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One-pot synthesis of end-functionalised soluble star-shaped polymers by living ring-opening metathesis polymerisation using a molybdenum-alkylidene catalyst†

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Precise synthesis of soluble star-shaped polymers has been achieved by adopting living ring-opening metathesis polymerisation (ROMP) using a molybdenum-alkylidene catalyst with sequential addition of norbornene and cross-linking agent; the method provides efficient one-pot synthesis of high molecular weight end-functionalised star-shaped polymers ($M_n = >1.37 \times 10^5$) with more arms (branching) with rather low PDI values ($M_w/M_n = 1.17\text{--}1.37$) under the optimised conditions.

Introduction

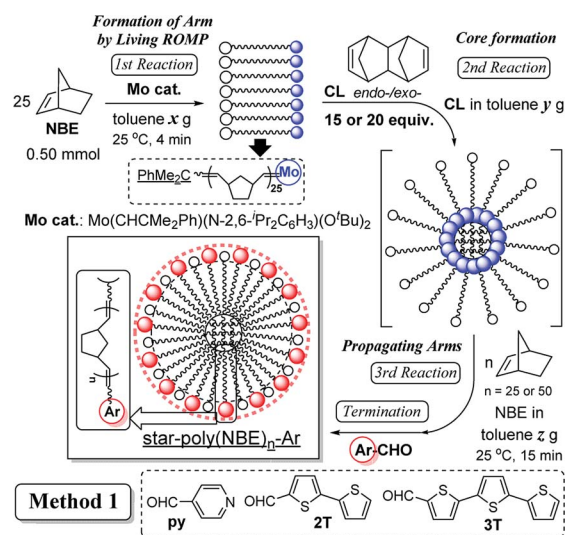
Star polymers containing multiple linear arms connected at a central branched core are one of the simplest nonlinear polymers,^{1–10} and development of precise synthesis methods by living polymerisation techniques attracts considerable attention.^{1–10} Reported examples for the synthesis by adopting living ring-opening metathesis polymerisation (ROMP)^{11–23} *via* arm (brush) first^{24–30} and core first (in-out)^{31–35} approaches by sequential addition of monomers/cross linkers (CLs) are known. Moreover, related examples for synthesis of cross-linked polymers (which are insoluble in common organic solvents) by ROMP are also known,^{36–39} especially in terms of application as monolith materials for separation. In particular, the approach by the sequential living ROMP of norbornene (NBE) and cross-linking reagent (1,4,4a,5,8,8a-hexahydro-1,4,5,8-*exo*-*endo*-dimethano-naphthalene, CL) using a Mo-alkylidene catalyst enables us to introduce functionality to the polymer chain ends (star surface) through cleavage of the polymer-metal double bonds with aldehyde *via* Wittig-type reaction.^{15,23,31–34,40–42} However, the previous reports^{31–34} adopting the so called Method 1 (shown in Scheme 1) only demonstrated synthesis of soluble polymers with a small number of arms under limited conditions (5 or 10 equiv. of CL,^{31–34} shown below in Table 1) due to the difficulty of molecular weight control, as also described below.

We thus herein demonstrate that the protocols for synthesis of soluble high molecular weight end-functionalised star-shaped polymers with more arms (branching) have been

developed by using the living ROMP technique under the carefully optimised conditions.⁴³ The synthetic protocols should contribute to providing new (or improved) properties by placement of more functionalities on the star surface.

Results and discussion, experimental

As reported previously,^{31–34} the method consists of 4 steps by sequential addition of NBE, CL, NBE, and the termination by addition of aldehyde (Scheme 1). In order to obtain the star-shaped polymers with more arms (branching), two approaches especially at the core formation step (2nd reaction



Scheme 1 Synthesis of star-shaped ROMP polymers by sequential addition of norbornene (NBE) and cross-linker (CL) in the presence of molybdenum-alkylidene catalyst (Mo cat.).

