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Controlled Preparation of Amphiphilic Triblock-Copolyether in a Metal- and Solvent-Free Approach for Tailored Structure-Directing Agents

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Under mild conditions, PPO-PEO-PPO ("reverse Pluronics") and PBO-PEO-PBO copolyether were generated by way of *N*-heterocyclic olefin-based organocatalysis. Reverse Pluronics with molar masses > 20 000 g/mol could be synthesized with excellent control ($Đ_M$ ≤ 1.03) and were converted into (ordered) mesoporous carbons via organic self-assembly to showcase the need for tailor-made copolymer as structure-directing agent.

Organopolymerization of cyclic ethers is a challenging matter. In contrast to cyclic esters (lactones) or carbonates, the range of suitable catalysts is still very limited.[1] Metal-free (anionic) polymerization of typical representatives such as propylene oxide (PO) or butylene oxide (BO) is usually hindered by slow polymerization rates, low conversion and turnover as well as by transfer-to-monomer, a side reaction which limits the molar masses and complicates the construction of more block-like polyether architectures (Scheme 1b).[2]

Early efforts focused on the application of Schwesinger's phosphazene bases for polymerization of ethylene oxide (EO) and PO.[3-7] While the considerable size of phosphazenium cations improved polymerization rates, this was also found to increase transfer-to-monomer.[6] Nonetheless, these investigations highlighted the potential of organocatalysis in this area; especially for phosphazene-mediated (alternating) copolymerizations of epoxides with other monomers a number of impressive advances have been achieved lately.[8-10]

The application of *N*-heterocyclic carbenes (NHCs) further improved the situation for EO as shown by Raynaud and Taton, resulting in metal-free polymerizations with excellent control over molar masses (M_n) with low polydispersity.[11] Even for the more challenging PO NHCs were found to be suitable catalysts, however, some limitations were also observed with regard to rather low conversion (30-40%) and slow reactions.[12]

In this context, we recently described the homopolymerization of PO using *N*-heterocyclic olefins (NHOs) as organocatalysts.[13] NHOs, which increasingly occupy a prominent role in polymerization catalysis[14-17] and other fields,[18-19] where shown to be excellently suited to synthesize PPO in high yields (up to 96%) in a setup without solvent or any other additives except an alcohol-based initiator. The received polyether was fully controlled with respect to molar masses, polydispersity and end groups. Importantly, transfer-to-monomer was also largely absent. Together, these observations recommend the use of NHO-catalysis for the construction of more complex, block-like copolyethers in a metal- and solvent-free, highly controlled process. Amid this versatile and promising class of polymers,[20-21] we considered this approach to be especially useful for amphiphilic triblock copolyether of the type PEO-*b*-PPO-*b*-PEO. Among the most widely employed polyether materials, used as lubricants, surfactants or in medical applications,[21] and known as poloxamers (sometimes marketed as "Pluronics"), these polymers also act as structure-directing agents (SDAs) for the formation of mesoporous materials.[22-26] For these applications, finely tailored properties (micelle formation, balance of lipophilic to hydrophilic blocks) are obviously indispensable. However, this requirement is at odds with the commercially available product, where only a certain number of block variations is available. For so-called reverse Pluronics (PPO-*b*-PEO-*b*-PPO) this situation is even more severe; the formation of micellar networks[27] complicates the generation of ordered phases while at the same time the commercial offers are even more limited. Consequently, tailor-made triblock copolyether as presented in this work was considered to facilitate access to defined mesoporous materials.

