



Cite this: *Polym. Chem.*, 2018, **9**, 4711

Received 27th June 2018,
Accepted 31st August 2018

DOI: 10.1039/c8py00953h

rsc.li/polymers

Yb(NTf₂)₃/HFIP induced high isotacticity in atom transfer radical polymerization of methyl methacrylate†

Sebastian Schaubach, Xiao-Yan Wang, * Jun-Fang Li, Xiu-Li Sun, Sunewang R. Wang and Yong Tang *

High triad isotacticity (mm = 69%) in copper/BOX mediated ATRP of MMA is achieved. The use of strong Lewis acid Yb(NTf₂)₃ (1.0–8.0 mol%) and HFIP as the solvent is the key for this isotactic stereocontrol. A dilute concentration and a relatively low temperature are beneficial for further improving the isotacticity.

The advent of controlled/living radical polymerization (CRP) has led to various advanced polymers with well-controlled molecular weight (MW) and diverse architectures as well as different functionalities.^{1–8} However, stereoregulation in CRP that predominantly modulates the stereochemical configuration of the polymers (Scheme 1), especially for methyl methacrylate (MMA), is still considered a great challenge in synthetic polymer chemistry, possibly due to the planar structure of the propagating chain-end radical.^{9,10} The use of bulky fluorinated alcohols as the solvent has been found to improve the triad syndioselectivity of radical polymerization of methacrylates^{11–14} through hydrogen bonding between the acidic alcoholic proton and the ester moieties of the monomer and the polymer chain.¹⁵ Recently, a BOX/copper catalyzed highly syndioselective atom transfer radical polymerization (ATRP) of MMA with rr over 90% by the use of a side arm strategy,¹⁶ borrowed from asymmetric catalysis in organic synthesis,^{17–20} has been also realized in our group.

On the other hand, through the coordination interaction with the polar functional groups, bulky Lewis acids have been found to significantly enhance the isotacticity in both free and controlled/living radical polymerization of (meth)acrylamides.^{21–26} However, as far as we know, only a slightly improved triad isotacticity (mm up to 22%) could be observed in either free or controlled radical polymerization of MMA by the addition of Lewis acids.^{25,27,28} Owing to the disfavored isotacticity for radical polymerization of MMA, some specific

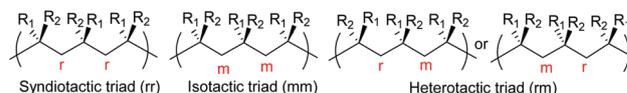
radical polymerization techniques, such as explicitly designed bulky methacrylates^{29,29,31–33} and molecularly templated synthesis,^{34–37} have been described. However, the general isotactic radical polymerization of MMA remains unsolved. We ascribed the above-mentioned inferior effect of Lewis acidic rare-earth triflates on isotactic radical polymerization of MMA to the weaker donor ability of methacrylates with respect to (meth)acrylamides, and thus the use of stronger Lewis acids may solve the long-standing isotacticity problem. Herein, we report an unprecedented high isotacticity in copper-mediated atom transfer radical polymerization (ATRP) of MMA with a catalytic amount of Yb(NTf₂)₃ in 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) under mild conditions.

Similar to our previous study,¹⁶ supplemental activator and reducing agent (SARA) method^{38–40} was also employed for ATRP of MMA in the current project. Specifically, zero-valent copper (a fine powder (99.9% metals basis)) as the reducing agent, ethyl 2-bromo-2-phenylacetate (EBPA) as the initiator, indane bisoxazoline (In-BOX) as the ligand, and CuBr₂ as the precatalyst were used. Initially, various solvents were screened in the presence of 5.0 mol% of Lewis acid Yb(OTf)₃ (Table 1).

