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Influence of functional groups on ring opening metathesis polymerisation and polymer properties

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Abstract

The polymerisation of exo,endo-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid esters initiated by $(H_2IMes)(PCy_3)(Cl)_2Ru$=CHPh was used as a model reaction to investigate the influence of various donor solvents on the polymerisation reaction and the polymer properties, by using a fast and simple screening method. The results revealed, that especially molecular weights and molecular weight distributions are strongly affected by the functional groups present in the reaction mixture. Thus, polymer properties can be effectively adjusted by addition of donor solvents to the reaction mixture. The method can also be used to estimate the influence of various functional groups on the course of the polymerisation reaction of functionalised monomers.

Keywords: ROMP; Ruthenium carbene complexes; Polynorbornenes; Solvent influence; Functional monomers

1. Introduction

Over the past decades, olefin metathesis has emerged as a mild and efficient method for the formation of carbon–carbon double bonds. In particular, the 'Grubbs Catalyst' $(PCy_3)_2(Cl)_2Ru$=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 [1–4]. Nevertheless, this ruthenium initiator is, as stated in literature [1], limited by incompatibility with basic functional groups, most notably nitriles and amines, although there are some reports using $(PCy_3)_2(Cl)_2Ru$=CHPh in the polymerisation of nitrile and amine containing monomers [5–10].

With the introduction of the 'Super-Grubbs' catalyst, $(H_2IMes)(PCy_3)(Cl)_2Ru$=CHPh (**1**) (H_2IMes=*N*,*N*-bis (mesityl) 4,5-dihydroimidazol-2-ylidene) not only the activity could be increased but also the functional group tolerance. Thus, reports on ring opening metathesis polymerisation (ROMP) [11–15], cross metathesis (CM) [16–18] and ring closing metathesis (RCM) [19–24] with nitriles, amines, sulfides and phosphines were published in the last years.

Although the position of the functional group in the molecules under investigation is also crucial [23,25], general knowledge of the influence of functionalities on the outcome of a ROMP reaction is lacking. Moreover, the use of donor solvents is sometimes necessary to guarantee homogenous reaction conditions during the polymerisation procedure, thus knowledge of the influence on polymer properties is desired. To shed some light on this issue we designed a test polymerisation reaction using 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 to examine the influence of the functional group on ROMP initiated with **1** (see Scheme 1**)** . There are two major advantages of this in a fast and efficient 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, which is a valuable information for rational polymer synthesis. Preliminary results of this work have been communicated previously [15].

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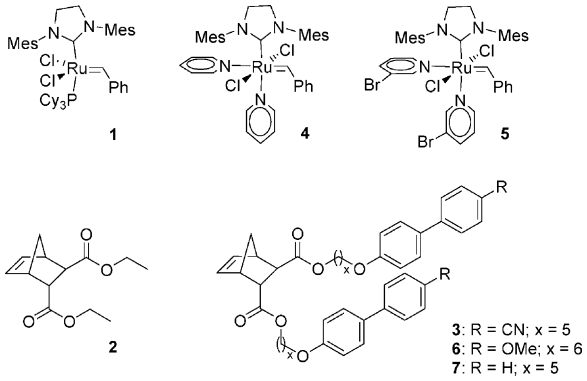


Scheme 1. Initiators and monomers under investigation.

2. Experimental

2.1. General

The weight average of molecular mass (M_W) and the polydispersity indices (PDI) were determined by gel permeation chromatography (a) with THF as the solvent using the following arrangement: Merck Hitachi L6000 pump, separation columns of Polymer Standards Service, 8 mm × 300 mm STV 5 μm grade size (10^6, 10^4 and 10^3 Å); refractive index detector from Wyatt Technology, model Optilab DSP Interferometric Refractometer or (b) with $CHCl_3$ as the solvent using a Merck Hitachi L6000A pump, 2 separation columns of PL, Plgel 5 μm Mixed-C, differential refractometer from Waters 410 and a photodiode array detector Waters 996. In both cases polystyrene standards purchased from Polymer Standard Service were used for calibration. ^{1}H NMR spectra were recorded on a Varian INOVA 500 MHz spectrometer operating at 499.803 MHz and were referenced to $SiMe_4$, the relaxation delay was set to 10 s. $^{13}C\{^1H\}$ NMR spectra were recorded on a Varian INOVA 500 MHz spectrometer operating at 125.687 MHz and were referenced to $SiMe_4$. Infrared (IR) spectra were recorded on a Perkin-Elmer spectrophotometer with a DTGS detector, ν_{max} (cm^{-1}). Bands are characterised as strong (s), medium (m) and weak (w).