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Table 1 Synthesis of star-shaped polymers by living ring-opening metathesis polymerisation (ROMP) using Mo(CHCMe₂Ph)(N-2,6-ⁱPr₂C₆-H₃)(O^tBu)₂ (Method 1)^a

Run	Toluene ^b /g	2nd			3rd		Ar ^e	M _n ^f × 10 ⁻⁴	M _w /M _n ^f	Yield ^g /%
	x/y/z	CL ^c /equiv.	Conc. ^d /×10 ⁻² M	Time/min	NBE ^c /equiv.					
1	3.0/4.0/4.0	10	6.36	50	25	py	8.9	1.18	95	
2	3.0/4.0/4.0	10	6.36	50	25	py	8.8	1.19	96	
3	3.0/4.0/4.0	10	6.36	50	25	py	8.8	1.19	96	
4	3.0/4.0/4.0	15	7.27	50	25	py	13.4	1.30	96	
5	3.0/4.0/4.0	15	7.27	70	25	py	20.8	2.88 ^h	94	
6	3.0/4.0/4.0	15	7.27	90	25	py	21.1	1.98 ^h	92	
7	3.0/4.0/4.0	15	7.27	120	25	py	23.5	2.09 ^h	94	
8	3.0/4.0/4.0	15	7.27	50	50	py	39.4	3.09 ^h	93	
9	3.0/4.0/4.0	15	7.27	50	50	py	39.1	3.37 ^h	90	
10	3.0/4.0/4.0	15	7.27	70	50	py	42.3	3.13 ^h	91	
11	3.0/4.0/4.0	15	7.27	70	50	py	41.4	3.42 ^h	92	
12	5.0/4.0/6.0	15	5.33	50	25	py	13.7	1.44	97	
13	5.0/4.0/6.0	15	5.33	70	25	py	14.4	1.46	99	
14	5.0/4.0/6.0	15	5.33	90	25	py	15.7	1.47 ^h	98	
15	5.0/4.0/6.0	15	5.33	120	25	py	16.9	1.38 ^h	98	
16	5.0/4.0/6.0	15	5.33	50	50	py	15.5	1.50 ^h	93	
17	5.0/4.0/6.0	15	5.33	70	50	py	16.4	1.60 ^h	95	
18	5.0/4.0/6.0	15	5.33	90	50	py	17.8	1.92 ^h	95	
19	5.0/4.0/6.0	15	5.33	120	50	py	19.0	1.86 ^h	94	
20	11.0/4.0/5.0	15	4.00	50	25	py	13.7	1.22	90	
21	11.0/4.0/5.0	15	4.00	70	25	py	14.9	1.37	94	
22	11.0/4.0/5.0	15	4.00	50	25	2T	15.5	1.33	88	
23	11.0/4.0/5.0	15	4.00	50	25	3T	15.2	1.29	81	
24	11.0/4.0/5.0	15	4.00	50	50	py	15.6	1.17	96	
25	11.0/4.0/5.0	15	4.00	70	50	py	16.4	1.28	94	
26	3.0/4.0/4.0	20	8.18	50	25	py	28.6	2.51 ^h	95	
27	3.0/4.0/4.0	20	8.18	50	25	py	30.7	2.37 ^h	95	
28	3.0/4.0/4.0	20	8.18	70	25	py	34.9	4.31 ^h	98	
29	3.0/4.0/4.0	20	8.18	90	25	py	28.6	2.19 ^h	90	
30	3.0/4.0/4.0	20	8.18	120	25	py	32.7	2.12 ^h	95	
31	5.0/4.0/6.0	20	6.00	50	25	py	19.4	1.99 ^h	92	
32	5.0/4.0/6.0	20	6.00	70	25	py	21.1	2.65 ^h	94	
33	5.0/4.0/6.0	20	6.0	90	25	py	24.1	2.05 ^h	98	
34	5.0/4.0/6.0	20	6.0	120	25	py	23.6	2.58 ^h	98	
35	11.0/4.0/5.0	20	4.50	50	25	py	14.9	1.44 ^h	90	
36	11.0/4.0/5.0	20	4.50	70	25	py	17.8	1.54 ^h	91	