While most of the tested solvents such as DCM, THF, aprotic polar solvents (runs 3–5) and various aromatic solvents (runs 6–9) showed little influence on the mm value, polyfluorinated alcohols such as trifluoroethanol (TFE) and HFIP improved the isoselectivity with respect to isopropanol (runs 10 vs. 11 and 12). The mm value marginally dropped back to 2.6% when reacted in HFIP without Yb(OTf)₃ (run 13), thus indicating that such isotactic preference originates in fact from the synergetic combination of Yb(OTf)₃ and HFIP. According to the reports of Matyjaszewski *et al.*,^{22,25,41} coordination of the Lewis acid with the last two segments of a

State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Lu, Shanghai 200032, China.
E-mail: tangy@sioc.ac.cn, wangxiaoyan@sioc.ac.cn

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c8py00953h



Scheme 1 Stereochemical configurations.

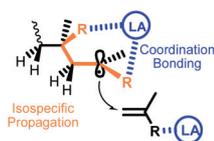
Table 1 Solvent effect on (SARA) ATRP of MMA with the addition of Yb(OTf)₃^a

Run	Solvent	Yield ^b (%)	M _n (×10 ³) ^c	D ^c	mm/mr/rr ^d (%)
1	DCM	32	10.8	1.18	3.2/29.2/67.6
2	THF	47	15.6	1.41	2.7/27.3/70.0
3	DMF	44	27.9	4.59	2.5/28.4/69.1
4	CH ₃ CN	5	9.90	1.20	2.6/27.8/69.6
5	DMSO	67	20.0	1.99	2.8/28.9/68.3
6	Toluene	26	10.5	1.19	2.5/29.2/68.3
7	Anisole	47	12.4	1.23	2.9/30.2/66.9
8	C ₆ H ₅ F	20	10.6	1.17	3.2/30.2/66.6
9	C ₆ F ₆	27	15.8	1.20	3.1/27.8/69.1
10	ⁱ PrOH	23	9.42	8.41	3.5/26.2/70.3
11	TFE	67	23.2	1.64	5.5/34.6/59.9
12	HFIP	50	41.8	2.21	9.2/42.0/48.8
13 ^e	HFIP	47	19.3	1.58	2.6/28.7/68.7

^a Conditions: 200 : 2 : 1 : 2 : 4 MMA : EBPA : CuBr₂ : In-BOX : Cu(0) ratio, 5.0 mol% of Yb(OTf)₃, solvent/MMA (4/1, v/v), RT. ^b Isolated yields. ^c Number-average molecular weights and polydispersity indices determined by GPC at 25 °C in THF vs. narrow PS standards ($D = M_w/M_n$). ^d Triad tacticity measured by ¹H NMR in CDCl₃. ^e Without Yb(OTf)₃.

growing polymer chain forces them into the meso configuration during the monomer addition and leads to isotactic polymers, even in the presence of catalytic amounts of Lewis acid (Scheme 2). Another explanation can be derived from the observation that methacrylate monomers with more bulky ester side chains display an increased tendency to form isotactic polymers which is rationalized by the increasing tendency for a helical polymer macrostructure that minimizes steric repulsion when the bulky sidechains are in an isotactic arrangement.⁴² For example, in the reports of Okamoto *et al.*,^{11,29,30} in both TFE and HFIP, higher triad isotacticity were produced in free radical polymerization of ethyl methacrylate (EMA) with respect to MMA. In accord to this notion, the coordination of Lewis acid to monomer MMA in TFE and HFIP (Scheme 2) can be regarded as a transient monomer with a bulky ester group that facilitates the isotacticity. Besides, both Yb(NTf₂)₃ and the polymer PMMA are highly soluble in HFIP, thereby guaranteeing a homogeneous reaction system even at high conversions of MMA and at relatively low temperatures (≤25 °C). Rationally, the Lewis acids with stronger acidity exhibit strengthened coordination interaction with the ester groups of MMA or the propagating segments, which is benefit for the enhancement of the isotacticity.

