | 15 | 32 |
| 0.8 | 0 | 0 | 7 | 8 | 7 |
| 0.8 | 30 | 0 | 32 | 27 | 48 |

[a]Conversion determined after five compression cycles by $^1$H NMR spectroscopy of the dissolved sample. Results of three experiments within one sample are given. Sample contains 74 wt % pTHF matrix, 15 wt % catalyst **1a**, and 11 wt % monomer **3**. [b]Applying pressure takes approximately 5 s.

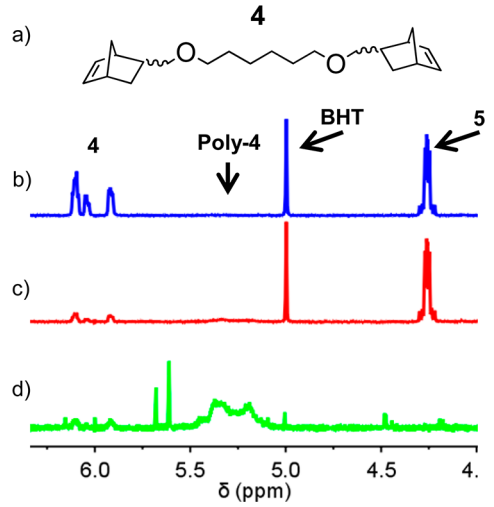



**Figure 4.** (a) Structure of bifunctional monomer **4**. (b,c) Part of $^1$H NMR spectra of (b) dissolved film (71 wt % pTHF matrix, 14 wt % catalyst **1a**, 5 wt % monomer **4**, 5 wt % internal standard **5**, and 4 wt % BHT) before compression and (c) $CDCl_3$ soluble fraction of five times compressed film. (d) Insoluble fraction of five times compressed film. Compression was done at 0.8 GPa, waiting 5 min between compression cycles.

Bis(2-ethylhexyl) terephthalate (**5**) was used as an internal standard, and BHT was added to inactivate radicals formed by homolytic bond cleavage of the pTHF matrix. After five compression cycles on a sample containing **4**, the product contained an insoluble fraction. $^1$H NMR spectroscopy of the liquid fraction showed a decrease of 84% (duplicate) in [**4**], while only a small peak ascribed to **poly-4** was observed (Figure 4). After washing the insoluble fraction three times with $CHCl_3$, the residue was swollen with $CDCl_3$. The solvent swollen particles were analyzed using HR-MAS $^1$H NMR spectroscopy using an Agilent Nanoprobe, a probe especially designed to obtain high-resolution spectra of semisolid samples.[29] In the spectrum in Figure 4d, the formation of polymer is evident. When control catalyst **1b** was used, only a 2.0% decrease (duplicate) in [**4**] was observed, proving the mechanical nature of catalyst activation. Compression of the pTHF matrix without catalyst led to <2% decrease in [**4**], indicating that radicals formed by homolytic bond scission of pTHF chains do not lead to cross-linking.


dx.doi.org/10.1021/mz400201c | ACS Macro Lett. 2013, 2, 613−616

In conclusion, mechanocatalyst **1a** is activated under compressive strain in a high molecular weight pTHF matrix. Up to 25% polymerization of monofunctional norbornene monomer **3** was reached after five compression cycles. When bifunctional monomer **4** was used, polymerization resulted in a cross-linked product. These results represent the first demonstration of in situ catalysis performed by a mechanocatalyst activated in the solid state. To develop this system further for autonomous self-healing materials, the current high modulus system should be replaced by a softer, chemically cross-linked material. Furthermore, addition of chain transfer agents will be beneficial to increase the number of polymer chains per scission event.[30] The research presented here is an important step toward a functional self-healing material, demonstrating polymerization and cross-linking reaction initiated by mechanical activation in the solid state.

## ■ ASSOCIATED CONTENT

### Supporting Information

Full experimental details, DSC traces, and stress−strain curves of polymer samples and GPC traces of samples upon compression. This material is available free of charge via the Internet at http://pubs.acs.org.

## ■ AUTHOR INFORMATION

### Corresponding Author

*E-mail: r.p.sijbesma@tue.nl.

### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

This work was supported by grants from Netherlands Organization for Scientific Research (NWO) and Dutch IOP Self Healing Materials (project SHM08748). We thank ir. M.M.L. Nieuwenhuizen for help with semisolid state NMR spectroscopy, E. Parodi for help with recording stress−strain curves, and Dr. L. E. Govaert for fruitful discussions.