2.2. Reagents

$(H_2IMes)(PCy_3)(Cl)_2Ru$=CHPh (**1**) and 1,5-dibromopentane were purchased from Aldrich and used as received. CH_2Cl_2, chlorobenzene, 2-butanone and DMF were purified and dried as described in literature [26]. $(H_2IMes)(pyridine)_2(Cl)_2Ru$=CHPh (**4**) [27], $(H_2IMes)(3\text{-bromopyridine})_2(Cl)_2Ru$=CHPh (**5**) [28] and the monomers **2** [29], **3** [30] and **6** [31] were prepared according to the literature.

2.3. Polymerisation procedure

To a solution of 300 eq. of **2** in a mixture of CH_2Cl_2 and the respective additive, 1 eq. of **1** dissolved in CH_2Cl_2 was added in an inert atmosphere of N_2. The reaction mixture was kept for 20 h at room temperature. The reaction progress was monitored by thin layer chromatography (TLC). Polymerisation was stopped by adding 50 eq. of ethylvinylether. After 30 min the reaction mixture was slowly added to vigorously stirred methanol. After reprecipitation from CH_2Cl_2/MeOH and drying in vacuum poly**2** was isolated with the yields given in Table 1.

^{1}H NMR (δ, 20 °C, $CDCl_3$): 5.52 (s, 1H, HC=CH_{trans}), 5.42–5.30 (m, 1H, HC=CH), 5.20 (s, 1H, HC=CH_{cis}), 4.08 (q, 4H, OCH_2CH$_3$), 3.28–2.75 (m, 4H, cyclopentane[1,2,3,4]), 1.96 (m, 2H, cyclopentane[5]), 1.23 (bs, 6H, OCH$_2$CH_3).

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

Entry	Additive	Eq.	Yield (%)	M_W	PDI
1	–	–	87	678,000	1.9
2	MeCN	300	89	378,900	1.8
3	MeCN	900	89	271,800	1.8
4	MeCN	2100	82	150,600	1.5
5	PhCN	300	88	383,600	2.1
6	PhCN	900	88	215,200	1.7
7	PhCN	1200	83	161,700	1.7
8	$HNEt_2$	150	80	138,800	1.6
9	$HNEt_2$[b]	300	80	70,500	1.2
10	NEt_3	300	95	618,900	2.3
11	NEt_3	600	93	537,100	2.0
12	NEt_3	900	89	472,600	2.1
13	Pyridine[b]	300	50	60,000	1.1
14	Pyridine[b]	600	0	–	–
15	Pyridine[c]	100	75	68,500	1.1
16	Lutidine	300	89	235,600	1.5
17	Lutidine	600	89	195,600	1.5
18	Lutidine	900	72	139,100	1.3
19	2,2′-Bipyridinyl	100	91	462,700	2.2
20	2,2′-Bipyridinyl	300	92	249,600	2.3
21	2,2′-Bipyridinyl	600	74	178,100	2.3
22	$PhCH_2SCN$	300	86	309,400	2.1
23	Dimethyl sulfoxyde	300	85	219,100	2.0
24	Dimethyl sulfoxyde	900	69	131,500	1.9
25	2-Propanethiol	300	60	153,370	2.4
26	2-Propanethiol	900	0	–	–
27	2-Propanol[d]	300	91	758,500	2.0
28	2-Propanol[d]	900	94	811,100	1.6
29	2-Propanol[d]	1500	86	842,500	1.9
30	Phenol[d]	300	88	441,700	2.1
31	Phenol[d]	900	80	266,400	2.0
32	Acetone[d]	300	90	793,500	2.0
33	Acetone[d]	900	91	562,200	2.0
34	Acetone[d]	1500	87	571,700	1.9
35	Acetylacetone[d]	100	87	683,000	1.9
36	Acetylacetone[d]	300	98	635,000	2.0
37	Acetylacetone[d]	600	98	523,900	2.6
38	Benzoic acid[e]	300	85	137,000	1.7
39	Benzoic acid[e]	900	87	110,600	1.5

[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.
[e] Two ml CH_2Cl_2 was used to dissolve the benzoic acid.