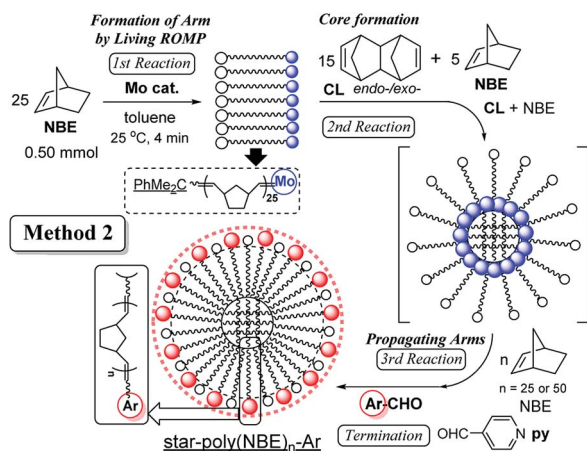
^a Conditions: toluene at 25 °C (detailed procedure, see Scheme 1). ^b Amount of toluene (in gram) in each step (shown in Scheme 1). ^c Equiv. to Mo. ^d Calculated concentration of NBE + CL charged (mmol L⁻¹) at the second stage (core formation). ^e ArCHO employed for the termination (py = 4-pyridine carboxaldehyde; 2T = 2,2'-bithiophene-5-carboxaldehyde; 3T = 2,2':5',2''-terthiophene-5-carboxaldehyde). ^f GPC data in THF vs. polystyrene standards (g mol⁻¹). ^g Isolated yield (%) as MeOH insoluble fraction. ^h Bimodal (or multi-modal) molecular weight distributions observed on GPC trace.

in Scheme 1), such as (i) the approach by increasing the CL under optimised conditions (Method 1, Scheme 1), (ii) the approach by reacting with CL in the co-presence of norbornene (NBE) (formation of different core size, Method 2, Scheme 2 shown below), have thus been considered. Mo(CHCMe₂Ph)(N-2,6-ⁱPr₂C₆H₃)(O^tBu)₂ (Mo cat.) has also been chosen as the initiator due to its ability to prepare the multi-block ring-opened copolymers in a precise manner with moderate propagation as well as with complete conversion of monomers.^{15,23,40–42} This is also due to that the initiator shows markedly higher reactivity toward strained cyclic olefins (norbornene derivatives) than the internal olefins (in the ring-opened polymers).^{15,23,40–42,44} 1,4,4a,5,8,8a-hexahydro-1,4,5,8-*exo-endo*-dimethanonaphthalene (CL, *exo* : *endo* = 0.15 : 1.00)⁴⁵ has also been chosen as the cross-linker, and the

polymerisation was terminated with 4-pyridine carboxaldehyde.^{31,34} The conditions for the first and the third ROMPs with NBE (4 and 15 minutes, respectively) were unchanged, because the NBE consumption should be completed based on our previous study.³¹ The results are summarised in Table 1.

It turned out that, as reported previously,^{31–34} the sequential ROMP with 10 equiv. of CL afforded ring-opened star-shaped polymers with rather low PDI values ($M_w/M_n = 1.18, 1.19$, runs 1–3) and the results are thus reproducible.⁴⁶ However, the PDI values in the resultant polymers eventually became broad if these polymerisations were conducted in the presence of 15 equiv. of CL under the same conditions ($M_w/M_n = 1.30–2.88$, runs 4–6); prolong the reaction time at the second (core formation) step led to increase in the M_n values with broad molecular weight distributions. Similarly, the PDI values in the





Scheme 2 Synthesis of star-shaped ROMP polymers (Method 2).

resultant polymers became broad if the polymerisations were conducted in the presence of 20 equiv. of CL under the same conditions ($M_w/M_n = 2.51, 2.37$, runs 26,27); it becomes more difficult to control the molecular weights (as well as to obtain the reproducibility).