Subsequently, effects of the ytterbium(III) salts with various counter anions on the selectivity were studied (Table 2). While only a slight difference was observed for sulfates with longer

**Scheme 2** Coordination interaction between Lewis acid and the ester groups of MMA or the segments of a growing polymer chain.**Table 2** Counterion effect of Yb(III) salts on (SARA) ATRP of MMA in HFIP^a

Run	X	Yield ^b (%)	M _n (×10 ³) ^c	D ^c	mm/mr/rr ^d (%)
1	OTf	67	20.4	1.62	14.2/40.9/44.9
2	ⁿ C ₄ F ₉ SO ₃	75	18.0	1.72	12.8/38.1/49.1
3	CF ₃ CO ₂	57	20.3	1.45	2.9/26.0/71.1
4	NTf ₂	66	17.3	1.53	38.8/28.3/32.9
5	SbF ₆	59	67.4	2.04	5.3/24.4/70.3
6	PF ₆	53	45.5	2.00	3.3/26.5/70.2

^a Conditions: 200 : 2 : 1 : 2 : 4 MMA : EBPA : Cu(NTf₂)₂ : In-BOX : Cu(0) ratio, 5.0 mol% of YbX₃, HFIP/MMA (4/1, v/v), RT. ^b Isolated yields. ^c Number-average molecular weights and polydispersity indices determined by GPC at 25 °C in THF vs. narrow PS standards ($D = M_w/M_n$). ^d Triad tacticity measured by ¹H NMR in CDCl₃.

perfluorinated alkyl chains, the weaker Lewis acid ytterbium trifluoroacetate led to a large decrease in the triad isotacticity (runs 1–3), indicating the important role of Lewis acidity of the Yb center. Thus, stronger Lewis acid Yb(NTf₂)₃ was then used, which showed a remarkably higher isotacticity, *i.e.* 38.8% mm (run 4). Due to the ill solubility of Yb(SbF₆)₃ and Yb(PF₆)₃ in HFIP, almost no improvement for the triad isoselectivity was observed with these Lewis acids (runs 5 and 6). The counter anions of the precatalyst Cu(II) salts also showed similar influence on the mm value (Table S1, in the ESI[†]). According to the potential anion exchange between the Lewis acid and the ATRP catalyst, Cu(NTf₂)₂ was found to be the most effective ATRP precatalyst for improving the isotacticity.

Effects of the temperature^{14,43,44} and the MMA concentration with the optimized catalytic system in HFIP were then studied. As shown in Table S2 (in the ESI[†]), the slightly lower temperature, for example, operating at 10 °C, was good for a higher triad isotacticity, *i.e.* 46.3% mm, with a slight broadening of the molecular weight distribution (run 3). As indicated in Table 3, polymerizations at the volume ratio of HFIP to MMA between 16/1 and 12/1 showed a steady and high mm selectivity (67.6%–69.0%) with a molecular weight distribution

Table 3 Effect of MMA concentration on (SARA) ATRP of MMA with Yb(NTf₂)₃ in HFIP^a

Run	HFIP/MMA (v/v)	Yield ^b (%)	M _n (×10 ³) ^c	D ^c	mm/mr/rr ^d (%)
1	4/1	50	36.4	1.87	46.3/24.5/29.2
2	6/1	48	28.9	1.84	57.1/21.7/21.2
3	8/1	42	35.2	1.88	59.9/22.2/17.9
4	12/1	37	36.7	1.88	68.5/18.5/13.0
5	16/1	38	54.6	1.99	67.6/18.2/14.2
6 ^e	12/1	47	46.5	2.03	69.0/18.6/12.4
7 ^f	12/1	50	39.7	1.80	63.7/21.0/15.2
8 ^g	12/1	29	31.5	1.77	28.9/24.6/46.5

^a Conditions: 200 : 2 : 1 : 2 : 4 MMA : EBPA : Cu(NTf₂)₂ : In-BOX : Cu(0) ratio, 5.0 mol% of Yb(NTf₂)₃, 10 °C. ^b Isolated yields. ^c Number-average molecular weights and polydispersity indices determined by GPC at 25 °C in THF vs. narrow PS standards ($D = M_w/M_n$). ^d Triad tacticity measured by ¹H NMR in CDCl₃. ^e With 8.0 mol% of Yb(NTf₂)₃. ^f Polymerized for 4 days. ^g With 1.0 mol% of Yb(NTf₂)₃.