## ■ REFERENCES

(1) Sohma, J. *Prog. Polym. Sci.* **1989**, *14*, 451−596.
(2) Beyer, M. K.; Clausen-Schaumann, H. *Chem. Rev.* **2005**, *105*, 2921−2948.
(3) James, S. L.; Adams, C. J.; Bolm, C.; Braga, D.; Collier, P.; Friscic, T.; Grepioni, F.; Harris, K. D. M.; Hyett, G.; Jones, W.; Krebs, A.; Mack, J.; Maini, L.; Orpen, A. G.; Parkin, I. P.; Shearouse, W. C.; Steed, J. W.; Waddell, D. C. *Chem. Soc. Rev.* **2012**, *41*, 413−447.
(4) Hickenboth, C. R.; Moore, J. S.; White, S. R.; Sottos, N. R.; Baudry, J.; Wilson, S. R. *Nature* **2007**, *446*, 423−427.
(5) Caruso, M. M.; Davis, D. A.; Shen, Q.; Odom, S. A.; Sottos, N. R.; White, S. R.; Moore, J. S. *Chem. Rev.* **2009**, *109*, 5755−5798.
(6) Suslick, K. S.; Price, G. J. *Annu. Rev. Mater. Sci.* **1999**, *29*, 295−326.
(7) Wiggins, K. M.; Brantley, J. N.; Bielawski, C. W. *Chem. Soc. Rev.* **2013**, DOI: 10.1039/C3CS35493H.
(8) Nguyen, T. Q.; Liang, Q. Z.; Kausch, H.-H. *Polymer* **1997**, *38*, 3783−3793.
(9) Kuijpers, M. W. A.; Iedema, P. D.; Kemmere, M. F.; Keurentjes, J. T. F. *Polymer* **2004**, *45*, 6461−6467.
(10) Kryger, M. J.; Ong, M. T.; Odom, S. A.; Sottos, N. R.; White, S. R.; Martinez, T. J.; Moore, J. S. *J. Am. Chem. Soc.* **2010**, *132*, 4558−4559.
(11) Klukovich, H. M.; Kean, Z. S.; Iacono, S. T.; Craig, S. L. *J. Am. Chem. Soc.* **2011**, *133*, 17882−17888.
(12) Brantley, J. N.; Wiggins, K. M.; Bielawski, C. W. *Science* **2011**, *333*, 1606−1609.
(13) White, S. R.; Sottos, N. R.; Geubelle, P. H.; Moore, J. S.; Kessler, M. R.; Sriram, S. R.; Brown, E. N.; Viswanathan, S. *Nature* **2001**, *409*, 794−797.
(14) Porter, R. S.; Casale, A. *Polym. Eng. Sci.* **1985**, *25*, 129−156.
(15) Smith, A. P.; Shay, J. S.; Spontak, R. J.; Balik, C. M.; Ade, H.; Smith, S. D.; Koch, C. C. *Polymer* **2000**, *41*, 6271−6283.
(16) Black, A. L.; Orlicki, J. A.; Craig, S. L. *J. Mater. Chem.* **2011**, *21*, 8460−8465.
(17) Potisek, S. L.; Davis, D. A.; Sottos, N. R.; White, S. R.; Moore, J. S. *J. Am. Chem. Soc.* **2007**, *129*, 13808−13809.
(18) Davis, D. A.; Hamilton, A.; Yang, J.; Cremar, L. D.; Van Gough, D.; Potisek, S. L.; Ong, M. T.; Braun, P. V.; Martinez, T. J.; White, S. R.; Moore, J. S.; Sottos, N. R. *Nature* **2009**, *459*, 68−72.
(19) Lenhardt, J. M.; Black, A. L.; Craig, S. L. *J. Am. Chem. Soc.* **2009**, *131*, 10818−10819.
(20) Lenhardt, J. M.; Black, A. L.; Beiermann, B. A.; Steinberg, B. D.; Rahman, F.; Samborski, T.; Elsakr, J.; Moore, J. S.; Sottos, N. R.; Craig, S. L. *J. Mater. Chem.* **2011**, *21*, 8454−8459.
(21) Chen, Y.; Spiering, A. J. H.; Karthikeyan, S.; Peters, G. W. M.; Meijer, E. W.; Sijbesma, R. P. *Nat. Chem.* **2012**, *4*, 559−562.
(22) Diesendruck, C. E.; Steinberg, B. D.; Sugai, N.; Silberstein, M. N.; Sottos, N. R.; White, S. R.; Braun, P. V.; Moore, J. S. *J. Am. Chem. Soc.* **2012**, *134*, 12446−12449.
(23) Piermattei, A.; Karthikeyan, S.; Sijbesma, R. P. *Nat. Chem.* **2009**, *1*, 133−137.
(24) Tennyson, A. G.; Wiggins, K. M.; Bielawski, C. W. *J. Am. Chem. Soc.* **2010**, *132*, 16631−16636.
(25) Wiggins, K. M.; Hudnall, T. W.; Tennyson, A. G.; Bielawski, C. W. *J. Mater. Chem.* **2011**, *21*, 8355−8359.
(26) Jakobs, R. T. M.; Sijbesma, R. P. *Organometallics* **2012**, *31*, 2476−2481.
(27) Dreyfuss, P. *Poly(tetrahydrofuran)*; Gordon & Breach: New York, 1982.
(28) Catalyst **1b** was fully soluble in pTHF; the UV−vis absorption in pTHF (650 g/mol, liquid at RT) and $CHCl_3$ was of similar intensity.
(29) Keifer, P. A.; Baltusis, L.; Rice, D. M.; Tymiak, A. A.; Shoolery, J. N. *J. Magn. Reson., Ser. A* **1996**, *119*, 65−75.
(30) Ivin, K. J.; Mol, J. C. *Olefin Metathesis and Metathesis Polymerization*; Academic Press: London, 1997.