In contrast, importantly, it turned out that the molecular weight distributions in the resultant polymers became unimodal when the polymerisation runs were conducted under diluted conditions ($M_w/M_n = 1.22\text{--}1.46$, runs 16–19, 20–23, Fig. 1). It should be noted that the polymerisation under high dilution (at the second step) afforded the high molecular weight star-shaped ROMP polymers with rather low PDI values [$M_n = 1.37 \times 10^5$, $M_w/M_n = 1.22$ (run 20); $M_n = 1.49 \times 10^5$, $M_w/M_n = 1.37$ (run 21), shown in Fig. 1]. Moreover, further increase of NBE (in the third step) also afforded the high molecular weight ROMP polymers with rather low PDI values [$M_n = 1.56 \times 10^5$, $M_w/M_n = 1.17$ (run 24); $M_n = 1.64 \times 10^5$, $M_w/M_n = 1.28$ (run 25)]. It seems that rather

low PDI values could be maintained under high dilution conditions (runs 20,21,24,25), whereas the PDI values became rather large when the ROMPs were conducted with 50 equiv. of NBE in the third step under conditions conducted in runs 12 and 13 ($M_w/M_n = 1.50\text{--}1.92$, Table 1, runs 16). The results could thus probably suggest that further cross-linking (like star-star coupling upon increasing the reaction time at the second step) would be controlled under these diluted conditions (in the presence of 15 equiv. of CL), which means that the monomer concentration at the core formation step seems critical for obtaining of star-shaped ROMP polymers with low PDI values. The resultant polymers are soluble in toluene, tetrahydrofuran (THF), chloroform, dichloromethane (for measurement of NMR spectra and/or ordinary GPC analysis), but insoluble in methanol, ethanol, water, *n*-hexane *etc.* at room temperature.

Upon presence of 20 equiv. of CL, the ROMPs under high dilution conditions only afforded the star-shaped polymers with rather low PDI values, and the M_n value increased upon increasing the reaction time at the second step with broadening the distribution [$M_n = 1.49 \times 10^5$, $M_w/M_n = 1.44$ (run 35), $M_n = 1.78 \times 10^5$, $M_w/M_n = 1.54$ (run 36)]. These results also suggest that certain optimisation (especially, concentration and the reaction time at the second step) should be necessary.

As shown in Table 1, the M_n values in the polymers (prepared under the optimised conditions) increased upon increasing the CL with rather low PDI values [$M_n = 8.9 \times 10^4$ (run 1, CL = 10), 1.37×10^5 (run 20, CL = 15) or 1.49×10^5 (run 21, CL = 15), 1.78×10^5 (run 36, CL = 20)], clearly suggesting that number of arms (branching) should be increasing upon increasing the amount of CL. Moreover, the M_n values also increased upon increasing amount of NBE in the third step (after formation of core), and the values are apparently higher than those in the linear ROMP polymers. The results clearly suggest that the resultant polymers are star-shaped polymers consisting of the core and arms. It also turned out that the similar polymerisations terminated with 2,2':5',2''-terthiophene-5-carboxaldehyde (3T-CHO), 2,2'-bithiophene-5-carboxaldehyde (2T-CHO) in place of 4-pyridine carboxaldehyde afforded the high molecular weight polymers with relatively low PDI values [$M_n = 1.55 \times 10^5$, $M_w/M_n = 1.33$ (run 22, terminated with 2T-CHO); $M_n = 1.52 \times 10^5$, $M_w/M_n = 1.29$ (run 23, terminated with 3T-CHO)]. The results also suggest that the method can be applied to synthesis of star-shaped ROMP polymers with different end-groups.

In order to change the core size for obtainment of the star-shaped ROMP polymers with more arms (branching), the reaction with CL was conducted in the co-presence of NBE (5.0 equiv.) under the optimised conditions (conducted in Table 1 under high dilution). The results (by Method 2, Scheme 2) are summarised in Table 2.

