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Ring opening metathesis polymerisation initiated by $RuCl_2$(3-bromopyridine)$_2$(H_2IMes)(CHPh) Scope and limitation in block copolymer synthesis

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Abstract

The scope and limitations of $RuCl_2$(3-bromopyridine)$_2$(H_2IMes)(CHPh) (H_2IMes = *N*,*N*-dimesityl-4,5-dihydroimidazol-2-ylidene) as the initiator for living ring opening metathesis polymerization (ROMP) of functionalized norbornenes are evaluated. While norbornene derivatives exhibiting different propagation rate constants could be successfully employed in the preparation of block copolymers irrespective of their sequence of addition, the usage of cyano functionalised monomers is restricted. This phenomenon could be rationalized by a coordination of the cyano group to the ruthenium centre.
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Keywords: Block copolymers; initiators; metathesis; norbornenes; ROMP

1. Introduction

Block copolymers (BCPs) have attracted attention as they have been recognized as materials that not only combine properties of different polymers in one material but can also lead to materials with even totally new characteristics [1]. Because the polymer blocks are tethered to each other, macroscopic phase separation cannot take place and structural organization occurs in domains in a range from 1 to 100 nm ("microphase separation"). BCPs with low molecular weight polydispersity often exhibit self-assembled morphologies with high order. This self-organisation can be used for the build up of hierarchically structured materials. Among the living polymerization techniques that allow a controlled build up of such BCPs, ring opening metathesis polymerization (ROMP) [2,3] is one of the most promising synthesis methods towards well-defined functional block copolymers [4].

In 1985, ROMP was used to synthesize block copolymers for the first time [5]. Since then, ROMP has proven to be a versatile tool for the preparation of BCPs with low polydispersity indices (PDIs). In many cases, Schrock-type molybdenum initiators, as depicted in Fig. 1, were used, as they are very active and provide complete initiation [6]. The main drawback of these compounds is their incompatibility with protic functional groups and their high reactivity with moisture and oxygen [7]. Ruthenium complexes, most prominently represented by $RuCl_2(PCy_3)_2$(CHPh), the 1st generation Grubbs initiator and $RuCl_2(PCy_3)$(H_2IMes)(CHPh) (H_2IMes = *N*,*N*-dimesityl-4,5-dihydroimidazol-2-ylidene), the 2nd generation Grubbs catalyst (Fig. 2, right), exhibit a higher tolerance of functionalities but are hampered due to a low activity in case of $RuCl_2(PCy_3)_2$(CHPh) and low initiation efficiency in case of $RuCl_2(PCy_3)$(H_2IMes)(CHPh).

Initiators providing high activity, complete initiation, high functional group tolerance and low sensitivity towards moisture and oxygen are represented by Grubbs initiators of the formula shown in Fig. 2. Initiator $RuCl_2$(pyridine)$_2$(H_2IMes)(CHPh) was prepared by Grubbs et al. [8] and identified as a fast initiating initiator in our group [9]. More recently, Love et al. presented $RuCl_2$(3-bromopyridine)$_2$(H_2IMes)(CHPh) (**1**), which was stated to be the fastest initiator available up to now [10].

Since then, numerous contributions reported on the use of **1** in the synthesis of well-defined block copolymers [11–15]. In this contribution, our aim is to demonstrate the scope but also the

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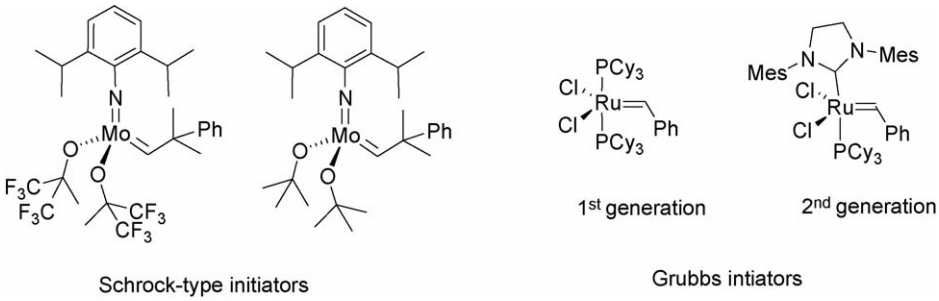

Fig. 1. Most utilized ROMP initiators.

