ChemComm

Influence of Solvent on Cyclic Polynorbornene Tacticity

Journal:	*ChemComm*
Manuscript ID	CC-COM-08-2023-004167.R1
Article Type:	Communication

COMMUNICATION

Influence of Solvent on Cyclic Polynorbornene Tacticity

Received 00th January 20xx,
Accepted 00th January 20xx

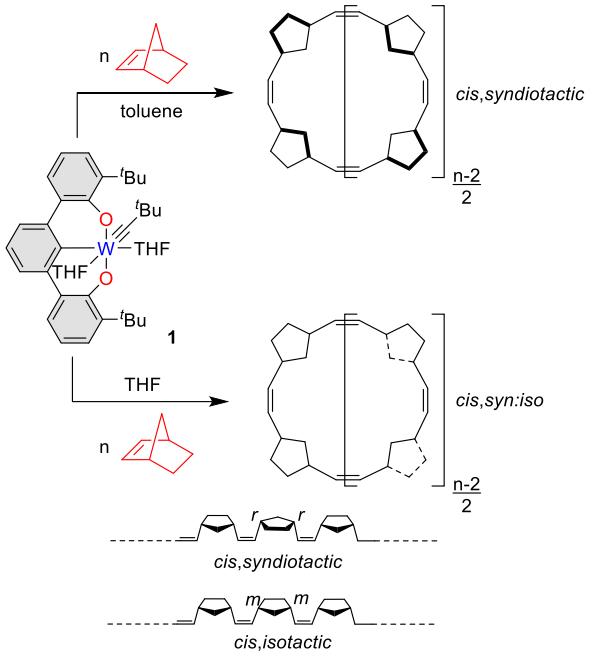
DOI: 10.1039/x0xx00000x

Sung-Min Hyun,[a] Arkadios Marathianos,[c] Parker T. Boeck,[a,d] Ion Ghiviriga,[b] Daniel W. Lester,[c] Brent S. Sumerlin,[d] Adam S. Veige*[a]

Tacticity is critical to polymer properties. The influence of solvent on tacticity in the catalytic synthesis of cyclic polynorbornene (c-PNB) is reported. In toluene *cis,syndiotactic* c-PNB forms; in THF, *cis,syn/iso* c-PNB forms.

The stereochemistry of repeat units in polymers significantly impacts their physical properties and is critical to their application.[1–9] A quintessential example is presented by atactic polypropylene being a soft and amorphous material, whereas isotactic polypropylene is highly crystalline with good thermal and mechanical properties.[3–9] It is desirable to access polymers in various tacticity. In metal-catalyzed insertion polymerization, tacticity results from the stereospecific approach of the enantioface of prochiral monomers. Modifying ligands to change the chiral environment of catalysts is a common approach to enriching tacticity.[7–18]

Polynorbornenes (PNB) are important commercial materials produced via ring-opening metathesis polymerization (ROMP)[12,19] of norbornene (NB) and have outstanding thermal and optical properties that find application in films and optical devices.[20] There are four possible regular structures of polynorbornenes: *cis,isotactic*,[12,14,16,21,22] *cis,syndiotactic*,[2,12–16,22,23] *trans,isotactic*,[12,23,24] and *trans,syndiotactic*.[21,25,26] Linear polymers of all the various tacticities are known. Previously, we reported various stereoselective ring-expansion metathesis polymerization (REMP) catalysts that produce highly *cis,syndiotactic* cyclic polynorbornene (c-PNB) containing nearly exclusively *rrrr* dyads.[27–29] Altering catalyst stereoselectivity through ligand modification has the advantage of rational design but can be tedious. Isotactic cyclic polynorbornene is unknown and new catalysts are likely needed to access this polymer. Here, we demonstrate *isotactic* (or *m* dyads) incorporation in highly *cis,syndiotactic* c-PNB by simply changing the solvent (Scheme 1).



Scheme 1. Catalytic REMP of norbornene to yield *cis,syndiotactic* c-PNB in toluene and *cis,syn:iso* c-PNB in THF (where [THF] changes the *syn*:*iso* ratio).