$^{13}C\{^1H\}$ NMR (δ, 20 °C, $CDCl_3$): 174-173 (2C, C=O), 134–130 (2C, H*C*=*C*H), 60.8 −60.6 (2C, O*C*H$_2$CH$_3$), 53.6, 52.8, 52.6, 52.4–51.6, 46.5, 44.8, 42.0, 41.6, 40.2, 39.5 (5C, cyclopentane), 14.5 (2C, OCH$_2$*C*H$_3$).

FTIR (NaCl, cm^{-1}): 2981 (s, ν_{CH}), 1731 (s, ν_{CO}), 1465 (m), 1447 (m), 1380 (m), 1329 (m), 1257 (m), 1179 (m), 1097 (m), 1031 (s), 972 (m, CH_{trans}), 860 (w), 735 (w, CH_{cis}).

Preparation of poly**3**, poly**6** and poly**7** was carried out analogously to poly**2** using 100 eq. of **3**, **6** or **7** with respect to the initiator.

2.4. Preparation of 4-(5-bromo-pentyloxy)-biphenyl

Preparation analogously to [32]: 3.0 g 4-hydroxybiphenyl (17.6 mmol), 6.0 g dibrompentane (26.4 mmol) and 3.65 g K_2CO_3 (26.4 mmol) were dissolved in 2-butanone (150 ml) and heated under reflux for 20 h. Solid components were removed by filtration and the filtrate was evaporated under reduced pressure. The crude product was purified by column chromatography (SiO_2, Cy:EE = 30:1; R_f (Cy:EE = 5:1) = 0.76) and subsequent recrystallisation from cyclohexane. Yield: 2.1 g (37%).

^1H NMR (δ, 20 °C, $CDCl_3$): 7.55 (m, 4 H, Ph$^{2,6,2',6'}$), 7.47 (m, 2 H, Ph$^{3',5'}$), 7.36 (m, 1 H; Ph$^{4'}$), 7.11 (m, 2 H, Ph^{3,5}), 4.02 (t, 2H, –C*H*$_2$O), 3.46 (t, 2H, BrC*H*$_2$), 1.99–1.82 (m, 4H, BrCH$_2$C*H*$_2$CH$_2$C*H*$_2$CH$_2$O), 1.66 (m, 2 H, BrCH$_2$CH$_2$C*H*$_2$CH$_2$CH$_2$O).

$^{13}C\{^1H\}$ NMR (δ, 20 °C, $CDCl_3$): 158.6 (1C, Ph^4), 140.9 (1C, Ph$^{1'}$), 133.8, 128.8, 128.2, 126.8, 126.7 (7C, Ph$^{2,6,2',3',5',6',4'}$), 114.8 (2C, Ph^{3,5}), 67.7 (*C*H$_2$O), 33.7, 32.6, 28.6 (Br*C*H$_2$*C*H$_2$CH$_2$*C*H$_2$CH$_2$O), 25.0 (1 C, BrCH$_2$CH$_2$*C*H$_2$CH$_2$CH$_2$O).

FTIR (NaCl, cm^{-1}): 3031 (w), 2941 (m), 2867 (m), 1609 (m), 1583 (w), 1568 (w), 1519 (m), 1487 (m), 1473 (m), 1450 (m), 1391 (w), 1290 (m), 1269 (m), 1246 (s), 1186 (m), 1175 (m), 1113 (w), 1044 (m), 1014 (w), 1004 (w), 910 (w), 833 (m), 763 (s), 718 (w), 697 (m), 639 (w).