For a first set of experiments, the NHOs **1** and **2** were investigated (Scheme 1a). It had been shown earlier that imidazole-derived NHOs are powerful catalysts for PO polymerization, while the saturated analogues are inactive under identical conditions.[13]

Catalyst **2** was initially expected to be the better choice, as it cleanly starts an anionic polymerization; in contrast,

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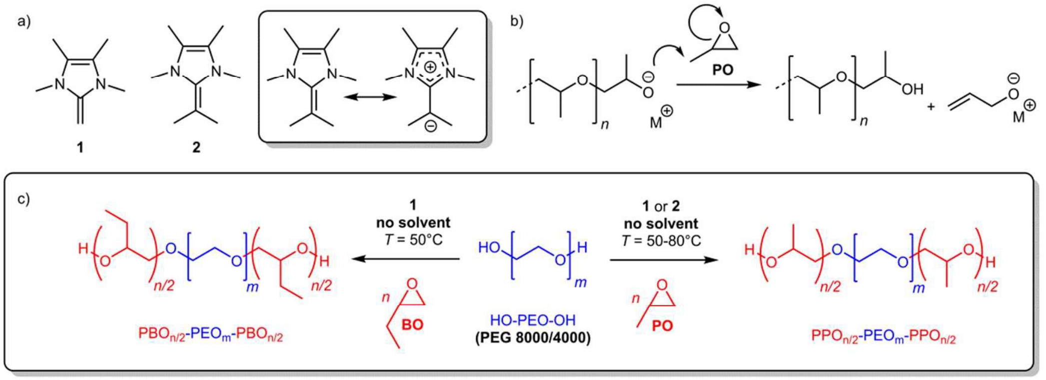

Scheme 1. (a) employed NHO organocatalysts; (b) transfer-to-monomer as side reaction; (c) preparative scheme for amphiphilic block-copolyethers.

Table 1. Polymerization results using NHO **1**.

#	Initi-ator	T [°C]	t [h]	[NHO]/[-OH]/[M]	M_n ($Đ_M$)$^{a)}$ [kg/mol]	Repeating units PO $^{b)}$
1	PEG 8k	80°C	1.0	1:5:1000	11.4 (1.03)	3
2	PEG 8k	80°C	3.5	1:5:1000	13.9 (1.02)	26
3	PEG 8k	80°C	5.0	1:5:1000	15.4 (1.02)	50
4	PEG 8k	80°C	14.5	1:5:1000	17.3 (1.03)	92
5	PEG 8k	80°C	25	1:5:1500	26.4 (1.02)	132
6	PEG 8k	80°C	45.5	1:5:1500	27.9 (1.03)	177
7	PEG 4k	80°C	1.0	1:5:1000	5.5 (1.03)	2
8	PEG 4k	80°C	6.0	1:5:1000	8.9 (1.02)	34
9	PEG 4k	80°C	9.0	1:5:1000	13.2 (1.02)	89
10	BnOH	50°C	3d	1:10:1000	1.2 (1.07)	20 $^{c)}$
11	PEG 8k	50°C	3d	2:5:1000	19.9 (1.02)	31 $^{c)}$
12	PEG 8k	50°C	5d	2:5:1000	21.3 (1.02)	53 $^{c)}$
13	PEG 8k	50°C	9d	2:5:1000	22.1 (1.02)	64 $^{c)}$

a) according to GPC ($CHCl_3$); b) determined *via* ^{1}H NMR; c) monomer = BO

homopolymerization of PO with **1** delivers a very small, but detectable "impurity" originating from zwitterionic polymerization.[13] The triblock copolymer was constructed from α,ω-dihydroxylated PEO (PEG 4000 and PEG 8000) as macroinitiator, on which blocks of PPO were grown (Scheme 1c). Catalyst loadings of 0.1 mol.-% and a ratio of [-OH termini]/[PO] = 1:200 resulted in a mixture that was fully homogeneous at typical reaction temperatures (T = 50-80°C), containing 500-700 mg of PEO and about 1.5 g of PO. Since no solvent was applied, PO acted not only as monomer substrate, but it also solubilized the initiator. For higher conversion the viscosity consequently rose considerably to honey-like appearance with a pale yellow to orange discoloration, depending on NHO concentration and reaction times.