REMP of norbornene using the tungsten alkylidyne [$^{t\text{Bu}}$OCO]W≡C^{t}Bu(THF)$_2$ (**1**)[27–37] in toluene with 500:1=[NB]:[**1**] (0.1 M of NB) yields *cis,syndiotactic* c-PNB (>99% by ^{1}H NMR spectroscopy) with M_n=326,000 g/mol, $Đ$=3.08 in 98% yield (Table 1).The observed high molecular weights are due to activating <1% of the initiator $k_{prop} >> k_{init}$.

Table 1. Polymerization of norbornene by initiator **1** in various solvents.

Solvent	M_n (g/mol)	$Đ$	%cis	Tacticity
toluene	326,000	3.08	95	>99% *syn*
Et_2O	325,000	3.59	>99	>99% *syn*
THF	87,000	2.03	>99	50% *syn*
2-MeTHF	8,000	3.86	97	>99% *syn*
pyridine	-	-	-	-

c-PNB exhibits longer elution times, lower intrinsic viscosity ([η]), and a smaller radius of gyration (R_g) compared to an analogous linear polymer at the same molecular weight (Figure 1). Size-exclusion chromatography, using refractive index and

[a] University of Florida, Department of Chemistry, Center for Catalysis, P.O. Box 117200, Gainesville, FL, 32611.
[b] University of Florida, Department of Chemistry, Center for NMR Spectroscopy, P.O. Box 117200, Gainesville, FL, 32611.
[c] Polymer Characterization Research Technology Platform, University of Warwick, Coventry CV4 7AL, United Kingdom.
[d] University of Florida, Department of Chemistry, George and Josephine Butler Polymer Research Laboratory, Center for Macromolecular Science and Engineering, Gainesville, FL 32611
Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

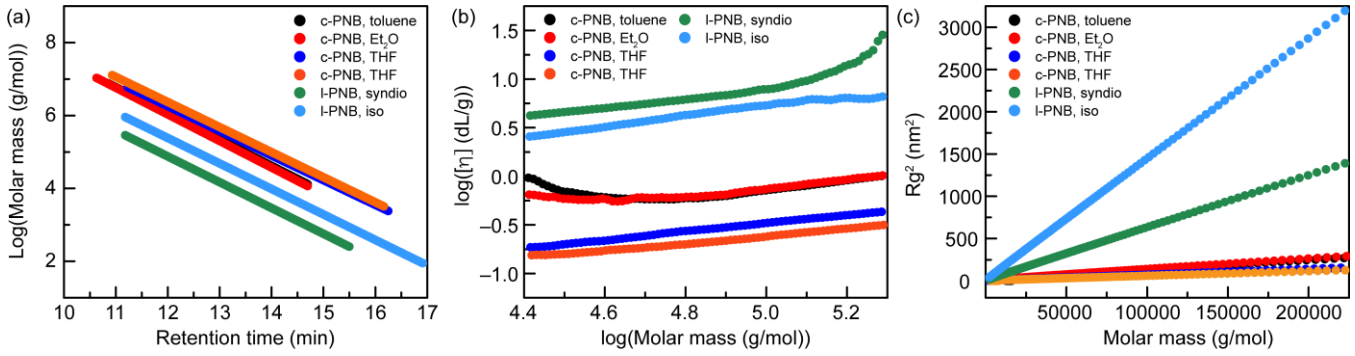


Figure 1. (a) Log of molar mass versus elution time (b) log of intrinsic viscosity ([η]) versus log of molar mass, and (c) mean square radius (R_g^2) versus molar mass for c-PNBs synthesized by **1** in various solvent and l-PNBs.