2.5. Preparation of (±)-exo,endo-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid bis-[5-(biphenyl-4-yloxy)-pentyl] ester (7)

1.5 g 4-(5-Bromo-pentyloxy)-biphenyl (4.70 mmol), 0.43 g (±)-*exo,endo*-bicyclo[2.2.1]hept-5-en-dicarboxylic acid (2.35 mmol) and 1.30 g K_2CO_3 (9.40 mmol) were dissolved in DMF (50 ml) and heated under reflux for 20 h. Solid components were removed by filtration and the filtrate was evaporated under reduced pressure. The crude product was purified by column chromatography (SiO_2, Cy:EE = 20:1; R_f (Cy:EE = 5:1) = 0.36). Yield: 1.30 g (84%).

^1H NMR (δ, 20 °C, $CDCl_3$): 7.53 (m, 8H, Ph$^{2',6',2,6}$), 7.41 (m, 4H, Ph$^{3',5'}$), 7.30 (m, 2H, Ph$^{4'}$), 6.96 (m, 4H, Ph^{3,5}), 6.29, 6.09 (dd, 1H, Nb^{5,6}), 4.16, 4.09 (m, 4H, OC*H*$_2$), 4.00 (t, 4H, C*H*$_2$OPh), 3.41 (t, 1H, Nb^2), 3.28 (s, 1H, Nb^1), 3.13 (s, 1H, Nb^4), 2.71 (dd, 1H, Nb^3), 1.86-1.82 (m, 4H, C*H*$_2$CH$_2$OPh), 1.77–1.69 (m, 4H, OCH$_2$C*H*$_2$), 1.63 (d, 1H, Nb^7), 1.59–1.55 (m, 4H, OCH$_2$CH$_2$C*H*$_2$), 1.47 (dd, 1H, Nb^7).

$^{13}C\{^1H\}$ NMR (δ, 20 °C, $CDCl_3$): 174.7, 173.5 (2C, C=O), 158.7 (2C, Ph^4), 141.0 (2C, C$^{1'}$), 137.8 (1C, –CH=CH–), 135.3 (1C, –CH=CH–), 133.8 (1C, Ph^1), 128.8, 128.3, 126.8 (7C, Ph$^{2,6,2',6',3',4',5'}$), 114.9 (4C, Ph^{3,5}), 67.8 (2C, *C*H$_2$OPh), 64.9, 64.6 (2C, O*C*H$_2$CH$_2$), 48.1 (1C, Nb^2), 47.9 (1C; Nb^4), 47.5 (1C, Nb^3), 47.4 (1C, Nb^7), 45.9 (1C, Nb^1), 29.0 (2C, *C*H$_2$CH$_2$OPh), 28.6 (2C, OCH$_2$*C*H$_2$), 22.8 (2C, OCH$_2$CH$_2$*C*H$_2$).

FTIR (NaCl, cm^{-1}): 3061 (w), 3031 (w), 2946 (m), 2869 (m), 1727 (s), 1609 (m), 1583 (w), 1569 (w), 1519 (m), 1488 (m), 1474 (m), 1451 (w), 1393 (w), 1332 (w), 1309 (m), 1289 (m), 1268 (s), 1246 (s), 1176 (s), 1113 (m), 1074 (m), 1042 (m), 1029 (m), 1014 (m), 1003 (m), 910 (w), 862 (w), 833 (m), 763 (s), 718 (m), 698 (m).

Characterisation of poly**7** (prepared by the general procedure presented above): ^1H NMR (δ, 20 °C, $CDCl_3$): 7.6–7.2 (m, 12 H, Ph$^{2,6,2',3',4',5',6'}$), 6.9–6.8 (m, 4 H, Ph$^{3',5'}$), 5.6–5.1 (m, 2 H, C*H*=C*H*), 4.2–3.8 (m, 8 H, COC*H*$_2$, C*H*$_2$OPh), 3.4–2.6 (m, 4 H, cyclopentane^{1,2,3,4}), 2.2–1.4 (m, 14 H, cyclopentane^5, OCH$_2$(C*H*$_2$)$_3$CH$_2$OPh).