When PEG 8000 was reacted with PO at 50°C using NHO **2** for 17 h, a clean shift to higher molar masses was observed while a very good control over polydispersity was achieved ($Đ_M$ = 1.02). ^{1}H NMR analysis showed that 46 repeating units of PO had been added, resulting in a structure with the average formula PPO_{23}-PEO_{180}-PPO_{23}. However, also a high-M_n impurity was reproducibly observed in GPC, with its M_n slightly higher than twice the value found for the main peak (42 kg/mol vs. 18 kg/mol). As determined from GPC peak areas, the corresponding integral ratio of impurity/main peak was 8:92 (Figure S3). The high molecular weight suggested that a condensation reaction takes place, base-catalyzed by the NHO; and since no similar impurity had been observed for PO homopolymerization,[13] it was assumed that the reaction directly involves two chain ends of macroinitiators (primary alcohols, while a growing PPO-chain is terminated by a secondary alcohol). Hence, after addition of a PO unit, condensation might not take place readily anymore, explaining why the desired product forms to a large majority. Indirect proof for this was obtained from control reactions: a melt of PEG 8000 at 80°C showed no formation of high molecular weight fractions in the absence of catalyst, while in its presence the side product occurred prominently (Figure S4). It should be noted that after condensation involving one terminus, the polymer can still grow, so its molecular weight will always be larger than the twofold M_n of the initiator itself (Figure S5 summarizes all (side-)reactions). Interestingly, mild introduction periods have been found for the polymerization (Figure S6), underlining that it is sensible to assume a certain life time of the pristine macroinitiator without any PO attached, in spite of the large excess of the monomer.

Obviously, suppression of this side reaction would be rewarded by gaining access to very well defined polymer. While a screening of different reaction conditions clearly influenced the proportion of condensation product in the polymerization mixture (down to 2:98, Table S1), it was the application of NHO **1** which delivered constantly better results in this regard, reliably delivering material with a purity >99.5%. This behaviour was attributed to the somewhat decreased basicity of **1**, a consequence of the absence of the electron donating exocyclic methyl groups. With this setup and elevated temperatures (80°C) a series of analogous polymerizations was conducted with the aim to synthesize PPO-PEO-PPO triblock copolyether with systematic variations of the lipophilic PPO moieties.

This succeeded at a loading of only 0.1 mol.-% of the organocatalyst, delivering polymer with very narrow molecular weight distribution (Table 1, entries 1-4, see Figure S7 for

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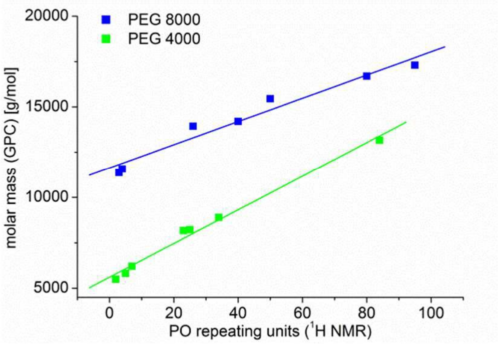

Figure 1. Correlation of PO repeating units and molar masses (M_n).

chromatograms). Closer inspection of polymerization time/M_n reveals an induction period of slow monomer conversion (Figure S6): after 2h, only about four repeating units have been added, while after 3.5 h this has expanded to 26 PO units. Potentially, this period of slow growth is caused by the transition of a primary (oxyanionic) chain end to a secondary one with increased basicity when the first PO is added to the PEO. With progressing reaction the conversion runs into saturation (after ca. 100 incorporated PO repeating units per chain, 50% conversion) as the polymerization mixture gets noticeably viscous. However, the preparation of higher molecular weight polymer is readily achieved by an increase of the initial monomer concentration; indeed, with a ratio of 1:5:1500 ([NHO]/[-OH]/[PO], = 0.067 mol.-% catalyst loading) viscosity increases at a later stage and the PPO block length is suitably increased to 130-180 repeating units (43-60% conversion, Table 1, entries 5-6). Hence, a polyether like PPO$_{90}$-PEO$_{180}$-PPO$_{90}$, with equal molarity of hydrophilic and lipophilic repeating units, is readily available and its homologues with systematic block length variation are accessible by simple adaption of reaction time and PO concentration. The same system can also be employed with another PEO-based macroinitiator (PEG 4000), displaying the same well-behaved properties ($Đ_M \leq 1.03$) and suggesting that the presented organocatalytic system can be employed in a general manner for a wide range of amphiphilic copolyether (Table 1, entries 7-9). Importantly, as documented by monomodal chromatograms, the excellent correlation of molecular weight and PPO repeating units (Figure 1) as well as NMR analysis, no PPO homopolymer is present in the final product. Traces of PPO, originating from zwitterionic initiation by NHO **1**, are quantitatively lost during work-up (precipitation form diethyl ether). No further purification is required.

