



Fluorinated Polymers via Para-Fluoro-Thiol and Thiol-Bromo Click Step Growth Polymerization

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Click reactions are utilized widely to modify chain ends and side groups of polymers while click polymerizations based on step-growth polymerization of bifunctional monomers have recently attracted increased attention of polymer chemists. Herein, the combination of two highly efficient click reactions, namely para-fluoro-thiol click and thiol-bromo substitution reactions, is demonstrated to form fluorinated polymers with tuned hydrophobicity owing to the nature of the dithiol linker compound. The key compound in this study is 2,3,4,5,6-pentafluoro benzyl bromide that provides the combination of thiol click reactions. The thiols used here are 4,4-thiobisbenzenthio, 2,2'-(ethylenedioxy) diethanethiol, and 1,2-ethanedithiol that allow tuning of the properties of obtained polymers. The step-growth click reaction conditions are optimized by screening the effect of reaction temperature, base, solvent, and stoichiometric ratio of the compounds. Thermal properties and hydrophobicity of synthesized polymers are determined via water contact angle, thermogravimetric analysis and differential scanning calorimetry measurements, showing thermal stability up to 300 °C, glass transition temperatures ranging from –25 to 82 °C and water contact angles ranging from 55 to 90 °C.

have been developed and thoroughly investigated for different applications involving gas separation membranes,^[2,3] artificial muscle actuators,^[1] photoresists,^[4] and optical waveguides.^[5] Fluorinated polymers are usually synthesized by either fluorination of polymers or direct polymerization of fluorine-containing monomers via chain-growth or step-growth methodologies. The fluorination approach is rarely employed due to the requirement of aggressive fluorination agents and non-quantitative degrees of fluorination of the post-polymerization modification.^[6] However, the direct polymerization of fluorinated monomers is widely employed to synthesize numerous commercially available fluorinated polymers.^[6,7] More recently, the synthesis of novel fluorinated monomers in combination with various polymerization methods has been subject of intensive research.^[3,8–10]

Fluorinated polymers are gaining increased attention in polymer chemistry since the discovery of polytetrafluoroethylene (PTFE) in 1938.^[1] The existence of carbon–fluorine bonds and the electronegative nature of fluorine atoms provide several noteworthy properties of fluorinated polymers such as good thermal stability, hydrophobicity, and chemical resistance. Besides PTFE, various fluorinated polymers with different backbone and side chain structures including poly(vinyl fluoride) (PVF), polychlorotrifluoroethylene (PCTFE), and poly(vinylidene fluoride) (PVDF)

Due to the potential for the synthesis of polymers on industrial scales, step-growth polymerization emerged as a powerful tool for the synthesis of materials with different heteroatoms across the backbone. The inherited high dispersity enables the facilitated processing of the obtained polymers.^[11,12] The advent of click chemistry opened avenues for the synthesis of step-growth polymers with novel architectures and properties.^[8,13–16] The prerequisites of click reactions^[13,17] such as high reaction kinetics, atom economy, orthogonality and modularity, are promising features for step-growth polymerization, allowing the synthesis of high molecular weight polymers in very short reaction times. Several different click reactions have been reported to produce step-growth polymers. In 2018, Mohapatra and coworkers reported synthesis of a linear polytriazole and cross-linked polymeric gel via copper catalyzed azide-alkyne cycloaddition (CuAAC) under ultrasound irradiation.^[18] Song and coworkers studied the synthesis of linear and hyperbranched polymers of difunctionalized azide and multifunctional alkynes via CuAAC and investigated the kinetics in 2016.^[19] Besides CuAAC, sulfonyl fluoride exchange (SuFEx) click reaction, which was coined by Sharpless in 2014, was applied to synthesize polysulfates and polysulfonates.^[20–22] Various bisphenol A (BPA) based disulfonyl compounds were used as monomers and the resulting polysulfates have shown good thermal properties and processability.^[20,21] The combination of orthogonal SuFEx and CuAAC click reaction has been reported by Yang and coworkers on the synthesis of sequence-regulated polymers on a solid phase utilizing solvent phase click