$^{13}C\{^1H\}$ NMR (δ, 20 °C, $CDCl_3$): 174 (2C, C=O), 158.7 (2C, Ph^4), 140.8 (2C,C$^{1'}$), not observed (–*C*H=*C*H–), 133.6 (1C, Ph^1), 128.8, 128.2, 126.7 (7C, Ph$^{2,6,2',6',3',4',5'}$), 114.8 (4C, Ph^{3,5}), 67.0 (2C, *C*H$_2$OPh), 64.7 (2C, O*C*H$_2$CH$_2$), 54–40 (4 C, cyclopentane^{1,2,3,4,5}), 29.1 (2C, *C*H$_2$CH$_2$OPh), 28.6 (2C, OCH$_2$*C*H$_2$), 22.6 (2C, OCH$_2$CH$_2$*C*H$_2$).

FTIR (NaCl, cm^{-1}): 3032 (w), 2946 (m), 2868 (m), 1889 (w), 1729 (s), 1608 (m), 1583 (w), 1569 (w), 1519 (m), 1488 (m), 1474 (m), 1450 (m), 1396 (m), 1369 (w), 1289 (m), 1269 (s), 1247 (s), 1175 (s), 1114 (w), 1075 (m), 1042 (m), 1029 (m), 1004 (w), 982 (w), 911 (w), 833 (m), 763 (s), 697 (m), 736 (m), 718 (w), 697 (m), 639 (w).

3. Results and discussion

Following a typical polymerisation procedure, a broad variety of additives was tested. The obtained polymers were characterised by ^1H- and $^{13}C\{^1H\}$ NMR, IR and GPC. The overall results are summarised in Table 1. In Fig. 1 the influence of the additives on the weight average of the molecular weights of the polymers made from **2** is shown.

3.1. Nitriles

Acetonitrile did not prevent the ROMP of **2** up to at least a seven-fold excess of the additive with respect to the monomer. The molecular weights and the polydispersity indices of poly**2** decreased with increasing MeCN concentration (Table 1, entries 2–4). An aromatic nitrile such as benzonitrile behaved similarly. Secondary amines, as exemplified by diethylamine, exhibited a more pronounced effect, slowing down the reaction substantially.

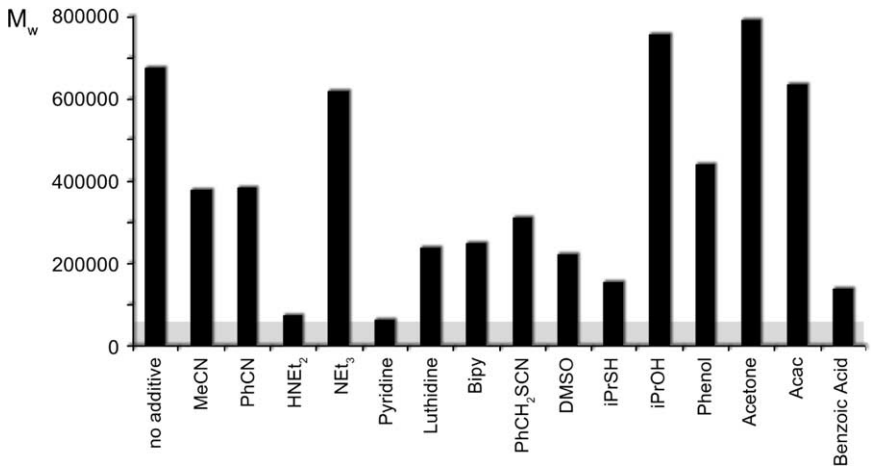


Fig. 1. Weight molecular weights of poly**2** prepared by addition of 300 eq. of the corresponding additive and initiation by **1**. The grey bar at the bottom marks the calculated molecular weight of poly**2** assuming complete initiation of **1**.

3.2. Amines

150 eq. of $HNEt_2$ were the upper limit for polymerising **2** under standard conditions up to high monomer conversion (Table 1, entry 8). Prolonging the reaction time to 72 h, 300 eq. 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 (Table 1, entry 9). Triethylamine was tolerated and hardly affected the M_W. Interestingly, the PDIs (Table 1, entries 10–12) were somewhat higher compared to the reference reaction (Table 1, entry 1).