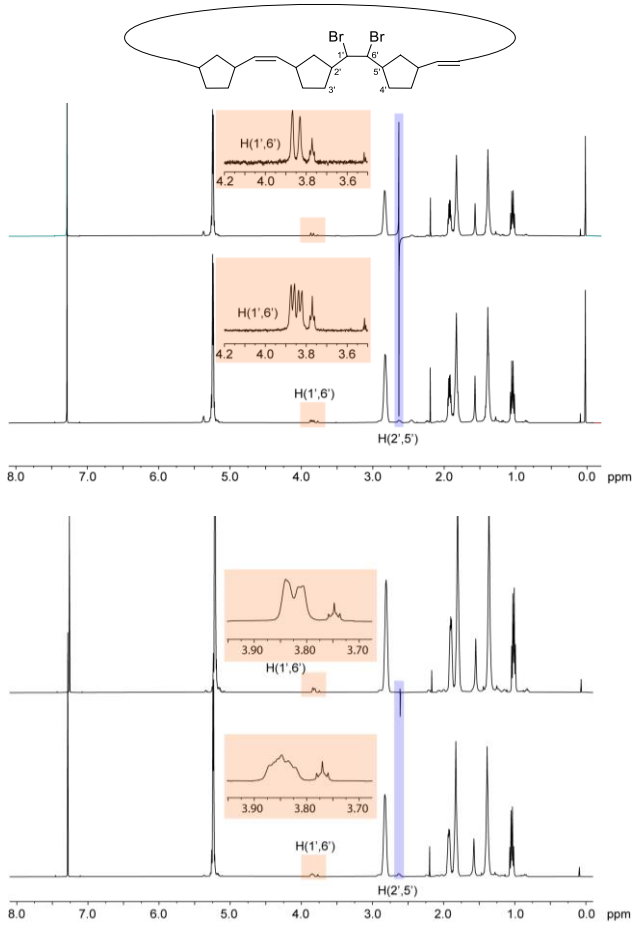


Figure 2. **TOP**: ^{1}H NMR spectra of partially brominated c-PNB synthesized in toluene with (top) and without (bottom) homonuclear decoupling at 2.61 ppm (blue). H(1',6') changes from two doublets to two singlets with decoupling, supporting *syndiotacticity*. **BOTTOM**: ^{1}H NMR spectra of partially brominated c-PNB synthesized in THF with (top) and without (bottom) homonuclear decoupling at 2.61 ppm (blue). H(1',6') changes from multiplets to four singlets with decoupling.

viscometry detectors to perform Universal analysis reveals that c-PNB$_{Et2O}$ has [η] and R_g measurements that overlap with c-PNB$_{tol}$. However, c-PNB$_{THF}$ results in even lower [η] and R_g at the same molecular weight than c-PNB$_{tol}$ and c-PNB$_{Et2O}$ (Figure 1). Tacticity can alter the chain conformation properties of polymers, thus the [η] difference observed for c-PNB$_{THF}$ suggests it has a different tacticity.In addition, the *Tg* of c-PNB$_{tol}$ = 67 °C and *Tg* of c-PNB$_{THF}$ = 59 °C, though the M_w of the samples are significantly different making this comparison tentative.

Evidence for *syndiotacticity* in c-PNB$_{tol}$ comes from partial bromination, as described by Schrock et al.[10] Figure 2 (TOP) depicts the ^{1}H NMR and decoupled spectra of partially brominated c-PNP$_{tol}$. The brominated polymer exhibits two doublets at 3.84 ppm (*J*=10.0 Hz) and 3.81 ppm (*J*=10.8 Hz), corresponding to two diastereotopic H(1',6') protons coupled with H(2',5'). As a consequence of *syndiotactic* stereochemistry, C2' and C5' have either the same *R* or *S* configuration; *trans*-bromination yields the same stereochemistry for C1' and C6', *R* or *S*, therefore H1' and H6' do not couple with each other but do with H2' and H5'. The two doublets observed in the spectrum correspond to *S*-C1,C6 and *S*-C2,C5 and to *S*-C1,C6 and *R*-C2,C5. Decoupling of H(2',5') at 2.61 ppm converts H(1',6') from two doublets to two singlets at 3.84 and 3.80 ppm (Figure 2, TOP). Also, a ^{13}C NMR spectrum of the sample agrees with the previously reported characterization of *cis,syndiotactic* l-PNB.[14]

We hypothesized that by altering the coordination environment of the active catalyst by choice of solvent, the stereochemistry may be controlled or changed. Solvents Et_2O, THF, 2-MeTHF and pyridine were used in REMP of norbornene using the same initiator **1**. Due to strong coordination that prevents initiator activation, REMP in pyridine does not result in polymer formation. REMP in Et_2O and THF with 500:1=[NB]:[**1**] (0.25 M) yields 87 and 98% of c-PNB with M_n=325,000 g/mol (*Đ*=3.59) and 87,000 g/mol (*Đ*=2.03), respectively (Table 1). ^{1}H NMR spectra of c-PNB samples obtained from toluene, Et_2O, and THF indicate the high *cis*-selectivity (>99%) is preserved (see ESI).

