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Ring opening metathesis polymerisation in donor solvents

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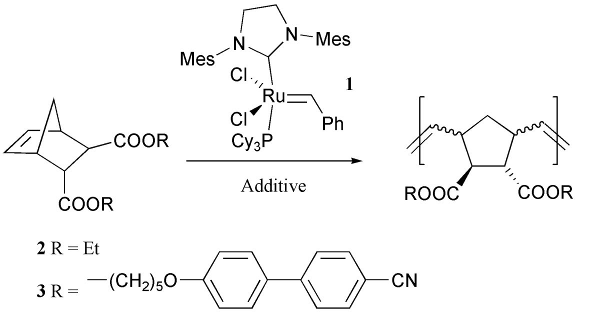
A screening concerning the functional group tolerance of the 'Super Grubbs' initiator (1) reveals that nitriles, amines or thiocyanates do not prevent ring opening metathesis polymerisation but strongly influence polymer properties.

Over the past decades, olefin metathesis has emerged as a mild and efficient method for the formation of carbon–carbon double bonds. In particular, $(PCy_3)_2(Cl)_2Ru{=}CHPh$ has found extensive use in organic and polymer chemistry due to its high reactivity towards olefins in the presence of a wide array of functional groups. Nevertheless, ruthenium catalysts are, as stated in literature,[1] limited by incompatibility with basic functional groups, most notably nitriles and amines. In past years a few isolated and very specialized reports of ring opening metathesis polymerisation (ROMP), cross metathesis (CM) and ring closing metathesis (RCM) with nitriles, amines, sulfides and phosphines have been published. In most of these reports the 'Super-Grubbs' catalyst, $(H_2IMes)(PCy_3)(Cl)_2Ru{=}CHPh$ (**1**) (H_2IMes = *N*,*N*-bis(mesityl)-4,5-dihydroimidazol-2-ylidene), was used.[2]

In the course of our studies towards side chain liquid crystal polymers (SCLCPs), we became interested in **1** as a substitute for various Schrock-type ROMP-initiators that have been used so far. To examine the functional group tolerance of **1** in a fast and efficient manner we designed a test polymerisation reaction of the model monomer (±)-*exo*,*endo*-bis(ethyl)bicyclo-[2.2.1]hept-5-ene-2,3-dicarboxylate (**2**) in the presence of an additive containing the functional group of interest (Scheme 1). Such additives included MeCN, $HNEt_2$ or pyridine (*cf*. Table 1). There are two major advantages of this strategy: the molar ratio of functional groups with respect to the initiator can be conveniently adjusted and the obtained polymers can be compared with regard to differences in molecular weights and molecular weight distributions. Therefore the influence of the functional groups on the polymer properties can be assessed.

Following a typical polymerisation procedure,[3] a broad variety of additives was tested. The obtained polymers were characterized by ^1H- and $^{13}C\{^1H\}$-NMR, IR and GPC. The results are summarized in Table 1. Acetonitrile did not prevent the ROMP of **2** up to at least a seven fold excess of the nitrile with respect to the monomer. The molecular weights and the polydispersity indices (PDI) of poly**2** decreased with increasing MeCN concentration. An aromatic nitrile such as benzonitrile behaved similarly. Secondary amines, as exemplified by diethylamine, exhibited a more pronounced effect, slowing down the reaction substantially. 150 equivalents of $HNEt_2$ were the upper limit for polymerising **2** under standard conditions and high conversion. Prolonging the reaction time to 72 h, 300 equivalents of $HNEt_2$ were tolerated and a poly**2** with a PDI as low as 1.2 and a molecular weight as low as 70 530 could be isolated in 80% yield. Triethylamine was tolerated and hardly affected the M_W. Interestingly, the PDIs were somewhat higher compared to the reference reaction (Entry 1). By contrast, for pyridine, the reaction rate of the polymerisation was the lowest observed in this series. Addition of 300 equiv. of pyridine yielded only 50% polymer after 72 h reaction time (conversion was 90%, the low yield is due to separation of unreacted **2**), but poly**2** from this reaction was nearly monodisperse and the M_W close to the calculated value (71484 g mol^{-1}). These results are remarkable, because the PDIs of polymers obtained from initiator **1** are generally high. The conversion and the yield of poly**2** could be improved by a combination of heating the polymerisation mixture to 80 °C and the usage of only 100 equivalents of pyridine (solvent: chlorobenzene; Entry 15). A reference polymerisation of **2** at 80 °C without additive is complete after 10 min yielding poly**2** in 91% with a M_W of 402 640 and a PDI of 2.1. In the case of sterically shielded 2,6-dimethylpyridine (lutidine) the reaction rate became higher, and the effects on M_W and the PDI were less pronounced compared to pyridine as the additive. Entry 19 demonstrates that the thiocyanate group was also tolerated. The molecular weight