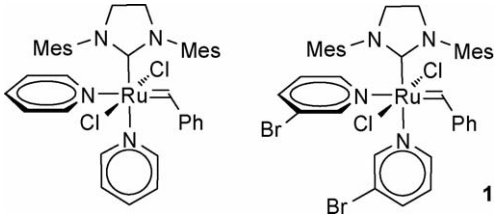

Fig. 2. Pyridine-based ROMP initiators.

limitations of this remarkable initiator. In a brief communication, we have already demonstrated that initiator **1** is well suited for the preparation of functional tri-block co-oligomers and copolymers with very low PDIs [11]. However, the polymerisation of a norbornene monomer bearing the liquid crystalline cyano-biphenyl group in the side chain leads only to blocks with comparatively high PDIs due to the interaction between the cyano-group and the ruthenium initiator [16]. Here we want to report on the preparation of well defined block copolymers focussing on two distinct topics: first we concentrate on the influence of different anchor groups on the preparation of defined block copolymers; second we investigate possibilities to reduce the polydispersity of cyanobiphenyl-bearing polymers.

2. Results and discussion

In order to study the influence of the anchor group on block copolymer synthesis we have chosen a series of different monomers exhibiting different rates of initiation and propagation (cf. Fig. 3) [17]. As the avenue to prepare defined (block co)polymers, i.e. (block co)polymers featuring low PDIs, is – amongst other factors – dependent on the relative rates of initiation and propagation (k_i and k_p) of every individual polymerisation event, we anticipated significant differences when preparing A/B and B/A block copolymers using the addressed monomers. Monomers **2** (k_p initiated with **1** $= 16 \times 10^{-3}$ L mol^{-1} s^{-1}), **3** ($k_p = 52 \times 10^{-3}$ L mol^{-1} s^{-1}) and **4** ($k_p = 4 \times 10^{-3}$ L mol^{-1} s^{-1}) were used to prepare the corresponding homopolymers and block copolymers [17]. The corresponding k_i*s* could not be determined using NMR spectroscopy, because of the fastness of the reaction – already in the first NMR spectrum acquired after addition of the monomer (i.e. after approximately 30 s) no signals for **1** could be observed. It can be estimated, that k_i exceeds k_p by the factor 1000 [17]. Under these circumstances, also the method used by Schrock and Feast et al. [18] based on work by Gold [19] is not applicable. The preparation is given in the experimental part and the outcome of the reactions is summarized in Table 1. As can be seen from entries 1, 2 and 5, almost monodisperse homopolymers could be obtained with all monomers suggesting again [17] that initiation is distinctly faster than propagation. Entries 3, 4, 6 and 7 illustrate the results for diblock copolymers. Similar to the homopolymers, polydispersities are remarkably low.

The outcome of the polymerisation is independent of the order of monomer addition (A/B or B/A), as evidenced by the similar PDIs for both types of block copolymers. Macroinitiators

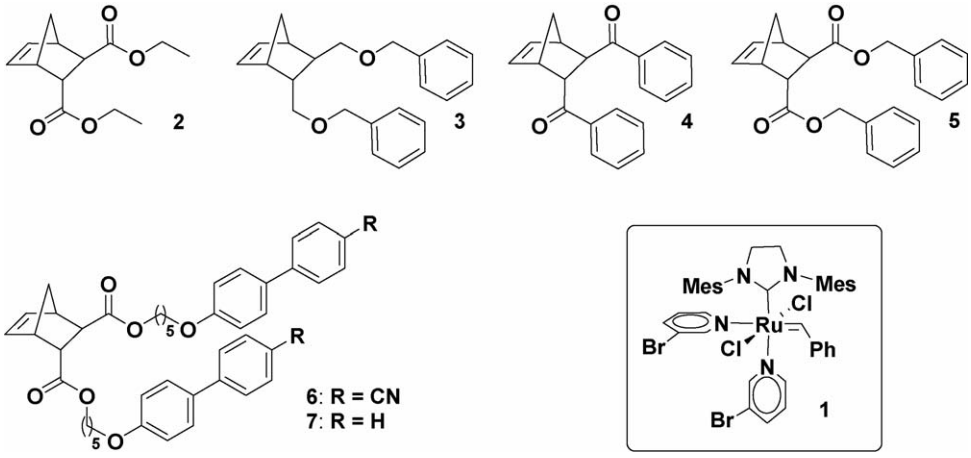

Fig. 3. Monomers and the initiator used in this study.