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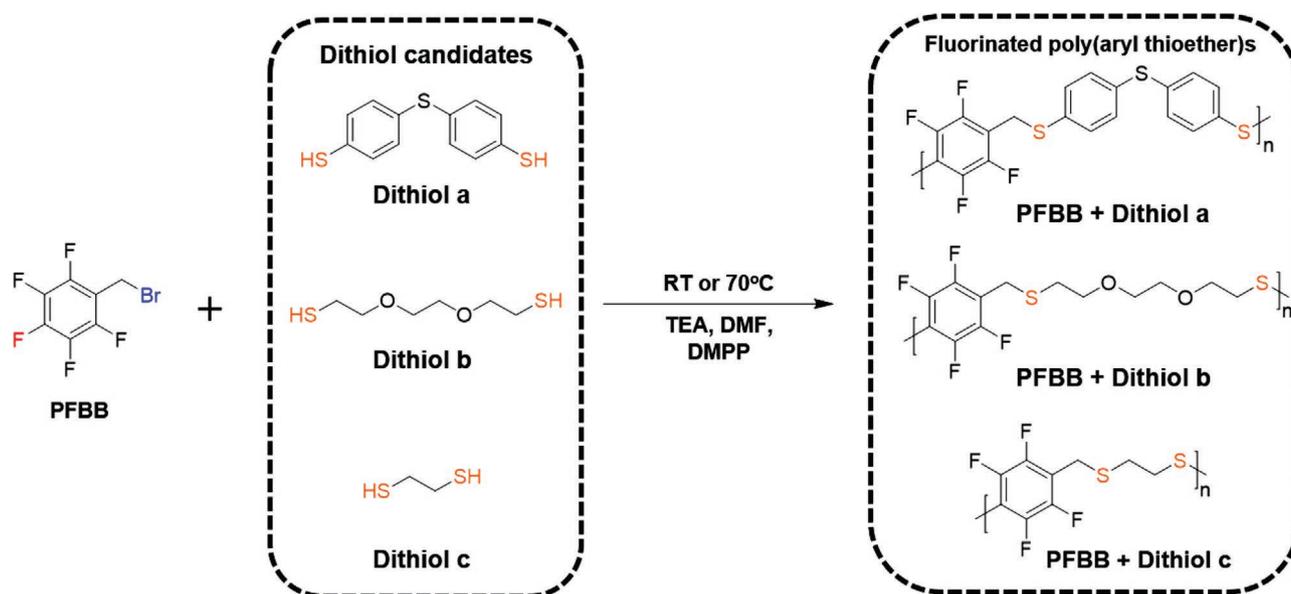
reaction.^[23] Recently, thiol-halogen nucleophilic substitution reactions, including para-fluoro-thiol click reaction (PFTR)^[24–26] and thiol-bromo click reaction^[27–30] attracted growing attention due to the increasing interest in incorporating sulfur-based compounds into polymeric materials. The commercial availability of a multitude of thiol compounds with diverse functionalities enables the synthesis of numerous different polymer compositions via PFTR and thiol-bromo click reactions.^[26] PFTR and thiol-bromo reactions are both base-activated coupling reactions with triethylamine (TEA) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) frequently employed to initiate the reaction.^[26,29–31] These two types of click reactions have been well investigated and reported for post-polymerization modification (PPM),^[8,25,26,28,29,31–34] yet only a handful of reports demonstrated the preparation of step-growth polymers.^[35–39] The fluorinated poly(aryl thioether) structures obtained from PFTR have great potential due to their remarkable physical properties^[39] such as high refractive index (RI) values,^[29] and low optical loss.^[10] Thus, in order to take advantage of efficient PFTR and thiol-bromo click reactions and investigate novel fluorinated polymer structures, a combination of these two click reactions has been utilized to synthesize fluorinated polymers from different monomer precursors.