3.3. Pyridines

For pyridine the polymerisation rate was the lowest observed in this series. Addition of 300 eq. of pyridine yielded only 50% polymer after 72 h reaction time (conversion was 90 %, the low yield is due to separation of unreacted **2**). Poly**2** from this reaction, on the other hand, was nearly monodisperse and the M_W close to the calculated value (71484 g/mol) (Table 1, entry 13). These results are remarkable, because the PDIs of polymers obtained from initiator **1** are generally high [33]. The conversion and yield of poly**2** could be improved by a combination of heating the polymerisation mixture to 80 °C and by lowering the amount of pyridine to 100 eq. (solvent: chlorobenzene; entry 15). A reference polymerisation of **2** at 80 °C without additive was complete after 10 min yielding 91% poly**2** with a M_W of 402,640 and a PDI of 2.1. Usage of 600 eq. pyridine gave no observable polymerisation at room temperature after 72 h (Table 1, entry 14). 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 (Table 1, entries 16–18). Surprisingly, the effect of 2,2′-bipyridyl on M_W was also less pronounced than that in case of pyridine. Weight average molecular weights were similar to those produced in presence of same amounts of luthidine and polydispersities were remarkably high. Moreover, reaction times of 20 h were sufficient for complete polymerisation of **2**. All these findings illustrate that 2,2′-bipyridyl is a poor ligand for the $(H_2IMes)(Cl)_2Ru{=}CHPh$ fragment compared to pyridine or diethylamine.

3.4. Thiocyanates

Entry 22 in Table 1 demonstrates that the thiocyanate group was also tolerated. The molecular weight of poly**2** was approximately half of that of the reference, but the PDI was somewhat higher.

3.5. Sulfur containing additives

Addition of DMSO gave polymers with fairly low molecular weights but virtually unchanged PDI compared to the reference polymerisation (Table 1, entries 23–24). 2-Propanethiol on the other hand drastically slowed down the polymerisation but was tolerated, yielding comparably short polymer chains with comparably high PDI (Table 1, entries 25–26).

3.6. Alcohols and phenols

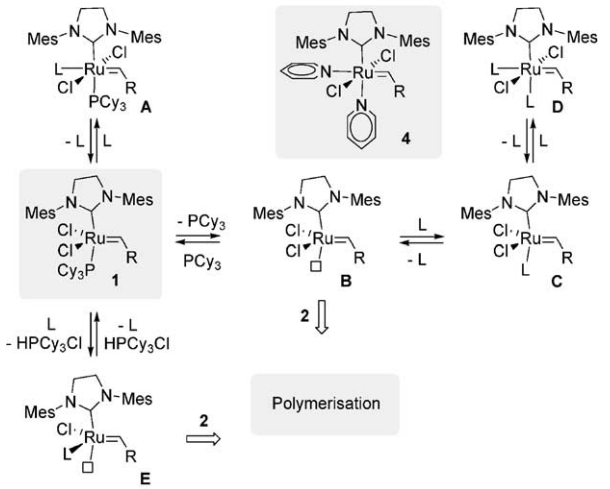
Also 2-propanol was tested, molecular weights and PDIs were higher than in the reference polymerisation. The molecular weights of poly**2** increased further with increasing 2-propanole amounts. On the other hand, the time needed for completing the reactions was substantially shorter (Table 1, entries 27–29). The more acidic phenol behaved differently. Molecular weights became smaller with higher phenol concentrations, while the PDI remained roughly unaffected (Table 1, entries 30–31).

3.7. Ketones and acids

For acetone and acetylacetone no significant differences on the polymer properties compared to the reference experiment were observed (Table 1, entries 32–36). Finally, benzoic acid was employed, yielding relatively low molecular weight polymers with fairly good PDI (Table 1, entries 37 and 38).

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 while slowing down the polymerisation rate [34] due to competition of the additive with the monomer and the PCy_3 ligand for the Ru centre during initiation and propagation [35]. Thus, the initiation rate is enhanced, the propagation rate is reduced and secondary metathesis reactions ("back-biting") are reduced, this being responsible for lower M_Ws and PDIs. We suppose, that in the presence of most of the additives, **1** is transformed according to Scheme 2. Dissociation of the PCy_3 ligand gives **B**, which is (in the presence of an additive) readily transformed into **C**. Moreover, **C** might be capable of co-ordinating another donor molecule yielding **D**. The same accounts for **1**, meaning that co-ordination of a donor molecule gives complexes of type **A**. All listed reactions are equilibriums leading to overall slower reaction rates. For additives like propanol, acetylacetone, phenol and benzoic acid a further reaction pathway leading to alkoholate or benzoate complexes with the general structure **E** (Scheme 2) might be possible. Related bis-alkoxy complexes had been synthesised by reacting **1** with potassium alkoxylates [36].