Table 1
Homo and block copolymers of **2**, **3** and **4** prepared by using **1** as the initiator (reaction conditions: CH_2Cl_2, 20 °C, reaction time: 1 h for each monomer)

Entry	Polymer	Monomer A/B	Molar ratio A/B/**1**	Yield (%)	M_n (g/mol)[a]	PDI[a]	A/B[b]
1	**Poly2**	**2** → –	200/–/1	65	29700	1.07	–
2	**Poly3**	**3** → –	200/–/1	68	30500	1.06	–
3	**Poly2/3**	**2** → **3**	200/200/1	80	59100	1.10	1/1.1
4	**Poly3/2**	**3** → **2**	200/200/1	81	51100	1.11	1.3/1
5	**Poly4**	**4** → –	200/–/1	92	34400	1.05	–
6	**Poly2/4**	**2** → **4**	200/200/1	96	58300	1.05	1/1.0
7	**Poly4/2**	**4** → **2**	200/200/1	99	60900	1.08	1.2/1

[a] Determined by GPC (solvent: THF; calibrated against polystyrene standards).
[b] Determined by NMR spectroscopy.

Table 2
Block copolymers of **2**, **5** and **6** prepared by using **1** as the initiator; reaction conditions: CH_2Cl_2 (4 mL × 1 mL); 20 °C

Entry	Polymer	Monomer A/B/C [reaction time in h]	Molar ratio A/B/C/**1**	Yield (%)	M_n (g/mol)[a]	PDI[a]
1	**Poly2/5/6**	**2** [1] → **5** [1] → **6** [6]	80/40/20/1	75	24890	1.1
2	**Poly5/6/2**	**5** [1] → **6** [1] → **2** [1]	40/20/80/1	73	24170	1.8[b]
3	**Poly6/2/5**	**6** [6] → **2** [1] → **5** [1]	20/80/40/1	84	54200, 7480	2.5[c]
4	**Poly6/2/5**	**6** [2] → **2** [1] → **5** [1]	20/80/40/1	83	38650, 8480	2.4[c]
5	**Poly5/2/6**	**5** [1] → **2** [1] → **6** [6]	40/80/20/1	85	17830	1.2
6	**Poly6/2/5**	**6** [20] → **2** [3] → **5** [3]	20/80/60/1	82	69290	2.5[c]

[a] Determined by GPC (solvent: THF; calibrated against polystyrene standards).
[b] Bimodal.
[c] Trimodal.

poly2-[**Ru**], **poly3**-[**Ru**] and **poly4**-[**Ru**] are structurally different featuring different anchor groups [17]. Nevertheless, in all cases similar initiation characteristics were observed in the polymerisation of the second monomer. This is an important requirement for a general applicability of **1** in block copolymer synthesis.

Based on the insights presented above, we tried to extend the usage of initiator **1** to the preparation of triblock copolymers comprising cyanobiphenyl mesogens in the side chain. During the preparation of the corresponding homopolymer of **6** (cf. Fig. 3) we encountered difficulties regarding the preparation of a polymer with a PDI below 1.1. This particular issue could be best explained by the ability of cyano groups to coordinate to the ruthenium centre and thus altering initiation and propagation behaviour of the initiator [16,20].