with molecular weight distributions between 1.88 and 2.03 (runs 4–6). Since dilution of MMA led to a lower yield of PMMA, a higher loading of $\text{Yb}(\text{NTf}_2)_3$ was attempted. To our delight, polymerization of MMA with 8.0 mol% of $\text{Yb}(\text{NTf}_2)_3$ or for a longer reaction time at a volume ratio of HFIP to MMA (12/1) gave PMMA in comparable yields to that with 5.0 mol% of $\text{Yb}(\text{NTf}_2)_3$ at a volume ratio of HFIP to MMA (4/1) (runs 1 vs. 6 and 7). Interestingly, even a 1.0 mol% loading of $\text{Yb}(\text{NTf}_2)_3$ produced PMMA in 29% yield with an isotacticity of 28.9% (run 8), which is a remarkable improvement in comparison to the previous results.^{25,27} Furthermore, $\text{Yb}(\text{NTf}_2)_3$ proved to be the most efficient Lewis acid in enhancing the triad isotacticity among a series of rare earth bis(trifluoromethane)sulfonamide salts examined in Table S3 (in the ESI†).

The In-BOX is a bidentate ligand and the cyclic voltammetry experiments in CH_3CN indicate a low K_{ATRP} of *ca.* 7.2×10^{-13} for $\text{CuBr}_2/\text{In-BOX}$ according to Matyjaszewski's work (Fig. S1†).⁴⁵ However, under the reaction conditions adopted in this work, the In-BOX ligand achieved a much higher polymerization rate and better controllability than the traditional highly active ligand Me_6TREN (Scheme S5†). Besides, In-BOX ligand based catalysts proved to be compatible with Lewis acid and works quite well with the addition of 5 mol% $\text{Yb}(\text{NTf}_2)_3$, while traditional highly active ATRP catalysts based on ligands such as Me_6TREN or TPMA failed to furnish any polymer under the same conditions (Table S5†).

It was found that the molecular weight distributions were relatively broad ($D = 1.8\text{--}2.0$) when the mm values are higher than 50%. According to literatures, it is difficult to simultaneously obtain high stereoselectivity and excellent molecular weight control in the ATRP of MMA with the addition of Lewis acid. For instance, in the report of Matyjaszewski *et al.*,²⁵ when the mm value in the ATRP of MMA reached 21%, the D was 2.0. We think that the broadening of D in our work might be mainly caused by the following two reasons: (i) the addition of Lewis acid makes the polymerization system sticky especially at the late stage of the polymerization and at a low temperature (10 °C), which hampers the diffusion of the catalytic system and damages its controllability on molecular weight; (ii) the HFIP/MMA ratios of 4/1–12/1 are necessary to achieve high mm values (>50%), and the diluted system is not conducive to the control of molecular weight, which is consistent with the result of our previous work.^{16,46}

Fig. 1 shows the ^1H NMR spectra of the polymers obtained in the absence and presence of $\text{Yb}(\text{NTf}_2)_3$. As compared to the previous reports,^{16,27,36} the spectra clearly confirmed the authentic structure of the resultant PMMA with significantly improved triad isotacticity, indicative of the stability of the ester group of PMMA towards strongly Lewis acidic $\text{Yb}(\text{NTf}_2)_3$ in HFIP. The silent ^{19}F NMR of these PMMAs further supported this. The well-resolved chemical shifts of the chain methylenic protons indicated a high content of tetrad isotactic units in the obtained PMMAs.³⁶ More importantly, the increasing triad tacticities of the resulting PMMAs determined from ^1H NMR spectra correlated well with the decreasing T_g measured by the DSC curves (Fig. 2 and Fig. S2†).^{47,48} Thus,