^{13}C NMR spectra of c-PNB synthesized in toluene (c-PNB$_{tol}$) and THF (c-PNB$_{THF}$) exhibit signals that overlap; however, c-PNB$_{THF}$ exhibits broad shoulders, implying the presence of multiple pentad combinations other than *mmmm* and *rrrr* (Figure S2).[7] Matching a previous report by Schrock,[16] the partially brominated c-PNB$_{THF}$ exhibits unresolved multiplets for H(1',6') protons at 3.87-3.83 ppm. Figure 2 (bottom) depicts the ^{1}H NMR and decoupled spectra of partially brominated c-PNP$_{THF}$ synthesized in THF. The spectra are clearly different than c-PNB$_{tol}$ indicating solvent does alter the tacticity. The ^{1}H NMR (Figure 2 bottom) contains a multiplet that when decoupled changes into a mixture of four singlets (where the *isotactic m*

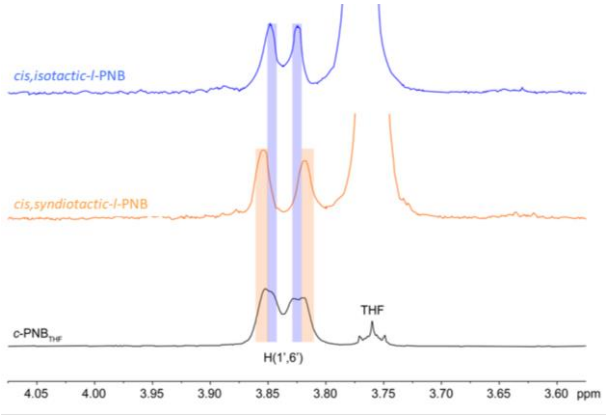


Figure 3. H(1′,6′) signal with homonuclear decoupling at 2.61 ppm in the ^{1}H NMR spectra of partially brominated *cis,syndiotactic*-l-PNB (orange) and *cis,isotactic*-l-PNB (blue), and *c*-PNB synthesized by **1** in THF. Note: *isotactic* H(1′,6′)s are two unresolved doublets with 2.5 Hz coupling, thus appearing as a singlet.

dyads are a poorly resolved pair of doublets (~2.5 Hz) that appear instead as two overlapping singlets). The four singlets are attributable to a mixture of *isotactic* (*mmmm* dyads) and *syndiotactic* (*rrrr* dyads).

Compelling evidence for the mixture of tacticities in c-PNB$_{THF}$ comes from comparing authentic samples of linear *cis,isotactic* and *cis,syndiotactic* PNB.[14] Figure 3 depicts the partially brominated decoupled spectra of *iso*-l-PNB, *syn*-l-PNB, and c-PNB$_{THF}$. The *iso*-l-PNB (blue) and *syn*-l-PNB (orange) exhibit two singlets that are separated enough to distinguish. When overlapped with a decoupled spectrum of c-PNB$_{THF}$ it is clear to see that the cyclic sample contains a mixture of *iso* and *syn*-PNB that match the pure tactic linear samples. Moreover, altering the ratio of THF in toluene permits control of *iso* incorporation. Polymerizing norbornene with **1** in 10, 25, and 50% of THF in toluene (V_{THF}:$V_{toluene}$), it is possible to synthesize c-PNBs with increased *isotactic m* dyads% (Figure 4 and Table 2). Linewidth analysis (see Figure S1) using the pure tactic linear samples as reference allows the %*m*/*r* dyads to be calculated. For example, in pure THF the %*m* dyad is 50%(±5%). A noticeable increase in *m* dyads also appears in the ^{13}C NMR spectra as the %THF increases; the signals become increasingly broad (See Figure S2).

Table 2. Calculated *iso*:*syn* ratio of c-PNBs synthesized by **1** in varying ratios of THF/toluene solutions. The precision of *iso*:*syn* ratio is ±10%.