Next, BO was investigated as monomer source for the lipophilic blocks. Precedent for organocatalytic polymerization of BO is scarce,[8-9] and also for NHOs this had not been reported to date, so homopolymerization experiments were first studied. In comparison to PO, BO is somewhat more electron-rich in its epoxide moiety and also sterically more hindered. This seems to also affect NHO-mediated catalysis. NHO **2** was unable to generate meaningful conversion, including reactions at 50-80°C over several days (BnOH as initiator). In contrast, with NHO **1** polymerization occurred, albeit considerably slower than found for PO (Table 1, entry 10). The resultant oligomeric PBO was found to be well-defined ($Đ_M$ = 1.07), with the end groups exclusively originating from the employed initiator as found by MALDI-ToF MS analysis (Figure S8). Based on these findings, the synthesis of PBO-PEO-PBO triblock copolyether was investigated, employing **1** in mildly increased concentration (0.2 mol.-% loading) and the α,ω-dihydroxylated PEG 8000. Allowing for the depressed polymerization rates, this fortunately resulted in block copolyether, analogously to the PO-based system (Table 1, entries 11-13). Again, polydispersity was nicely controlled ($Đ_M$ = 1.02) and the number of incorporated BO units linearly correlated with the M_n of the copolymer (Figure S9). Hence, the different degrees of polymerization can be addressed exactly and copolymer structures up to PBO$_{32}$-PEO$_{180}$-PBO$_{32}$ (entry 13) were prepared in this manner. NMR analysis can be found in the SI (Figure S10-S12).

As a proof-of-principle, reverse Pluronics were subsequently applied as SDA, following the organic-organic self-assembly approach developed by Dai and Zhao for the preparation of mesoporous carbons (MCs),[28-29] using the EISA (Evaporation Induced Self-Assembly) process. This methodology is based on the use of polar and H-bonding crosslinking agents (oligomerized phenolic resins, formaldehyde), which stabilize – and influence – the formation of ordered mesophases in combination with Pluronic micelles by interaction with the hydrophilic PEO-blocks. Thermopolymerization at 100°C then forms a stable carbon precursor matrix, from which the non-crosslinked parts can finally be burned off (T = 700°C) under protective gas, engendering porosity and carbonization. Experimental details and a scheme of the self-organisation process are provided in Figure S2. Usually, to tailor the desired morphology and pore size, indirect, process-related measures are taken, such as variation of oven temperatures or a change in the ratio of SDA to formaldehyde.[29] The ability to prepare tailor-made polyether SDAs with systematically varied block lengths enabled us to work from the opposite direction, keeping reaction conditions strictly constant to prepare MCs, with only the polyether being changed (PPO$_n$-PEO$_{180}$-PPO$_n$ including n = 20, 25, 40, 50, 66 and 90). All samples showed 25-27% mass retention after carbonization. SAXS measurements were applied to investigate the regularity of the carbon material. Excitingly, this immediately highlighted the need for tailored SDAs: under the applied conditions for self-assembly, only the sample based on PPO$_{66}$-PEO$_{180}$-PPO$_{66}$ delivered an *ordered* MC (Figure S13, middle). In this case the SAXS profile shows two broad scattering maxima at q_1 = 0.91 nm^{-1} and q_2 = 1.36 nm^{-1}, the q-ratio of which however does not match the ratio of $1/\sqrt{3}$ required for the (10) and (11) peaks of a 2D hexagonal lattice. We thus propose a short-range ordered arrangement of pores on a 2D rectangular or distorted hexagonal lattice. This is clearly supported by scanning electron microscopy (Figure S14). N_2 gas sorption data (Figure 2) also fit to a well-ordered material. A specific surface area of 790 m^2/g was found, alongside a total pore volume of 0.65 cm^3/g and an average pore size of 6.2 nm (adsorption, 4.4 nm from desorption). Importantly, for longer and shorter PPO-