We now became interested whether it is possible to obtain block copolymers with a narrow molecular weight distribution with this particular monomer. For that reason we prepared triblock copolymers with the monomers **2**, **5** and **6** and changed the sequence of addition of the monomers. Experimental details are given in the experimental section and the caption of Table 2. The results are summarized in Table 2. As it can be seen from entries 1 to 6, satisfactory PDIs and monomodal block copolymers can only be prepared when **6** is employed as the third monomer. In case of employing **6** for preparation of the middle block (i.e. as the second monomer) a bimodal molecular weight distribution was determined. Finally, when **6** is used as the first monomer only trimodal gel permeation chromatograms were obtained (Table 2, entries 3, 4 and 6).

To provide evidence of the responsibility of the cyano group for the above-described difficulties, we employed **7** as a model monomer in the block copolymer synthesis. **7** is essentially identical with **6** except the cyano group in **6** is substituted for a proton in **7** (cf. Fig. 3). Indeed, block copolymers featuring a first or a second block made of **7** are both monomodal and are characterized by a low PDI (cf. Table 3).

As a consequence, monomers featuring functional units prone to interfere with the ruthenium centre entail difficulties in the synthesis of block copolymers. The only answer to this problem up to now is to employ such particular monomers to polymerize the last segment of the desired block copolymer. In due consequence, access to several polymer architectures, e.g. a triblock copolymer with the middle segment made from **6**, is restricted.

To possibly overcome this limitation we studied the influence of a donor additive namely acetonitrile and pyridine on the out-

Table 3
Block copolymers of **7** and **2** prepared by using **1** as the initiator (Reaction conditions: CH_2Cl_2 (3 × 1 mL); 20 °C; reaction time: 3 h for **7** and **2**)

Entry	Polymer	Monomer A/B	Molar ratio A/B/**1**	Yield (%)	M_n (g/mol)[a]	PDI[a]	A/B[b]
1	**Poly7**	**7** → –	100/–/1	69	38100	1.06	–
2	**Poly2/7**	**2** → **7**	80/20/1	72	29500	1.08	4/1
3	**Poly7/2**	**7** → **2**	20/80/1	74	25300	1.11	1/3.9

[a] Determined by GPC (solvent: THF; calibrated against polystyrene standards).

Table 4
Block copolymers of **6** and **5** prepared by using **1** as the initiator (reaction conditions: CH_2Cl_2 (3 mL × 1 mL); 20 °C; molar ratio: **6**:**5**:**1** = 20:40:1; reaction time: 6 h for **6** and 16 h for **5**)

Entry	Polymer	Additive	Amount additive/init. (mol/mol)	Yield (%)	M_n (g/mol)[a]	PDI[a]
1	**Poly6/5**	–	–	84	12160	1.8[b]
2	**Poly6/5**	CH_3CN	300/1	86	13700	1.8[b]
3	**Poly6/5**	Pyridine	50/1	71	9760	1.9[b]

[a] Determined by GPC (solvent: THF; calibrated against polystyrene standards).
[b] Bimodal.

Table 5
Block copolymers of **6** and **2** prepared by using **1** as the initiator (Reaction conditions: THF (3 mL × 1 mL); 20 °C; molar ratio: **6**:**2**:**1** = 100:200:1; reaction time: 2 h for **6** and 1 h for **2**)

Entry	Polymer	Temperature (°C)	Yield (%)	M_n (g/mol)[a]	PDI[a]
1	**Poly6/2**	0	78	57600	2.8[b]
2	**Poly6/2**	20	82	54300	3.0[b]
3	**Poly6/2**	40	78	51900	2.7[b]
4	**Poly6/2**	60	74	51200	3.6[b]

[a] Determined by GPC (solvent: THF; calibrated against polystyrene standards).
[b] Bimodal.

come of a block copolymer synthesis starting with **6** as the first monomer. As outlined, the ability of cyano groups to coordinate to the ruthenium centre might be the reason for problems encountered above. We hoped by adding additional coordinating additives to slow down the overall propagation rate and herewith to prevent fast polymerisation of macro-initators not affected by CN coordination. This principle was used with success for the improvement of polydispersity indices of, e.g. **poly6** (best PDI = 1.2) in an earlier work [16]. Now we wish to achieve a well-defined growing on of the second block segment employing this strategy.