THF:toluene	*iso:syn* ratio
1:0	1.0 : 1.0
1:1	0.9 : 1.0
1:3	0.4 : 1.0
1:9	0.1 : 1.0
0:1	0 : 1

In a control experiment, 2-methyltetrahydrofuran (2-MeTHF) was used as the solvent. 2-MeTHF has similar polarity to THF but is a weaker coordinating solvent.[38] REMP of norbornene in 2-MeTHF yields 32% of c-PNB with 97% *cis*-selectivity using 500:1=[NB]:[**1**]. ^{1}H NMR (brominated sample) and ^{13}C NMR spectra indicate c-PNB$_{2\text{-MeTHF}}$ is *cis,syndiotactic*, indicating that coordination of THF, not polarity, is the key for tacticity change (Table 1 and Figure S3).

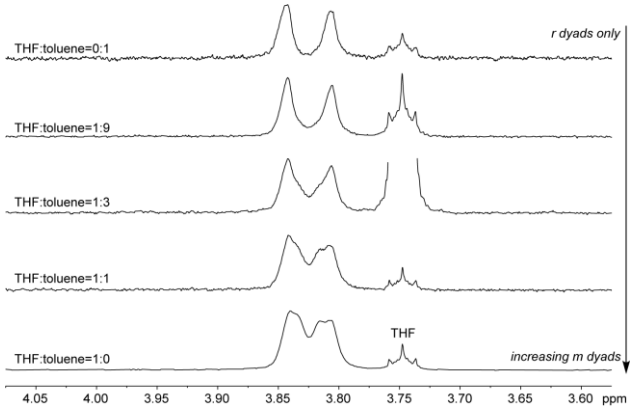
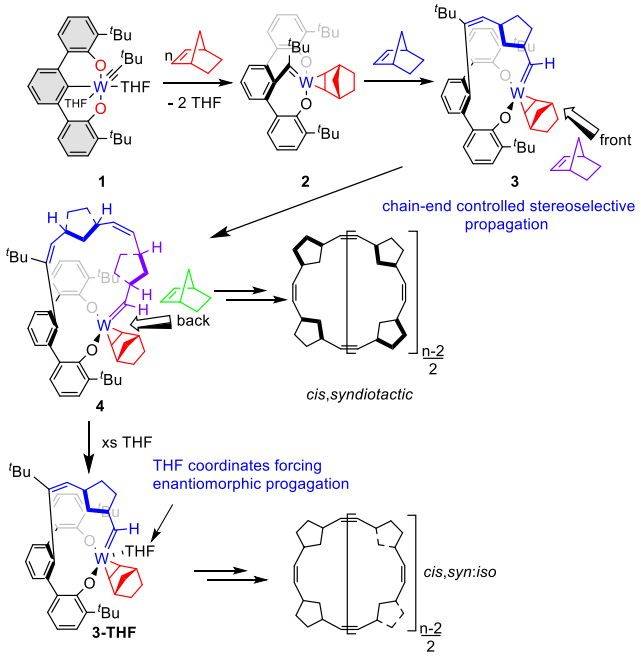


Figure 4. H(1′,6′) signal in the ^{1}H NMR spectra of partially brominated c-PNBs synthesized by 1 in varying ratio of THF:toluene. Upon lowering THF in solvent mixture, *m* dyad% decreases.

Initiator **1** and all others within this class[27–30,35–37] of catalysts produce highly *cis,syndiotactic* c-PNB in toluene. This work reveals the origins of stereoselectivity, and some clear conclusions emerge. Scheme 2 depicts a proposed mechanism for initiation and propagation of norbornene with complex **1**. Ample precedent[27,28,30–34] indicates upon exposure to unsaturated substrates, the alkylidyne in **1** rapidly inserts into the M–C bond of the OCO pincer ligand to provide a *tethered* alkylidene with a bound norbornene. Based on precedent with other unsaturated substrates, one norbornene may remain coordinated during the polymerization. Attack and insertion of subsequent monomers in alternating enantiofaces leads to *syndiotactic* polymers.[1] Due to the tethered alkylidene, chain-end control dominates the next insertion thus leading to *syndiotacticity* in polymers initiated with **1**. After each ring opening the monomer must approach from the opposite