It seems that the M_n values increased upon co-presence of NBE [ex. 1.49×10^5 (run 21) vs. 1.53×10^5 (run 38)], and the difference became more significant upon addition of 50 equiv. of NBE after the core formation [third step, 1.64×10^5 (run 25) vs. 2.02×10^5 (run 40)], suggesting that the resultant polymers prepared in Method 2 possess more arm numbers compared to those in Method 1. The resultant polymers possessed relatively low PDI values ($M_w/M_n = 1.28\text{--}1.45$), therefore, the method can

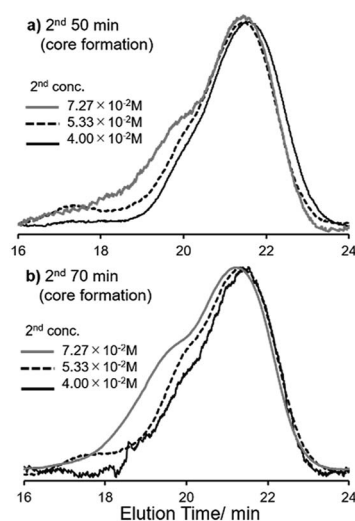


Fig. 1 Selected GPC traces of star-shaped ROMP polymers conducted under different concentration conditions, different time in the 2nd reaction (core formation, Scheme 1). The reaction time (2nd step): (a) 50 min (runs 4, 12, 20, Table 1); (b) 70 min (runs 5, 13, 21, Table 1). The heights in the GPC traces were normalized.



Table 2 Synthesis of star-shaped polymers by living ring-opening metathesis polymerisation (ROMP) using $\text{Mo}(\text{CHCMe}_2\text{Ph})(N\text{-}2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)(\text{O}^i\text{Bu})_2$ (Method 2)^a

Run	2nd			3rd		$M_n^c \times 10^{-4}$	M_w/M_n^c	Yield ^d /%
	CL ^b /equiv.	NBE ^b /equiv.	Time/min	NBE ^b equiv.				
20	15	—	50	25		13.7	1.22	90
21	15	—	70	25		14.9	1.37	94
37	15	5.0	50	25		14.5	1.28	91
38	15	5.0	70	25		15.3	1.39	96
24	15	—	50	50		15.6	1.17	96
25	15	—	70	50		16.4	1.28	94
39	15	5.0	50	50		19.1	1.36	98
40	15	5.0	70	50		20.2	1.45	99

^a Conditions: toluene (total 20 g, shown in runs 20–25) at 25 °C, 4-pyridine carboxaldehyde was used for the termination (detailed procedure, see Scheme 2). ^b Equiv. to Mo. ^c GPC data in THF vs. polystyrene standards (g mol^{-1}). ^d Isolated yield (%) as MeOH insoluble fraction.

also be applied to controlled synthesis of star-shaped ROMP polymers with more branching.⁴⁷

We have shown that protocols for facile and efficient synthesis of high molecular weight “soluble” star-shaped polymers with more branching (arms) have been developed by adopting the living ROMP with sequential addition of NBE and cross-linker using the molybdenum-alkylidene initiator under the optimised conditions (high dilution). The methods should provide a controlled synthesis of highly branched star-shaped ROMP polymers with different end groups (modification of the star surface), and interesting properties such as unique emission by interaction of the end group with the initiating fragment,³³ supported concerted catalysts³⁴ (by placement of different end groups/ligand or catalyst precursor) *etc.* can be thus highly expected. We are now exploring the possibility by introduction of various end groups into the star shaped ROMP polymers by adopting the present methods.