Herein, three commercially available dithiol building blocks and pentafluoro benzyl bromide were employed in the synthesis of fluorinated polymers with aryl thiol ether segments via simultaneous PFTR and thiol-bromo click reaction. (Scheme 1) The effect of base activation has been investigated and it was shown that the base is not acting catalytically in this polymerization. The obtained materials were tested on their thermal stability and hydrophobicity via thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and water contact angle, respectively.

Initial kinetic investigation of step-growth polymerization of 2,3,4,5,6-pentafluoro benzyl bromide (PFBB) with 4,4-thiobisbenzenethiol (dithiol a), 2,2'-(ethylenedioxy) diethanethiol (dithiol b), and 1,2-ethanedithiol (dithiol c) was performed in *N,N*-Dimethylformamide (DMF) at 70 °C or ambient temperature (Figure 1).

TEA was selected as the base to initiate both para-fluoro-thiol click reaction and thiol-bromo reaction and act as the acid scavenger. These three dithiols were selected because the polymers obtained would have aromatic, aliphatic, and heteroatom backbones which could be representative, while the nucleophilicity difference of these three dithiols could assist the investigation on reaction rate to monomer nucleophilicity. To prevent disulfide bridge formation, which affects stoichiometry, dimethylphenylphosphine (DMPP) was added to the mixture of PFBB and dithiol DMF solution before the slow addition of TEA to the mixture. T₀ samples were taken before addition of the base to prevent inaccurate t₀ trace because of rapid reaction. A swift exothermic was observed in room temperature reactions. Gel permeation chromatography (GPC) in THF showed the formation of polymers and molar mass values were calculated relative to PS standards, ranging from 2300 g mol⁻¹ for 1,2-ethanedithiol (dithiol c) to 4700 g mol⁻¹ for 4,4-thiobisbenzenethiol (dithiol a). These values indicate a calculated extent of reaction of 12–15 for these polymers. For dithiol a and dithiol c, the polymer chain growth stops in less than 20 min, while due to relatively weak nucleophilicity of 2,2'-(ethylenedioxy) diethanethiol (dithiol, b), the polymerization continues over 10 h, which is anticipated as the nucleophilic substitution mechanism of both click reactions employed. (Figure 1) The reactivity of the corresponding thiolate ion of dithiol b might be hampered by the strong electronegativity of two backbone oxygen atoms while dithiol a benefits from the aromatic ring resonance and dithiol c has a very low steric hindrance. Comparing the kinetics graph under 70 and 25 °C, at higher temperature, shorter time was required to reach the completion of polymerization and the molar masses of polymers produced were slightly higher. This could be the consequence of elevated temperature accelerating the deprotonation of thiol groups into thiolate ions and the nucleophilic attack that leads to polymer growth.

When analyzing the reaction kinetics of PFBB with dithiol b under 25 °C by ¹H and ¹⁹F NMR, full monomer conversion for thiol-bromo reaction was observed within minutes (Figure S1,



Scheme 1. Synthesis of fluorinated poly(aryl thioether)s via thiol-bromo and thiol-para fluoro click reactions.