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block analogues (*n* = 50, 90) no ordered structure was observed, which clearly localizes the window for the preparation of ordered MCs under the described conditions. Clearly, only in the case of PPO_{66}-PEO_{180}-PPO_{66} all polymer parameters (balance of hydrophilic to lipophilic units, molar mass) are suitable for the generation of an ordered structure in the given self-assembly system. Nonetheless, in all cases mesoporous carbons were formed. With respect to specific surface area and pore size (distribution), also the disordered materials displayed characteristic properties, as found by N_2 sorption (Figure S15, for PPO_{40}-PEO_{180}-PPO_{40}). This setup might also be of interest to other types of self-assembly.[30-31]

In summary, a novel catalytic setup for the preparation of amphiphilic copolyether was described. NHOs are employed as organocatalysts in a solvent-free and excellently controllable synthesis. Polymerization succeeds with PO and BO. As a consequence of the low polydispersity ($Đ_M \leq 1.03$) and the high degree of control, the SDA can be tailored towards a specific mesoporous structure, rather than tailoring preparative conditions to suit a specific, commercially available Pluronic-type SDA. This approach was demonstrated for (ordered) mesoporous carbons, where few experiments with a set of defined "reverse Pluronic"-type copolyethers quickly identified a suitable candidate for an ordered structure; defined mesoporous materials, solely based on "reverse Pluronic"-SDAs as described in this work, remain rare to date.[32-34]

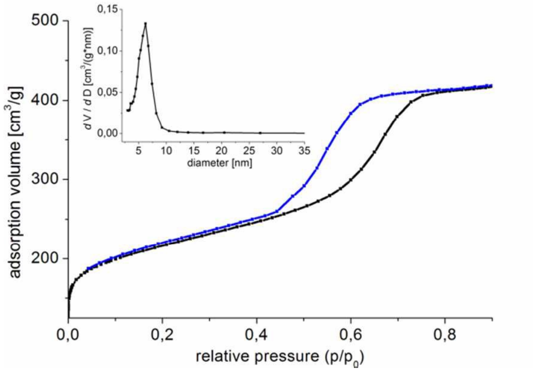

Figure 2. N_2 adsorption/desorption isotherms for ordered MC based on PPO_{66}-PEO_{180}-PPO_{66}. Inserts: Pore size distribution (adsorption) and detail from SEM analysis.

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Conflicts of interest

There are no conflicts to declare.