A representative of type **D** (cf. Scheme 2) $(H_2IMes)(py)_2(Cl)_2Ru{=}CHPh$ (**4**) is isolable and was prepared according to the literature [27] by treating **1** with excess of pyridine. For comparison reason, **4** was used as the initiator for the polymerisation of **2** under standard reaction conditions outline above. Characterisation of the obtained poly**2** (Yield: 82%) revealed a M_W of 71,400 and a PDI of 1.1. These values



Scheme 2. Proposed reactions of donor additives (L) with **1**.

Table 2
ROMP of biphenylmonomers **3**, **6** and **7**[a] initiated by 1 mol% of **1**, **4** or **5**

Entry	Initiator	Monomer	Additive	Eq.	Yield (%)	M_W	PDI
1	**1**	**3**	–	–	77	101,700	2.4
2	**1**	**3**	MeCN	300	81	50,500	1.6
3	**1**	**3**	MeCN	600	79	41,300	1.7
4	**1**	**3**	Pyridine[b]	50	90	31,600	1.2
5	**1**	**3**	Pyridine[c]	50	72	33,600	1.4
6	**4**	**3**	–	–	94	42,500	1.2
7	**5**	**3**	–	–	86	49,000	1.3
8	**5**	**6**	–	–	77	44,900[d]	1.12[d]
9	**5**	**7**	–	–	75	40,300	1.06
10	**5**	**7**	PhCN	200	88	39,000	1.09

[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 in THF against polystyrene.
[b] Reaction time: 45 h.
[c] Reaction time: 20 h; temperature: 80 °C; solvent: chlorobenzene.
[d] GPC in $CDCl_3$ against polystyrene.

are very similar compared to the values for poly**2** prepared by addition of 100 eq. pyridine to initiator **1** (c.f. Table 1, entry 15).

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**) a liquid crystal monomer used to obtain side chain liquid crystal polymers in our laboratories. Results are summarised in Table 2. The monomer bears two nitrile groups per norbornene unit and, therefore, should be polymerised without problems 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 101,700 g/mol in 78% yield after workup. Addition of acetonitrile (300 eq.) resulted in bisection of M_W (50,500 g/mol) and lowered the PDI to 1.6. By the addition of 50 eq. pyridine and a prolonged reaction time of 45 h the weight average molecular weight of isolated poly**3** was further reduced to 31,600 g/mol and a narrow molecular weight distribution of 1.2 was obtained. It has to be noted that the calculated molecular weight of poly**3** is 70,988. The underestimation of M_W by GPC results from an unfavourable comparison of the polymer with the polystyrene standards used for the calibration of the GPC. Molecular weights determined by GPC using universal calibration (yielding "absolute mass numbers") are approximately twice as high as the values determined by using polystrene as [37]. Upon heating (80 °C, chlorobenzene,) the polymerisation is complete after 20 h, yielding poly**3** with a similar M_W and PDI. Conclusively, the addition of pyridine leads to relatively monodisperse polymers with M_W close to the calculated value (Table 2, entry 4 and 5). In comparison, poly**3** was isolated in 94% yield featuring a M_W of 42,500 and a PDI of 1.2 using **4** as the initiator at room temperature. Solely the time necessary for completing the polymerisation was significantly lower. As determined by endgroup analysis and by following the