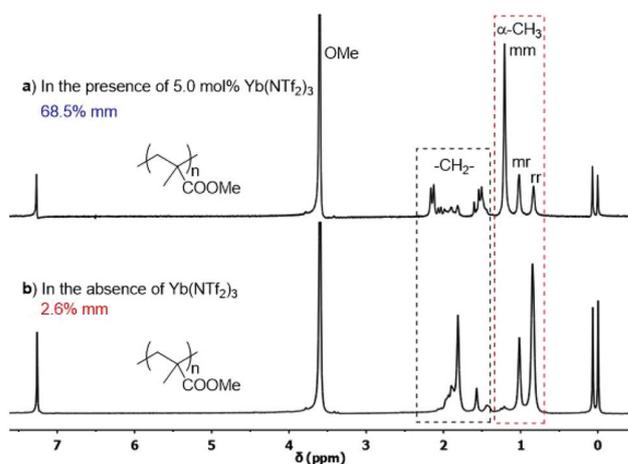


Fig. 1 A comparison of ^1H NMR spectra of PMMA prepared from (SARA) ATRP of MMA (a) in the presence of 5.0 mol% $\text{Yb}(\text{NTf}_2)_3$ (Table 3, run 4) and (b) in the absence of Lewis acid in HFIP (Table 1, run 13).

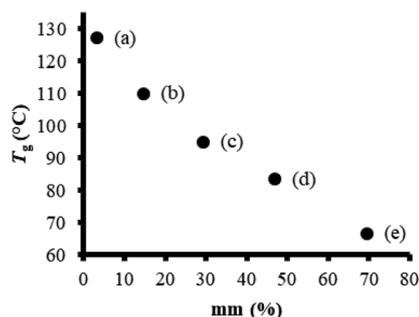


Fig. 2 Plot of T_g over triad isotacticity (mm) for PMMAs with increasing mm: (a) $T_g = 128$ °C, mm = 2.6% (Table 1, run 13). (b) $T_g = 111$ °C, mm = 14.2% (Table 2, run 1). (c) $T_g = 96$ °C, mm = 28.9% (Table S4,† run 2). (d) $T_g = 84$ °C, mm = 46.3% (Table 3, run 1). (e) $T_g = 67$ °C, mm = 69.0% (Table 3, run 6).

the catalytic amount of Lewis acids combined with the polyfluorinated alcohol solvents were found to be effective in enhancing the isotacticity in ATRP of MMA.

We conducted several experiments to demonstrate that all the polymerizations in this work proceeded *via* a radical mechanism. As shown in Scheme S1,† a conventional radical polymerization was set up using $\text{Et}_3\text{B}/\text{O}_2$ as the radical initiator system for the conventional radical polymerization of MMA in the presence of 5% $\text{Yb}(\text{NTf}_2)_3$ in HFIP at 10 °C, achieving a comparable mm value with the (SARA) ATRP. The radical character of the polymerizations was also underlined by a control experiment in which the reaction was efficiently suppressed in the presence of 10 mol% TEMPO (Scheme S2†). We also set up a polymerization without the addition of $\text{Cu}(0)$ where no yield was detected, underlining the SARA process (Scheme S3†). We have submitted several other monomers to our conditions, including acrylamide, *n*-butyl methacrylate and *n*-propyl methacrylate. As shown in Table S6,† for all the ATRP reactions of methacrylates and acrylamide, the isotacticity of the polymers

could be significantly improved *via* the addition of 5 mol% Yb(NTf₂)₃ and the employment of HFIP as the solvent, indicating that the approach to improve isotacticity described in this work is suitable for the ATRP of different methacrylate monomers and acrylamide.

In summary, highly efficient bulky Lewis acid Yb(NTf₂)₃ for a high triad isoselectivity in bisoxazoline/copper mediated atom transfer radical polymerization of MMA in HFIP is described. Specifically, the triad isotacticity was improved from 22% to 69% and the loading of the Lewis acid was lowered from 30.0 mol% to 5.0–8.0 mol% with acceptable yields of PMMA.²⁵ The strengthened coordination interaction in HFIP between the ester groups of MMA or the propagating chain and Yb(NTf₂)₃, a stronger Lewis acid than the previously used rare earth triflates, is very critical for this achievement, which may also serve as a practical strategy for stereospecific controlled radical polymerization of other challenging polar monomers in synthetic polymer chemistry.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

The authors are grateful for financial support by Shanghai Sailing Program (18YF1429000), the National Natural Science Foundation of China (21690072, 21672237), the Chinese Academy of Sciences (XDB 20000000, QYZDB-SSWSLH016) and the National Key Research and Development Program (2016YFA0202900) as well as the Science and Technology Commission of Shanghai Municipality (17JC1401200).