Experimental

1. General procedure

All experiments were carried out under a nitrogen atmosphere in a Vacuum Atmospheres dry-box or using standard Schlenk techniques. All chemicals used were of reagent grades and were purified by the standard purification procedures. Anhydrous grade toluene (Kanto Chemical Co., Inc.) was transferred into a bottle containing molecular sieves (mixture of 3A 1/16, 4A 1/8 and 13X 1/16) in the drybox, and was stored over sodium/potassium alloy, and was used after passing through an alumina short column under nitrogen flow prior to use. $\text{Mo}(\text{CHCMe}_2\text{Ph})(N\text{-}2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)(\text{O}^i\text{Bu})_2$ (ref. 48) and 1,4,4a,5,8,8a-hexahydro-1,4,5,8-*exo-endo*-dimethanonaphthalene (CL, *exo* : *endo* = 0.15 : 1.00)⁴⁵ were prepared according to the literature. 4-Pyridinecarboxaldehyde and 2,2':5',2''-terthiophene-5-carboxaldehyde (3T-CHO) and 2,2'-bithiophene-5-carboxaldehyde (2T-CHO) were used in the dry-box as received (Aldrich Chemical Co.) without further purification.

Molecular weights and the molecular weight distributions of the resultant polymers were measured by gel-permeation chromatography (GPC). HPLC grade THF (Wako Pure Chemical Ind., Inc.) was used for GPC and was degassed prior to use.

GPC were performed at 40 °C on a Shimadzu SCL-10A using a RID-10A detector (Shimadzu Co. Ltd.) in THF (containing 0.03 wt% 2,6-di-*tert*-butyl-*p*-cresol, flow rate 1.0 mL min⁻¹). GPC columns (ShimPAC GPC-806, 804 and 802, 30 cm × 8.0 mm ϕ) were calibrated *versus* polystyrene standard samples. All ¹H and ¹³C NMR spectra were recorded on a Bruker AV500 spectrometer (¹H, 500.13 MHz; ¹³C, 125.77 MHz), and all chemical shifts are quoted in ppm and are referenced to SiMe₄. Obvious multiplicities and routine coupling constants are usually not listed, and all spectra were obtained in the solvent indicated at 25 °C.

2. General polymerisation procedure

Typical polymerisation procedure (run 20, Method 1, Table 1) is as follows. A toluene solution (1.0 g) containing $\text{Mo}(\text{CHCMe}_2\text{Ph})(N\text{-}2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)(\text{O}^i\text{Bu})_2$ (2.00×10^{-5} mol) was added in one portion to a rapidly stirred toluene solution (10.0 g) containing the norbornene (25 equiv. to Mo) at room temperature (25 °C), and the solution was stirred for 4 min. A toluene solution (4.0 g) containing 1,4,4a,5,8,8a-hexahydro-1,4,5,8-*exo-endo*-dimethanonaphthalene (CL, 15 equiv. to Mo) was then added into the solution, and the mixture was stirred for prescribed time (50 min). Then a toluene solution (5.0 g) containing norbornene (25 equiv. to Mo) was then added in one portion to the mixture, and the reaction solution was further stirred for 15 min. The polymerisation was quenched by adding 4-pyridine carboxaldehyde (*ca.* >10 mg, excess), and the solution was stirred for 1 h for completion. The mixture was then removed *in vacuo* until it was dissolved in the minimum amount of toluene. The solution was poured dropwise into methanol to afford pale white precipitates. The polymer was then collected by filtration and dried *in vacuo*. In Method 2, the basic procedure was the same except that a toluene solution containing CL and norbornene (5.0 equiv. to Mo) was added in the second step.

¹H NMR (in CDCl₃ at 25 °C): δ 5.35 and 5.21 (br.s, 2H olefinic), 2.79 and 2.43 (br.s, 2H), 1.85 and 1.03 (m, 2H), 1.78 and 1.36 (m, 4H) ppm. Moreover, resonances ascribed to pyridine end group [8.54 and 8.50 (d) ppm] or oligo(thiophene) (2T, 3T, 7.00–7.40) were also observed. ¹³C NMR (in CDCl₃ at 25 °C): δ 133.9, 133.0, 128.2, 43.1, 38.6, 33.2, 32.2 ppm. Selected NMR spectra are shown in the ESI.†



Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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References