Scheme 2. Proposed initiation and role of THF in REMP of norbornene with **1**. In toluene both enantiofaces are open allowing norbornene to approach alternating faces creating *syndiotactic* PNB. In THF, one enantioface is blocked forcing approach at the same face creating *isotactic* blocks.

enantioface in a perfectly alternating sequence (>99% *syndiotactic*). Enantiomorphic site control leads to *cis*,*isotactic* polymers, where after each ring opening, the metal-coordination environment forces the monomer to approach the same chiral (*rac*) face of the alkylidene during each propagation step. By employing a coordinating solvent, a change in the *r*:*m* dyad ratio in c-PNB synthesis occurs. In pure THF, a 50:50 ratio results, whereas in non-coordinating toluene, >99% *r*-dyads form. The tacticity change is directly related to the ability of solvent to coordinate. Pyridine completely shuts down the polymerization, presumably by binding too strongly. Coordination of THF to block one enantioface must be key to inducing isotactic *mmmm* propagation because polymerization with sterically hindered 2-MeTHF as the solvent retains high *syndiotacticity*. These observations are consistent with the hypothesis that by blocking a coordination site, monomer must approach the same face of the alkylidene, thus switching to enantiomorphic polymerization. Stereocontrolled synthesis of cyclic polymers remains uncommon; for example, *isotactic* c-PNB is unknown. This work demonstrates that solvent can play an important role that will complement future catalyst design.

Acknowledgements

Financially supported by the National Science Foundation (NSF) CHE-2108266. There are no conflicts to declare.

Notes and references

1 S. Negash, Y. B. Tatek and M. Tsige, *J. Chem. Phys*, 2018, **148**, 134705.

2 L. E. Rosebrugh, V. M. Marx, B. K. Keitz and R. H. Grubbs, *J. Am. Chem. Soc.*, 2013, **135**, 10032–10035.

3 P.-N. Tzounis, D. V Argyropoulou, S. D. Anogiannakis and D. N. Theodorou, *Macromolecules*, 2018, **51**, 6878–6891.

4 C. De Rosa and F. Auriemma, *Prog. Polym. Sci.*, 2006, **31**, 145–237.

5 A. J. De Vries, *Polym. Eng. Sci.*, 1983, **23**, 241–246.

6 M. Farina, G. Di Silvestro and P. Sozzani, *Macromolecules*, 1993, **26**, 946–950.

7 L. S. Baugh and J. A. M. Canich, *Stereoselective Polymerization with Single-Site Catalysts*, CRC Press, Boca Raton, 1st Edition., 2007.

8 G. W. Coates and R. M. Waymouth, *Science (1979)*, 1995, **267**, 217–219.

9 S. A. Miller and J. E. Bercaw, *Organometallics*, 2006, **25**, 3576–3592.

10 R. M. Waymouth, G. Coates, A.-L. Mogstad, K. Stein, D. Fischer and S. Borkowsky, *Macromol. Symp.*, 1995, **98**, 221–222.

11 G. W. Coates, *Chem. Rev.*, 2000, **100**, 1223–1252.

12 R. R. Schrock, *Acc. Chem. Res.*, 2014, **47**, 2457–2466.

13 B. Autenrieth, H. Jeong, W. P. Forrest, J. C. Axtell, A. Ota, T. Lehr, M. R. Buchmeiser and R. R. Schrock, *Macromolecules*, 2015, **48**, 2480–2492.

14 B. Autenrieth and R. R. Schrock, *Macromolecules*, 2015, **48**, 2493–2503.

15 H. Jeong, V. W. L. Ng, J. Börner and R. R. Schrock, *Macromolecules*, 2015, **48**, 2006–2012.

16 J. Hyvl, B. Autenrieth and R. R. Schrock, *Macromolecules*, 2015, **48**, 3148–3152.

17 W. P. Forrest, J. G. Weis, J. M. John, J. C. Axtell, J. H. Simpson, T. M. Swager and R. R. Schrock, *J. Am. Chem. Soc.*, 2014, **136**, 10910–10913.