As can be retrieved from Table 4, the anticipated effect could not be observed. Neither the addition of acetonitrile nor the addition of pyridine improved the outcome of the block copolymer synthesis using **6** and **5** as monomers. Bimodal molecular weight distributions were observed for **poly6/5** regardless of which additive was used. These experiments show, that the adverse effect of CN coordination is rather a sort of deactivation of the affected macroinitiators then a question of different initiation rates of CN-coordinated and uncoordinated macroinitiators with the second monomer. The observation of the rather unexpected trimodal polymer weight distributions for, e.g. **poly6/2/5** (cf. Table 2) can also be rationalized with this working hypothesis.

Another way to potentially influence the k_i/k_p ratio, but also to reactivate CN-coordinated macroinitiators, is to alter the reaction temperature. We therefore prepared block copolymers of monomers **6** and **2** at various temperatures. THF was used as the solvent. Results are summarized in Table 5. Again no influence of the temperature on the outcome of the block copolymer synthesis could be noted. All reaction conditions resulted in a bimodal molecular weight distribution. PDI were even pronounced higher then using CH_2Cl_2 as the solvent. A similar experiment, i.e. varying the temperature to improve the PDI was made by Grubbs et al. The polymerisation of norbornene with **1** gave the corresponding polymer with a PDI of 1.65 at 20 °C but with a PDI as low as 1.08 when the reaction temperature was held at −20 °C. This phenomenon was explained by reduced chain transfer reaction at the lower temperature [12].

3. Conclusion

In conclusion we have demonstrated that initiator **1** is capable of producing block copolymers from norbornenes with different anchor groups. Although these monomers exhibit different rate constants of propagation well defined polymers can be obtained irrespective of the sequence of addition. We further documented difficulties in block copolymer synthesis when utilizing norbornenes bearing functional groups prone to interact with the ruthenium centre during the reaction. The difficulties could be overcome when using such monomers to synthesise the last block, but possible strategies (adding a donor additive and changing the temperature) to resolve this restriction failed. Indications for a deactivation of CN coordinated macroinitiators were found and used to explain the failure of cyano-group containing monomer **6** in the synthesis of well-defined block copolymers.

4. Experimental

Initiator **1** [10] and the monomers (±)-*endo*,*exo*-bicyclo-[2.2.1]hept-5-ene-2,3-dicarboxylic acid diethyl ester (**2**) [21], (±)-*endo,exo*-5,6-bis-benzyloxymethyl-bicyclo[2.2.1]hept-2-ene (**3**) [22], (±)-*endo,exo*-(3-benzoylbicyclo[2.2.1]hept-5-en-2-yl)(phenyl)methanone (**4**) [23], (±)-*endo*,*exo*-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid dibenzyl ester (**5**) [24], (±)-*endo*,*exo*-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid bis-[5-(4′-cyano-biphenyl-4-yloxy)-pentyl] ester (**6**) [25], (+/−)-*endo*,*exo*-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid bis-[5-(biphenyl-4-yloxy)-pentyl] ester (**7**) [16] were prepared according to the literature. Other chemicals were obtained from commercial sources and were used as received. CH_2Cl_2 was distilled over P_2O_5 under nitrogen atmosphere. The preparation

of the oligomers and the polymers was done under nitrogen atmosphere in a glove box or using Schlenk techniques. GPC: the weight and number average molecular weights (M_W and M_n) as well as polydispersity indices (PDIs) were determined by gel permeation chromatography with THF as the solvent using the following arrangement: Merck Hitachi L6000 pump, separation columns (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, Optilab DSP Interferometric Refractometer, 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. Were necessary 2D techniques were used to assign the corresponding signals.

4.1. General preparation for *poly2*, *poly3*, *poly2/3*, *poly3/2*, *poly4*, *poly2/4*, *poly4/2*

To a solution of monomer A (i.e. the first monomer according to Table 1) (0.60 mmol) in CH_2Cl_2 (1 mL) a solution of **1** (0.003 mmol) in CH_2Cl_2 (1 mL) was added and stirred at room temperature for 1 h. (As monitored by TLC, the reaction was complete after approximately 20 min.) Afterwards, the reaction mixture was split into two parts with equal volume. The first part was treated with ethyl vinyl ether (100 μL, excess) and precipitated upon addition of MeOH. Reprecipitation of a CH_2Cl_2 solution from MeOH and drying in vacuum yielded the corresponding homopolymer.