- For example, *Macromolecular Engineering: From Precise Macromolecular Synthesis to Macroscopic Materials Properties and Applications*, ed. K. Matyjaszewski, Y. Gnanou and L. Leibler, Wiley-VCH, Weinheim, Germany, 2007.
- For example (ref. 2–10), N. Hadjichristidis, M. Pitsikalis, S. Pispas and H. Iatrou, *Chem. Rev.*, 2001, **101**, 3747–3792.
- A. Hirao, M. Hayashi, S. Loykulnant, K. Sugiyama, S. W. Ryu, N. Haraguchi, A. Matsuo and T. Higashihara, *Prog. Polym. Sci.*, 2005, **30**, 111–182.
- N. Hadjichristidis, H. Iatrou, M. Pitsikalis and J. Mays, *Prog. Polym. Sci.*, 2006, **31**, 1068–1132.
- M. Ouchi, T. Terashima and M. Sawamoto, *Acc. Chem. Res.*, 2008, **41**, 1120–1132.
- H. Gao and K. S. Matyjaszewski, *Prog. Polym. Sci.*, 2009, **34**, 317–350.
- K. Matyjaszewski and N. V. Tsarevsky, *Nat. Chem.*, 2009, **1**, 276–288.
- K. Khana, S. Varshney and A. Kakkar, *Polym. Chem.*, 2010, **1**, 1171–1185.
- K. Matyjaszewski and N. V. Tsarevsky, *J. Am. Chem. Soc.*, 2014, **136**, 6513–6533.
- J. M. Ren, T. G. McKenzie, Q. Fu, E. H. H. Wong, J. Xu, Z. An, S. Shanmugam, T. P. Davis, C. Boyer and G. G. Qiao, *Chem. Rev.*, 2016, **116**, 6743–6836.
- Examples for metathesis polymerisation (ref. 11–23), M. R. Buchmeiser, *Chem. Rev.*, 2000, **100**, 1565–1604.
- Handbook of Metathesis*, ed. R. H. Grubbs, Wiley-VCH, Weinheim, Germany, 2003, vol. 3.
- Metathesis Polymerisation*, ed. M. Buchmeiser, Springer-Verlag, Berlin Heidelberg, Germany, 2005.
- S. Hilf and A. F. M. Kilbinger, *Nat. Chem.*, 2009, **1**, 537–546.
- K. Nomura and M. M. Abdellatif, *Polymer*, 2010, **51**, 1861–1881.
- A. Leitgeb, J. Wappel and C. Slugovc, *Polymer*, 2010, **51**, 2927–2946.
- M. R. Buchmeiser, *Macromol. Symp.*, 2010, **298**, 17–24.
- H. Mutlu, L. M. de Espinosa and M. A. R. Meier, *Chem. Soc. Rev.*, 2011, **40**, 1404–1445.
- P. Atallah, K. B. Wagener and M. D. Schulz, *Macromolecules*, 2013, **46**, 4735–4741.
- M. D. Schulz and K. B. Wagener, *Macromol. Chem. Phys.*, 2014, **215**, 1936–1945.
- Handbook of Metathesis*, ed. R. H. Grubbs and E. Khosravi, Wiley-VCH, Weinheim, Germany, 2nd edn, 2015, vol. 3.
- D. J. Lunn, E. H. Discekici, J. R. de Alaniz, W. R. Gutekunst and C. J. Hawker, *J. Polym. Sci., Part A: Polym. Chem.*, 2017, **55**, 2903–2914.
- Y. Chen, M. M. Abdellatif and K. Nomura, *Tetrahedron*, 2018, **74**, 619–643.
- R. S. Saunders, R. E. Cohen, S. J. Wong and R. R. Schrock, Arm (brush) first approach by addition of cross-linked reagent(s) at the final stage, *Macromolecules*, 1992, **25**, 2055–2057, ref. 24–30.
- J. Liu, A. O. Burts, Y. Li, A. V. Zhukhovitskiy, M. F. Ottaviani, N. J. Turro and J. A. Johnson, *J. Am. Chem. Soc.*, 2012, **134**, 16337–16344.
- L. Liao, J. Liu, E. C. Dreaden, S. W. Morton, K. E. Shopsowitz, P. T. Hammond and J. A. Johnson, *J. Am. Chem. Soc.*, 2014, **136**, 5896–5899.