Scheme 1

Table 1 ROMP of **2** initiated by 0.33 mol% **1**[a]

Entry	Additive	Equiv.	Yield (%)	M_W	PDI
1	—	—	87	678 000	1.9
2	MeCN	300	89	378 860	1.8
3	MeCN	900	89	271 780	1.8
4	MeCN	2100	82	150 560	1.5
5	PhCN	300	88	383 570	2.1
6	PhCN	900	88	215 160	1.7
7	PhCN	1200	83	161 690	1.7
8	$HNEt_2$	150	80	138 800	1.6
9	$HNEt_2$[b]	300	80	70 530	1.2
10	NEt_3	300	95	618 860	2.3
11	NEt_3	600	93	537 080	2.0
12	NEt_3	900	89	472 600	2.1
13	Pyridine [b]	300	50	60 040	1.1
14	Pyridine [b]	600	0	—	—
15	Pyridine[c]	100	75	68 530	1.1
16	Lutidine	300	89	235 620	1.5
17	Lutidine	600	89	195 630	1.5
18	Lutidine	900	72	139 110	1.3
19	$PhCH_2SCN$	300	86	309 380	2.1
20	2-Propanol[d]	300	91	758 510	2.0
21	2-Propanol[d]	900	94	811 120	1.6
22	2-Propanol[d]	1500	86	842 450	1.9

[a] General conditions: **1** (0.004 mmol) and **2** (1.26 mmol) in 1 mL solvent (additive in CH_2Cl_2) reaction time: 20 h; temperature 20 °C; Yields are given for the isolated products; GPC against polystyrene. [b] Reaction time: 72 h, conversion not complete. [c] Reaction time: 22 h; temperature: 80 °C; solvent: chlorobenzene. [d] Reaction time: 3 h.

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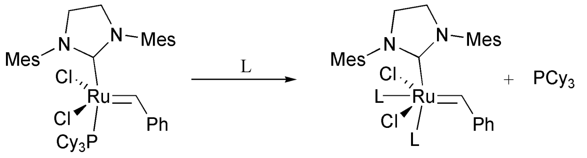
was half of the reference, but the PDI was somewhat higher. Finally, 2-propanol was tested, surprisingly molecular weights and PDIs were higher than in the reference polymerisation shown in Entry 1.

The influence of the additives on the polydispersity indices and the molecular weights of the polymers can be explained by enhancement of the initiation efficiency and an attenuation of the polymerisation rate,[4] due to competition of the additive with the monomer and the PCy_3 ligand for the Ru center during initiation and propagation.[5] Thus, the initiation rate is enhanced, the propagation rate is reduced and secondary metathesis reactions ("back-biting") are suppressed, this being responsible for lower M_Ws and PDIs. We suppose, that in the presence of the additive, **1** is transformed according to Scheme 2. In the case of L = py, $(H_2IMes)(py)_2(Cl)_2Ru{=}CHPh$ (**4**) is isolable and was prepared according to literature[6] by treating **1** with an excess of pyridine. For comparison, **4** was used as the initiator for the polymerisation of **2** under the standard reaction conditions[3] without additive. Characterization of the obtained poly**2** (yield: 82%) revealed a M_W of 71 400 and a PDI of 1.1. These values are closely related to the values for poly**2** prepared by addition of 100 equivalents of pyridine to initiator **1** (*cf.* Entry 15).