To the second part of the reaction mixture a solution of monomer B (i.e. the second monomer according to Table 1) (0.30 mmol) in CH_2Cl_2 (1 mL) was added and stirred at room temperature for 1 h. The reaction was quenched by adding ethylvinylether (100 μL, excess) and the product purified by precipitation from methanol. Subsequent reprecipitation and drying in vacuum yielded the corresponding block copolymer. Yields are given in Table 1. Selected NMR data for the block copolymers are given below. NMR spectra of **poly3/2** and **poly4/2** were very similar except of the relative intensities of the signals stemming from the different polymer-blocks. Data for the homo polymers have been published [17].

Poly2/3: ^{1}H NMR (500 MHz, 20 °C, $CDCl_3$): δ = 7.3–7.1 (m, 11H, *Ph*), 5.6–5.2 (m, 4.2H, CH=CH), 4.5–4.3 (m, 4.4H, –CH_2OCH_2Ph), 4.3–4.0 (m, 4H, –OCH_2CH_3), 3.5–2.5 (m, 10.6H, –CH_2OCH_2Ph, cPen), 2.3–1.1 (m, 12.4H, cPen, –OCH_2CH_3). ^{13}C{^{1}H} NMR (125 MHz, 20 °C, $CDCl_3$): δ = 174.1–173.1, 139.2, 134.2–130.0, 128.5, 127.5, 73.1, 72.2, 60.8–60.6, 53.1–51.9, 49.8–39.0, 14.5. FT-IR (NaCl, cm^{-1}): 2981 (m), 2937 (m), 2861 (m), 1729 (s), 1602 (w), 1584 (w), 1496 (w), 1452 (m), 1380 (m), 1370 (m), 1270 (m), 1183 (s), 1098 (m), 1070 (m), 1028 (m), 972 (m), 907 (w), 860 (w), 737 (m), 714 (m), 698 (m).

Poly2/4: ^{1}H NMR (500 MHz, 20 °C, $CDCl_3$): δ = 7.8–6.8 (m, 10H, *Ph*), 5.6–4.6 (m, 4H, CH=CH), 4.2–2.5 (m, 12H, –OCH_2CH_3, cPen), 2.2–1.7 (m, 2H, cPen), 1.6–1.3 (m, 2H, cPen), 1.2–1.0 (m, 6H, –OCH_2CH_3). ^{13}C{^{1}H} NMR (125 MHz, 20 °C, $CDCl_3$): δ = 202.4, 200.7, 174.1–173.1, 137.6, 133.5–129.2, 129.0, 128.7, 60.8–60.6, 53.3–51.9, 50.8.2–39.0, 14.5. FT-IR (NaCl, cm^{-1}): 2980 (m), 1729 (s, ν_{CO}), 1672 (s), 1596 (m), 1580 (m), 1447 (m), 1379 (m), 1213 (s), 1180 (s), 1027 (m), 688 (m).

4.2. General preparation for *poly2/5/6*, *poly5/2/6*, *poly5/6/2*, *poly6/2/5*

To a solution of **2** (100 mg, 0.42 mmol) in CH_2Cl_2 (1 mL) a solution of **1** (4.65 mg, 0.0052 mmol) in CH_2Cl_2 (1 mL) was added and stirred at room temperature. After the reaction was complete, as monitored by TLC, a solution of **5** (76 mg, 0.21 mmol) in CH_2Cl_2 (1 mL) was added. After the reaction was complete (as monitored by TLC), a solution of **6** (76 mg, 0.10 mmol) in CH_2Cl_2 (1 mL) was added and the reaction mixture was stirred at room-temperature until the reaction was complete (as monitored by TLC). After termination of the reaction with ethyl vinyl ether (100 μL, excess), the polymer was purified by precipitation and subsequent reprecipitation from methanol. The other polymers were prepared similarly using a different order of monomer addition. Yields and reaction times for each block are given in Table 2. The NMR spectrum of **poly2/5/6** is given below, the chemical shifts for all other polymers are the same but with variable internsities.