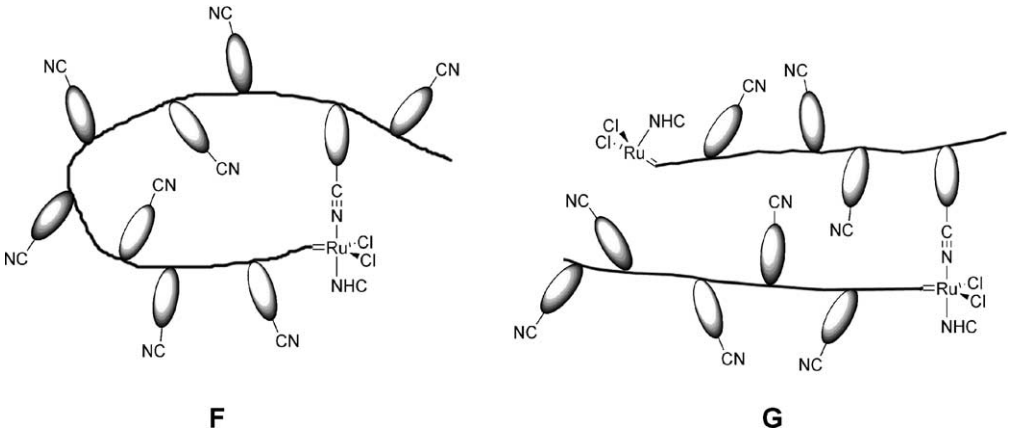


Fig. 2. "Back co-ordination" (F) or "coordinative cross-linking" (G) during the polymerisation of CN-side chain monomers.

polymerisation by ^{1}H NMR (conditions: solvent $CDCl_3$ with **4**: **3** = 1: 10) **4** also provided complete initiation. Nevertheless, there is still room for improvement with respect to polydispersity (Table 2, entry 6).

3.8. *Influence on the polydispersity*

In hope to reduce the PDI of poly**3** down to values below 1.1 we utilised **5**, which is the ruthenium benzylidene compound with the highest initiation rates known so far and, in addition, is capable of polymerising a broad variety of norbornene monomers with PDIs smaller than 1.1 [28]. But even with **5** the goal was missed (Table 2, entry 7). We therefore used two other biphenyl-based monomers (6 and 7 cf. Scheme 1) to elucidate the role of the cyano-group in **3**. The methoxy-group containing monomer **6** could be polymerised with initiator **5** into a well defined material characterised by a M_W of 44,900 and a PDI of 1.12 (Table 2, entry 8). Moreover, monomer **7** having no additional functional group, yielded a polymer with a polydispersity as low as 1.06 (Table 2, entry 9). To check if the cyanide group present in monomer **3** is responsible for the higher PDIs of poly**3**, 200 eq. of benzonitrile were added to a polymerisation of **7** by **5**. The PDI of the resulting polymer was determined to be 1.09, meaning that a cyano group present in the reaction mixture did not cause the high PDI values obtained for poly**3**. These findings led us to the assumption, that already formed poly**3** hampered a very well defined polymerisation of monomer **3** by deactivating the propagating species. The reason for this deactivation might have several reasons, two of them we want to discuss in more detail: generally steric effects or reduced solubility of such species might be responsible for the partial deactivation. In case of "back-co-ordination" of the CN-group (Fig. 2, example **F,** the vicinity of the bulky side-groups at the growing monomer and the donor ligand which is again a bulky side chain of the monomer reduces the accessibility of the active site, in case **G** not only the accessibility is reduced but also the solubility because of intermediate cross-linking as long as the second chain is coordinatively connected to the growing chain end. As this intramolecular "back co-ordination" (**F**) or the intermolecular "coordinative crosslinking" (**G**) can be suppressed by addition of another low molecular nitrile (e.g. acetonitrile or benzonitrile) this yields better PDI values but for the price of low reaction rates. In addition the sterical accessibility should be much better in case of co-ordinated small solvent molecule compared to a bulky voluminous monomer.

4. Conclusion

In summary we demonstrated that $(H_2IMes)(PCy_3)(Cl)_2$ Ru=CHPh (**1**) tolerates functional groups such as nitriles or amines, which are known to poison $(PCy_3)_2(Cl)_2$Ru=CHPh. Using a fast simple screening method, the influence of donor solvents on the polymerisation reaction and the polymer properties was investigated. Especially molecular weights and molecular weight distributions are strongly affected by the functional groups of the additives present in the reaction mixture. This opens the general possibility to adjust molecular weights and polydispersity by addition of donor solvents to the reaction mixture. In case of donor groups being bonded to the monomer "back co-ordination" or "co-ordinative crosslinking" reduces the polymerisation rate and increases the PDI values.

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