- A. O. Burts, A. X. Gao and J. A. Johnson, *Macromol. Rapid Commun.*, 2014, **35**, 168–173.
- J. C. Barnes, P. M. Bruno, H. V.-T. Nguyen, L. Liao, J. Liu, M. T. Hemann and J. A. Johnson, *J. Am. Chem. Soc.*, 2016, **138**, 12494–12501.
- H. V.-T. Nguyen, Q. Chen, J. T. Paletta, P. Harvey, Y. Jiang, H. Zhang, M. D. Boska, M. F. Ottaviani, A. Jasanoff, A. Rajca and J. A. Johnson, *ACS Cent. Sci.*, 2017, **3**, 800–811.
- Y. Shibuya, H. V.-T. Nguyen and J. A. Johnson, *ACS Macro Lett.*, 2017, **6**, 963–968.
- Core first (in and out) approach (ref. 31–34): K. Nomura, Y. Watanabe, S. Fujita, M. Fujiki and H. Otani, *Macromolecules*, 2009, **42**, 899–901.
- H. Otani, S. Fujita, Y. Watanabe, M. Fujiki and K. Nomura, *Macromol. Symp.*, 2010, **293**, 53–57.
- K. Takamizu and K. Nomura, *J. Am. Chem. Soc.*, 2012, **134**, 7892–7895.
- K. Nomura, K. Tanaka and S. Fujita, *Organometallics*, 2012, **31**, 5074–5080.
- J. A. Kalow and T. M. Swager, *ACS Macro Lett.*, 2015, **4**, 1229–1233.
- (reviews, ref. 36–39), S. Lubbad and M. R. Buchmeiser, *Macromol. Rapid Commun.*, 2003, **24**, 580–584.
- M. Mayr, D. Wang, R. Kröll, N. Schuler, S. Prühs, A. Fürstner and M. R. Buchmeiser, *Adv. Synth. Catal.*, 2005, **347**, 484–492.
- M. R. Buchmeiser, in *Handbook of Metathesis*, ed. R. H. Grubbs, Wiley-VCH, Weinheim, Germany, 2003, vol. 3, p. 226.
- M. R. Buchmeiser, *Chem. Rev.*, 2009, **109**, 303–321.
- For example (ref. 40–42), R. R. Schrock, in *Handbook of Metathesis*, ed. R. H. Grubbs, Wiley-VCH, Weinheim, 2003, vol. 1, p. 8.
- R. R. Schrock, in *Metathesis Polymerisation of Olefins and Polymerisation of Alkynes*, ed. Y. Imamoglu, NATO ASI Series, Kluwer Academic Publishers, 1998, pp. 1–27 and 357–380.
- R. R. Schrock, *Chem. Rev.*, 2009, **109**, 3211–3226.



- 43 The results were partly introduced in the Asian Polyolefin Workshop 2017 (APO2017), Tianjin, China, October, 2017 and the 8th International Conference on Polymer Chemistry (PC2018), Changchun, China, June, 2018.
- 44 For example, J. J. Murphy, H. Furusho, R. M. Paton and K. Nomura, *Chem.-Eur. J.*, 2007, **13**, 8985–8997.
- 45 J. K. Stille and D. A. Frey, *J. Am. Chem. Soc.*, 1959, **81**, 4273–4275.
- 46 Selected NMR spectra in the resultant polymers are shown in the ESI.†
- 47 It should be noted that the polymerisation with 2 step additions [CL + NBE (15 + 5.0 equiv.) and CL (5.0 equiv.)] in the second step afforded the ROMP polymers with broad molecular weight distributions. Some of the resultant polymers became hardly soluble in toluene, tetrahydrofuran (probably due to highly cross-linking).
- 48 R. R. Schrock, J. S. Murdzek, G. C. Bazan, J. Robbins, M. Dimare and M. B. O'Regan, *J. Am. Chem. Soc.*, 1990, **112**, 3875–3886.