^{1}H NMR (500 MHz, 20 °C, $CDCl_3$): δ = 7.7–7.1 (m, 33H, –CH_2*Ph*, biph-CN$^{3,3',6,6',7,7'}$), 7.0–6.8 (m, 4H, biph-CN$^{2,2'}$), 5.6–4.8 (m, 22.6H, –CH=CH–, –CH_2Ph), 4.3–3.8 (m, 24H, –OCH_2CH_3, –$OCH_2(CH_2)_3CH_2O$–), 3.4–2.6 (m, 28.4H, cPen), 2.2–1.1 (m, 50.2H, cPen, –OCH_2CH_3, –$OCH_2(CH_2)_3CH_2O$–). ^{13}C{^{1}H} NMR (125 MHz, 20 °C, $CDCl_3$): δ = 173, 159.7, 145.0, 132.7, 131.5, 128.4, 127.1, 119.1, 115.1, 110.3, 67.8, 64.7, 60.7, 54–52, 39–38, 29.0, 28.5, 22.6, 14.4. FT-IR (NaCl, cm^{-1}): 2929 (m), 2224 (w), 1729 (s), 1603 (m), 1495 (m), 1455 (m), 1380 (m), 1251 (m), 1179 (s), 1029 (m), 822 (m), 737 (m), 697 (m).

4.3. General preparation for *poly7*, *poly2/7* and *poly7/2*

Poly7, **poly2/7** and **poly7/2** were prepared similarly to **poly2/3** (cf. above) using 0.15 mmol **7** and 0.0038 mmol **1** for **poly7** and 0.30 mmol **2**, 0.0038 mmol **1** and 0.076 mmol **7** for **poly2/7** and **poly7/2**. Yields are given in Table 3.

Poly7: ^{1}H NMR (500 MHz, 20 °C, $CDCl_3$): δ = 7.6–7.2 (m, 12H, Ph$^{2,6,2',3',4',5',6'}$); 6.9–6.8 (m, 4H, Ph$^{3',5'}$); 5.6–5.1 (m, 2H, –CH=CH–); 4.2–3.8 (m, 8H, –$COCH_2$, –CH_2OPh); 3.4–2.6 (m, 4H, cPen); 2.2–1.4 (m, 14H, cPen, –$OCH_2(CH_2)_3CH_2$OPh). ^{13}C{^{1}H} NMR (125 MHz, 20 °C, $CDCl_3$): δ = 174, 158.7, 140.8, 133.6, 128.8, 128.2, 126.7, 114.8, 67.0, 64.7, 54–40, 29.1, 28.6, 22.6. FT-IR (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).

Poly2/7: ^{1}H NMR (500 MHz, 20 °C, $CDCl_3$): δ = 7.6–7.2 (m, 4H, Ph$^{2,6,2',3',4',5',6'}$); 6.9–6.8 (m, 1H, Ph$^{3',5'}$); 5.6–5.1 (m, 2.5H, –CH=CH–); 4.2–3.8 (m, 6.0H, –$COCH_2$, –CH_2OPh); 3.4–2.6 (m, 5.0H, cPen); 2.2–1.4 (m, 5.5H, cPen, –$OCH_2(CH_2)_3CH_2$OPh); 1.3–1.1 (m, 6H, –CH_2CH_3).

$^{13}C\{^1H\}$ NMR (125MHz, 20 °C, $CDCl_3$): δ = 174.2–173.0, 158.7, 140.8, 133.7–130.0, 128.8, 128.2, 126.7, 114.8, 67.0, 64.7, 60.8–60.5, 54–39, 29.1, 28.6, 22.6, 14.4.

FT-IR (NaCl, cm^{-1}): 2980 (m), 2942 (m), 2869 (m), 1729 (s), 1609 (m), 1583 (w), 1519 (m), 1487 (m), 1474 (m), 1449 (m), 1379 (m), 1289 (m), 1268 (m), 1247 (s), 1176 (s), 1097 (m), 1030 (m), 909 (w), 860 (w), 833 (m), 763 (m), 737 (m), 698 (m).