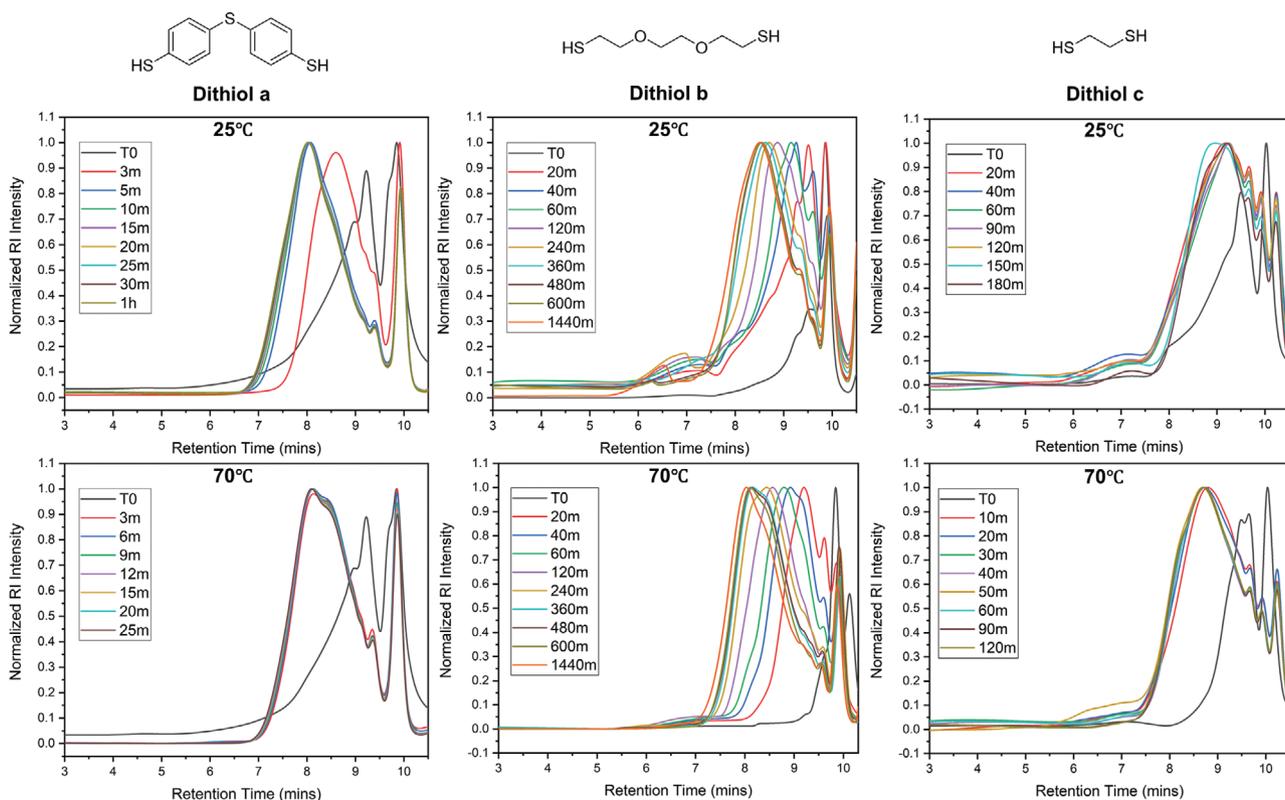


Figure 1. GPC traces of step-growth polymerization of PFBB and dithiol a, dithiol b, and dithiol c at various time intervals at 25 and 70 °C, respectively.

Supporting Information), shown by the shift of hydrogens of PFBB from 4.50 to 3.89 which indicates the removal of electron drawing bromine, while ^{19}F NMR shows the para-fluoro-thiol click reaction, proceeds and allows the formation of polymer chains (Figures S2 and S3, Supporting Information). That suggests the possibility of fast thiol-bromo reaction leading to the formation of an AB type precursor followed by the PFTR

dominated chain growth process as a consequence of weak nucleophilicity of dithiol b, while also suggesting higher reactivity of the C–Br bond in the nucleophilic substitution. The conversion versus time and $M_{n,\text{GPC}}$ versus conversion plots (Figure 2a,b) were drawn based on the quantitative ^{19}F NMR kinetics where the conversion was determined by the change of integration value of para-fluoro peak in ^{19}F NMR; examples