Notes and references

- 1 K. Matyjaszewski, *Macromolecules*, 2012, **45**, 4015–4039.
- 2 K. Matyjaszewski and J. Spanswick, *Mater. Today*, 2005, **8**, 26–33.
- 3 W. A. Braunecker and K. Matyjaszewski, *Prog. Polym. Sci.*, 2007, **32**, 93–146.
- 4 K. Matyjaszewski and J. Xia, *Chem. Rev.*, 2001, **101**, 2921–2990.
- 5 M. Ouchi, T. Terashima and M. Sawamoto, *Chem. Rev.*, 2009, **109**, 4963–5050.
- 6 G. Moad, E. Rizzardo and S. H. Thang, *Aust. J. Chem.*, 2005, **58**, 379–410.
- 7 C. J. Hawker, A. W. Bosman and E. Harth, *Chem. Rev.*, 2001, **101**, 3661–3688.
- 8 M. Kamigaito, *Polym. J.*, 2011, **43**, 105–120.
- 9 X. Su, Z. Zhao, H. Li, X. Li, P. Wu and Z. Han, *Eur. Polym. J.*, 2008, **44**, 1849–1856.
- 10 K. Satoh and M. Kamigaito, *Chem. Rev.*, 2009, **109**, 5120–5156.
- 11 Y. Isobe, K. Yamada, T. Nakano and Y. Okamoto, *Macromolecules*, 1999, **32**, 5979–5981.
- 12 S. Habaue and Y. Okamoto, *Chem. Rec.*, 2001, **1**, 46–52.
- 13 Y. Miura, T. Satoh, A. Narumi, O. Nishizawa, Y. Okamoto and T. Kakuchi, *Macromolecules*, 2005, **38**, 1041–1043.
- 14 Y. Miura, T. Satoh, A. Narumi, O. Nishizawa, Y. Okamoto and T. Kakuchi, *J. Polym. Sci., Part A: Polym. Chem.*, 2006, **44**, 1436–1446.
- 15 İ. Değirmenci, S. Eren, V. Aiyente, B. De Sterck, K. Hemelsoet, V. Van Speybroeck and M. Waroquier, *Macromolecules*, 2010, **43**, 5602–5610.
- 16 X.-Y. Wang, X.-L. Sun, F. Wang and Y. Tang, *ACS Catal.*, 2017, **7**, 4692–4696.
- 17 S. Liao, X.-L. Sun and Y. Tang, *Acc. Chem. Res.*, 2014, **47**, 2260–2272.
- 18 J.-B. Zhu, H. Chen, S. Liao, Y.-X. Li and Y. Tang, *Org. Chem. Front.*, 2014, **1**, 1035–1039.
- 19 Q.-J. Liu, J. Zhu, X.-Y. Song, L. Wang, S. R. Wang and Y. Tang, *Angew. Chem., Int. Ed.*, 2018, **57**, 3810–3814.
- 20 X.-K. Kuang, J. Zhu, L. Zhou, L. Wang, S. R. Wang and Y. Tang, *ACS Catal.*, 2018, **8**, 4991–4995.
- 21 Y. Isobe, D. Fujioka, S. Habaue and Y. Okamoto, *J. Am. Chem. Soc.*, 2001, **123**, 7180–7181.
- 22 J.-F. Lutz, D. Neugebauer and K. Matyjaszewski, *J. Am. Chem. Soc.*, 2003, **125**, 6986–6993.
- 23 Y. Sugiyama, K. Satoh, M. Kamigaito and Y. Okamoto, *J. Polym. Sci., Part A: Polym. Chem.*, 2006, **44**, 2086–2098.
- 24 J. Jiang, X. Lu and Y. Lu, *Polymer*, 2008, **49**, 1770–1776.
- 25 J.-F. Lutz, W. Jakubowski and K. Matyjaszewski, *Macromol. Rapid Commun.*, 2004, **25**, 486–492.
- 26 T. Hirano, T. Saito, Y. Kurano, Y. Miwa, M. Oshimura and K. Ute, *Polym. Chem.*, 2015, **6**, 2054–2064.
- 27 (a) Y. Isobe, T. Nakano and Y. Okamoto, *J. Polym. Sci., Part A: Polym. Chem.*, 2001, **39**, 1463–1471; (b) Y. Okamoto, S. Habaue, Y. Isobe and T. Nakano, *Macromol. Symp.*, 2002, **183**, 83–88.
- 28 B. B. Noble, L. M. Smith and M. L. Coote, *Polym. Chem.*, 2014, **5**, 4974–4983.
- 29 T. Nakano, M. Mori and Y. Okamoto, *Macromolecules*, 1993, **26**, 867–868.
- 30 K. Ishitake, K. Satoh, M. Kamigaito and Y. Okamoto, *Polym. Chem.*, 2012, **3**, 1750–1757.
- 31 T. Nakano, Y. Satoh and Y. Okamoto, *Polym. J.*, 1998, **30**, 635–640.
- 32 T. Nakano, Y. Shikisai and Y. Okamoto, *Polym. J.*, 1996, **28**, 51–60.
- 33 T. Nakano, A. Matsuda and Y. Okamoto, *Polym. J.*, 1996, **28**, 556–558.
- 34 R. Buter, Y. Y. Tan and G. Challa, *J. Polym. Sci., Part A-1: Polym. Chem.*, 1972, **10**, 1031–1049.
- 35 R. Buter, Y. Y. Tan and G. Challa, *Polym. Sci., Polym. Chem. Ed.*, 1973, **11**, 1003–1011.
- 36 T. Serizawa, K.-i. Hamada and M. Akashi, *Nature*, 2004, **429**, 52–55.
- 37 J. Hwang, H.-C. Lee, M. Antonietti and B. V. K. J. Schmidt, *Polym. Chem.*, 2017, **8**, 6204–6208.