Notes and references

1 W. N. Ottou, H. Sardon, D. Mecerreyes, J. Vignolle and D. Taton, *Progr. Polym. Sci.*, 2016, **56**, 64–115.
2 S. Carlotti and F. Peruch in N. Hadjichristidis and A. Hirao, *Anionic Polymerization*, Springer Japan, Tokyo, 2015.
3 B. Esswein and M. Möller, *Angew. Chem. Int. Ed.*, 1996, **35**, 623–625.
4 F. Schacher, M. Müllner, H. Schmalz and A. H. E. Müller, *Macromol. Chem. Phys.*, 2009, **210**, 256–262.
5 B. Esswein, N. M. Steidl and M. Möller, *Macromol. Rapid Commun.*, 1996, **17**, 143–148.
6 O. Rexin and R. Mülhaupt, *J. Polym. Sci. A Polym. Chem.*, 2002, **40**, 864–873.
7 H. Schlaad, H. Kukula, J. Rudloff and I. Below, *Macromolecules*, 2001, **34**, 4302–4304.
8 J. Zhao, D. Pahovnik, Y. Gnanou and N. Hadjichristidis, *Macromolecules*, 2014, **47**, 3814–3822.
9 S. Hu, G. Dai, J. Zhao and G. Zhang, *Macromolecules*, 2016, **49**, 4462–4472.
10 H. Li, J. Zhao and G. Zhang, *ACS Macro Lett.*, 2017, 1094–1098.
11 J. Raynaud, C. Absalon, Y. Gnanou and D. Taton, *J. Am. Chem. Soc.*, 2009, **131**, 3201–3209.
12 J. Raynaud, W. N. Ottou, Y. Gnanou and D. Taton, *Chem. Commun.*, 2010, **46**, 3203–3205.
13 S. Naumann, A. W. Thomas and A. P. Dove, *Angew. Chem. Int. Ed.*, 2015, **54**, 9550–9554.
14 S. Naumann, A. W. Thomas and A. P. Dove, *ACS Macro Lett.*, 2016, **5**, 134–138.
15 Q. Wang, W. Zhao, J. He, Y. Zhang and E. Y.-X. Chen, *Macromolecules*, 2017, **50**, 123–136.
16 S. Naumann and D. Wang, *Macromolecules*, 2016, **49**, 8869–8878.
17 S. Naumann, K. Mundsinger, L. Cavallo and L. Falivene, *Polym. Chem.*, 2017, **8**, 5803–5812.
18 R. D. Crocker and T. V. Nguyen, *Chem. Eur. J.*, 2016, **22**, 2208–2213.
19 M. M. D. Roy and E. Rivard, *Acc. Chem. Res.*, 2017, **50**, 2017–2025.
20 R. Klein and F. R. Wurm, *Macromol. Rapid Commun.*, 2015, **36**, 1147–1165.
21 J. Herzberger, K. Niederer, H. Pohlit, J. Seiwert, M. Worm, F. R. Wurm and H. Frey, *Chem. Rev.*, 2016, **116**, 2170–2243.
22 J. M. Kim, Y. Sakamoto, Y. K. Hwang, Y.-U. Kwon, O. Terasaki, S.-E. Park, G. D. Stucky, *J. Phys. Chem. B* **2002**, *106*, 2552-2558.
23 S. Förster, M. Antonetti, *Adv. Mater.* **1998**, *10*, 195-217.
24 C. Liang, Z. Li, S. Dai, *Angew. Chem. Int. Ed.* **2008**, *47*, 3696-3717.
25 N. D. Petkovich, A. Stein, *Chem. Soc. Rev.* **2013**, *42*, 3721-3739.
26 D. Zhao, W. Zhou, Y. Wan, *Ordered mesoporous materials*, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, **2013**.
27 K. Mortensen, W. Brown, E. Jorgensen, *Macromolecules* **1994**, *27*, 5654-5666.
28 C. Liang, S. Dai, *J. Am. Chem. Soc.* **2006**, *128*, 5316-5317.
29 Y. Meng, D. Gu, F. Zhang, Y. Shi, L. Cheng, D. Feng, Z. Wu, Z. Chen, Y. Wan, A. Stein et al., *Chem. Mater.* **2006**, *18*, 4447-4464.
30 Y. Mai and A. Eisenberg, *Chem. Soc. Rev.*, 2012, **41**, 5969–5985.
31 M. Wagner, M. J. Barthel, R. R. A. Freund, S. Hoeppener, A. Traeger, F. H. Schacher and U. S. Schubert, *Polym. Chem.*, 2014, **5**, 6943–6956.
32 Y. Huang, H. Cai, T. Yu, F. Zhang, F. Zhang, Y. Meng, D. Gu, Y. Wan, X. Sun, B. Tu et al., *Angew. Chem. Int. Ed.* **2007**, *46*, 1089-1093.
33 P. Li, Y. Song, Q. Guo, J. Shi, L. Liu, *Material Lett.* **2011**, *65*, 2130-2132.
34 P. Li, Y. Song, Q. Lin, J. Shi, L. Liu, L. He, H. Ye, Q. Guo, *Microporous Mesoporous Mat.* **2012**, *159*, 81-86.