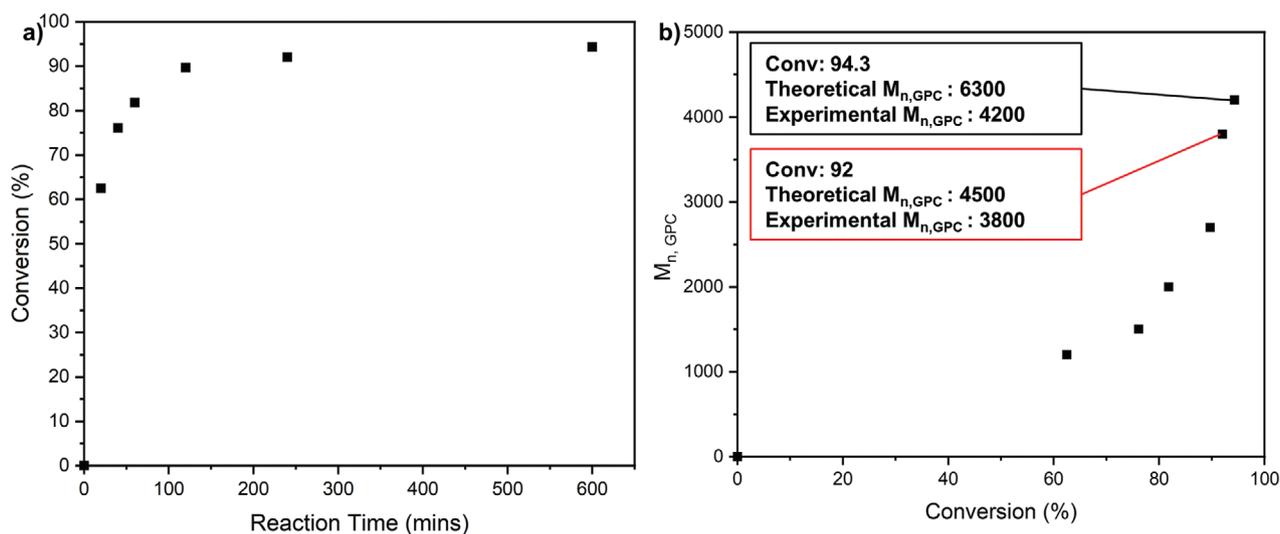


Figure 2. a) Conversion versus time and b) number average molecular weight versus conversion plots. The conversion of monomer was calculated using quantitative ^{19}F NMR.

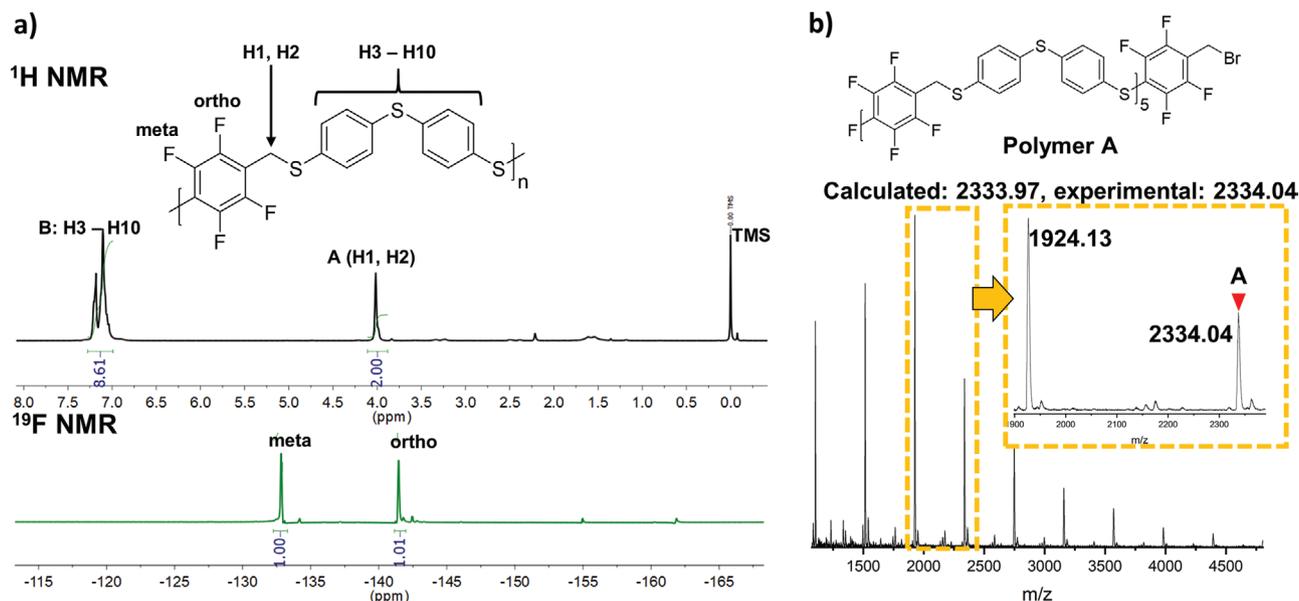


Figure 3. a) ^1H NMR, ^{19}F NMR and b) MALDI-ToF MS analysis of polymer of PFBB and dithiol a.