1

4: L = py

Scheme 2

With this information at our disposal, we investigated **1** as an initiator for the polymerisation of (+/−)-*exo,endo*-bis{5-[(4′-cyanobiphenyl-4-yl)oxy]pentyl}bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate (**3**). Results are summarized in Table 2. This monomer bears two nitrile groups per norbornene-unit and therefore should be easily polymerised according to Table 1, Entry 5. Indeed, smooth polymerisation took place upon addition of **1** giving poly**3** with a PDI of 2.4 and a M_W of 101 650 g mol^{-1} in 78% yield after workup.[7] Addition of acetonitrile (300 equiv.) resulted in bisection of M_W (50 500 g mol^{-1}) and a distinctly lower PDI of 1.6. By the addition of 50 equivalents of pyridine and a prolonged reaction time of 45 h the weight average molecular weight of isolated poly**3** was reduced to 31 600 g mol^{-1} and a narrow molecular weight distribution of 1.2 was obtained.[8] Upon heating (80 °C, chlorobenzene) the polymerisation is complete after 20 h, yielding poly**3** with a similar M_W and PDI. Thus, upon addition of pyridine, relatively monodisperse polymers with M_Ws close to the calculated value can be isolated, which is in good agreement with theoretical values assuming 'living' conditions.

Table 2 ROMP of **3** initiated by 1 mol% **1**[a]

Entry	Additive	Equiv.	Yield (%)	M_W	PDI
1	—	—	77	101 650	2.4
2	MeCN	300	81	50 500	1.6
3	MeCN	600	79	41 330	1.7
4	Pyridine[b]	50	90	31 600	1.2
5	Pyridine[c]	50	72	33 550	1.4

[a] General conditions: **1** (0.0014 mmol) and **2** (0.14 mmol) in 1 mL solvent (additive in CH_2Cl_2) reaction time: 20 h; temperature 20 °C; Yields are given for the isolated products; GPC against polystyrene. [b] Reaction time: 45 h. [c] Reaction time: 20 h; temperature: 80 °C; solvent: chlorobenzene.

Finally, **3** was polymerised with initiator **4**[7]. Poly**3** was isolated in 94% yield featuring a M_W of 42 510 and a PDI of 1.2. As seen by endgroup analysis and following the polymerisation by ^{1}H-NMR (conditions: solvent $CDCl_3$ with **4**:**3** = 1:10; characterization of poly**3**: M_W = 6 630; PDI = 1.1) **4** also provided complete initiation.[9]

In summary, we have demonstrated that $(H_2IMes)(PCy_3)(Cl)_2Ru{=}CHPh$ (**1**) tolerates functional groups such as nitriles or amines, which are known to poison the initiator $(PCy_3)_2(Cl)_2Ru{=}CHPh$,[1] using a fast and very simple screening method. Moreover, this methodology permits the investigation of the influence of donor solvents on the polymerisation reaction and the polymer properties. Especially molecular weights and molecular weight distributions are affected by the functional groups present in the reaction mixture. Thus, molecular weights and polydispersity can be effectively adjusted by addition of donor solvents to the reaction mixture. During this study, we also discovered that **4** is the first initiator of the 'Super-Grubbs'-family, which provides complete initiation with the monomers under investigation.

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4 M. S. Sanford, J. A. Love and R. H. Grubbs, *J. Am. Chem. Soc*, 2001, **123**, 6543.

5 C. W. Bielawski and R. H. Grubbs, *Macromolecules*, 2001, **34**, 8838.

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7 Preparation of poly**3** was made analogously to poly**2** using 100 equiv. of **3** with respect to the initiator.

8 M_{calc} is 70 888 — Molecular weights determined by GPC using universal calibration are approximately the double of the values determined using polystrene as the reference. M. Ungerank, B. Winkler, E. Eder and F. Stelzer, *Macromol. Chem. Phys.*, 1995, **196**, 3623.

9 Similar results with **4** as the initiator in ROMP of norbornene monomers were presented by Robert H. Grubbs at the of the ACS Boston National Meeting, August 18–22, 2002.