18 M. J. Benedikter, G. Frater and M. R. Buchmeiser, *Macromolecules*, 2018, **51**, 2276–2282.

19 O. M. Ogba, N. C. Warner, D. J. O'Leary and R. H. Grubbs, *Chem. Soc. Rev.*, 2018, **47**, 4510–4544.

20 B.-G. Shin, T.-Y. Cho, D. Y. Yoon and B. Liu, *Macromol. Res.*, 2007, **15**, 185–190.

21 R. O'Dell, D. H. McConville, G. E. Hofmeister and R. R. Schrock, *J. Am. Chem. Soc.*, 1994, **116**, 3414–3423.

22 M. M. Flook, L. C. H. Gerber, G. T. Debelouchina and R. R. Schrock, *Macromolecules*, 2010, **43**, 7515–7522.

23 M. M. Flook, J. Börner, S. M. Kilyanek, L. C. H. Gerber and R. R. Schrock, *Organometallics*, 2012, **31**, 6231–6243.

24 M. J. Benedikter, R. Schowner, I. Elser, P. Werner, K. Herz, L. Stöhr, D. A. Imbrich, G. M. Nagy, D. Wang and M. R. Buchmeiser, *Macromolecules*, 2019, **52**, 4059–4066.

25 G. C. Bazan, E. Khosravi, R. R. Schrock, W. J. Feast, V. C. Gibson, M. B. O'Regan, J. K. Thomas and W. M. Davis, *J. Am. Chem. Soc.*, 1990, **112**, 8378–8387.

26 G. C. Bazan, J. H. Oskam, H. N. Cho, L. Y. Park and R. R. Schrock, *J. Am. Chem. Soc.*, 1991, **113**, 6899–6907.

27 S. A. Gonsales, T. Kubo, M. K. Flint, K. A. Abboud, B. S. Sumerlin and A. S. Veige, *J. Am. Chem. Soc.*, 2016, **138**, 4996–4999.

28 V. Jakhar, D. Pal, I. Ghiviriga, K. A. Abboud, D. W. Lester, B. S. Sumerlin and A. S. Veige, *J. Am. Chem. Soc.*, 2021, **143**, 1235–1246.

29 S. S. Nadif, T. Kubo, S. A. Gonsales, S. VenkatRamani, I. Ghiviriga, B. S. Sumerlin and A. S. Veige, *J. Am. Chem. Soc.*, 2016, **138**, 6408–6411.

30 K. P. McGowan, M. E. O'Reilly, I. Ghiviriga, K. A. Abboud and A. S. Veige, *Chem. Sci.*, 2013, **4**, 1145–1155.

31 C. D. Roland, T. Zhang, S. VenkatRamani, I. Ghiviriga and A. S. Veige, *Chem. Commun.*, 2019, **55**, 13697–13700.

32 V. K. Jakhar, A. M. Esper, I. Ghiviriga, K. A. Abboud, C. Ehm and A. S. Veige, *Angew. Chem. Int. Ed.*, 2022, **61**, e202203073.

33 C. D. Roland, S. VenkatRamani, V. K. Jakhar, I. Ghiviriga, K. A. Abboud and A. S. Veige, *Organometallics*, 2018, **37**, 4500–4505.

34 C. D. Roland, H. Li, K. A. Abboud, K. B. Wagener and A. S. Veige, *Nat. Chem.*, 2016, **8**, 791–796.

35 S. Sarkar, A. R. Carlson, M. K. Veige, J. M. Falkowski, K. A. Abboud and A. S. Veige, *J. Am. Chem. Soc.*, 2008, **130**, 1116–1117.

36 V. K. Jakhar, Y.-H. Shen, S.-M. Hyun, A. M. Esper, I. Ghiviriga, K. A. Abboud, D. W. Lester and A. S. Veige, *Organometallics*, 2023, **42**, 1339–1346.

37 a) S. Sarkar, K. P. McGowan, S. Kuppuswamy, I. Ghiviriga, K. A. Abboud and A. S. Veige, *J. Am. Chem. Soc.*, 2012, **134**, 4509–4512. b) V. K. Jakhar, Y.-H. Shen, S.-M. Hyun, A. M. Esper, I. Ghiviriga, K. A. Abboud, D. W. Lester and A. S. Veige, *Organometallics*, 2023, **42**, 1339–1346.

38 D. F. Aycock, *Org. Process Res. Dev.*, 2007, **11**, 156–159.