4.4. General preparation for ***poly6/5***

To a solution of monomer **6** (0.070 mmol) in CH_2Cl_2 (1 mL) a solution of **1** (0.0035 mmol) in CH_2Cl_2 (1 mL) and the corresponding additive (cf. Table 3) was added and stirred at room temperature for 6 h. Afterwards, a solution of monomer **5** (0.14 mmol) in CH_2Cl_2 (1 mL) was added and stirred at room temperature for 16 h. The reaction was quenched by adding ethyl vinyl ether (100 μL, excess) and the product was purified by precipitation from methanol. Subsequent reprecipitation and drying in vacuo yielded the corresponding block copolymer. Yields are given in Table 4.

^1H NMR (500 MHz, 20 °C, $CDCl_3$): δ = 7.7–7.2 (m, 22H, CH_2Ph, $Ph^{2,6,2',3',4',5',6'}$); 6.9–6.8 (m, 4H, $Ph^{3',5'}$); 5.9–5.1 (m, 6H, –CH=CH–); 5.7–4.8 (m, 8H, CH_2Ph); 4.2–3.8 (m, 4H, CH_2OPh); 3.4–2.6 (m, 12H, cPen); 2.2–1.6 (m, 20H, cPen, $–OCH_2(CH_2)_3CH_2OPh$). $^{13}C\{^1H\}$ NMR (125MHz, 20 °C, $CDCl_3$): δ = 174.2–171.7, 158.7, 140.8, 134.8, 133.7–128.8, 128.2, 127.5–127.0, 126.7, 114.8, 67.0, 64.7, 65.3, 54–38, 29.2, 28.6, 22.6. FT-IR (NaCl, cm^{-1}): 3090–2957 (m), 2931 (m), 2225 (m), 1730 (s), 1608 (m), 1601 (m), 1498 (m), 1455 (m), 1394 (m), 1380 (m), 1328 (m), 1261 (m), 1257 (m), 1250 (m), 1179 (s), 1103 (m), 1031 (m), 974 (m), 910 (m), 823 (m), 802 (w), 732 (m), 695 (m).

4.5. General preparation for ***poly6/2***

To a solution of monomer **6** (0.14 mmol) in THF (1 mL) a solution of **1** (0.0014 mmol) in THF (1 mL) was added and stirred at different temperatures (cf. Table 4) for 2 h. Afterwards, a solution of monomer **2** (0.28 mmol) in THF (1 mL) was added and stirred at room temperature for 1 h. The reaction was quenched by adding ethyl vinyl ether (100 μL, excess) and the product purified by precipitation from methanol. Subsequent reprecipitation and drying in vacuum yielded the corresponding block copolymer. Yields are given in Table 5.

^1H NMR (500 MHz, 20 °C, $CDCl_3$): δ = 7.6–7.2 (m, 12H, $Ph^{2,6,2',3',4',5',6'}$); 6.9–6.8 (m, 4H, $Ph^{3',5'}$); 5.6–5.1 (m, 6H, –CH=CH–); 4.2–3.8 (m, 12H, $–COCH_2$, $–CH_2OPh$); 3.4–2.6 (m, 12H, cPen); 2.2–1.4 (m, 20H, cPen, $–OCH_2(CH_2)_3CH_2OPh$); 1.3–1.1 (m, 12H, $–CH_2CH_3$). $^{13}C\{^1H\}$ NMR (125MHz, 20 °C, $CDCl_3$): δ = 174.0–173.0, 159.7, 145.0, 133.9–130.1, 128.4, 127.1, 119.1, 115.1, 110.3, 67.8, 64.7, 60.7–60.5, 54–38, 29.0, 28.5, 22.6, 14.4.

FT-IR (NaCl, cm^{-1}): 2929 (m), 2224 (m), 1729 (s), 1603 (m), 1495 (m), 1455 (m), 1380 (m), 1251 (m), 1179 (s), 1029 (m), 822 (m), 737 (m), 697 (m).

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