- 38 W. Jakubowski and K. Matyjaszewski, *Macromolecules*, 2005, **38**, 4139–4146.
- 39 R. Luo and A. Sen, *Macromolecules*, 2008, **41**, 4514–4518.
- 40 H. Jiang, L. Zhang, J. Pan, X. Jiang, Z. Cheng and X. Zhu, *J. Polym. Sci., Part A: Polym. Chem.*, 2012, **50**, 2244–2253.
- 41 *ACS Symp. Ser.*, ed. K. Matyjaszewski, 2003, vol. 854.
- 42 B. B. Noble and M. L. Coote, *Adv. Phys. Org. Chem*, ed. I. H. Williams and N. H. Williams, 2015, vol. 49, pp. 189–258.
- 43 R. Buter, Y. Y. Tan and G. Challa, *Polym. Sci., Polym. Chem. Ed.*, 1973, **11**, 1013–1024.
- 44 L. M. Smith and M. L. Coote, *J. Polym. Sci., Part A: Polym. Chem.*, 2013, **51**, 3351–3358.
- 45 W. Tang, Y. Kwak, W. Braunecker, N. V. Tsarevsky, M. L. Coote and K. Matyjaszewski, *J. Am. Chem. Soc.*, 2008, **130**, 10702–10713.
- 46 X.-Y. Wang, X.-L. Sun, Z.-H. Chen, F. Wang, S. R. Wang and Y. Tang, *Polym. Chem.*, 2018, **9**, 4309–4315.
- 47 E. V. Thompson, *J. Polym. Sci., Part A-2: Polym. Phys.*, 1966, **4**, 199–208.
- 48 L. R. Denny, R. F. Boyer and H.-G. Elias, *J. Macromol. Sci., Phys.*, 1986, **25**, 227–265.