were shown in Figure S4a,b, Supporting Information. The overall trend fits the prediction of Carothers equation despite at high conversion the experimental $M_{n,\text{GPC}}$ being lower than the theoretical $M_{n,\text{GPC}}$, which might be the consequence of cyclic polymer production and stoichiometry distortion which would be discussed later with NMR and MALDI-ToF evidence. ^1H NMR, ^{19}F NMR, and MALDI-ToF analysis of the purified polymer revealed the existence of desired polymer structure.

As shown in **Figure 3**, using PFBB-dithiol a polymer as an example, formation of desired polymer backbone structure was confirmed by MALDI-ToF; the experimental mass number matches the calculated mass with desired repeating unit structure with penta-fluoro and tetrafluoro benzyl bromide as end groups; the stoichiometry ratio of meta and ortho fluorine and the mass of the repeating unit shown in MALDI indicates the formation of a linear polymer backbone with no meta- or ortho- fluorine substitution occurring during polymerization. Polymers of PFBB with other two thiols (b and c) were also purified and characterized to show the desired structures have been obtained (Figure S5, Supporting Information), although polymer of (PFBB-dithiol c) does not show a clean MALDI-ToF signal, which might be due to the high content of fluorinated aromatic ring.

The calculated moderate extent of reaction values indicates achieving full conversion might be hampered. Possible reasons include cyclisation, imbalanced stoichiometry, and side reactions. MALDI-ToF analysis effectively shows the mass that corresponds to the repeat unit as well as by performing end group analysis, the existence of cyclized polymer chains was easily determined. The possibility of cyclisation is evidenced further with MALDI-ToF data in the ESI. ^1H NMR of mixed PFBB stock solution and dithiol a stock solution (Figure S6, Supporting Information) has shown that without the addition of base even with the most nucleophilic dithiol a, no click reaction would happen and allows the monitoring of stoichiometry by ^1H NMR. The molar ratio of both reactants can be calculated via

integration, where the ratio of PFBB to dithiol a is 0.98:1 and the theoretical extent of reaction should be 50 if the reaction reaches full conversion. The difference between the theoretical extent of reaction based on stoichiometry calculated from ^1H NMR and the molar mass gained from the GPC indicates existence of other hindrances. To investigate possible side reactions, dithiol a was selected as the model compound for step-growth polymerization with PFBB in DMF with TEA assistance and different reaction procedures were executed. It was revealed that no significant difference of resulting polymer molar mass was observed while adding PFBB to a mixture of dithiol and TEA, comparing to the original approach where PFBB and dithiol were mixed first. However, when mixing PFBB with TEA and subsequently adding dithiol a, significantly restricted polymer growth was observed (**Figure 4a**). To investigate the reason of this limited chain growth, 1 equivalent of PFBB and 2.05 equivalents of TEA were mixed in DMF for 30 min. ^{19}F NMR characterization demonstrated the formation of secondary distribution for ortho-, meta-, and para-fluoro pattern, which corresponds with the shift of TEA and PFBB peaks in ^1H NMR spectrum (Figure 4b) where the $-\text{CH}_2-$ hydrogens from PFBB shifted from 4.50 to 4.94, indicating the presence of a stronger electron drawing group comparing to bromine, the methyl hydrogens of TEA shifted from 1.03–1.07 to 1.51–1.55 and the methylene hydrogens of TEA shifted from 2.53–2.59 to 3.59–3.64. These shifts suggest possible formation of quaternary salt of PFBB and TEA, which might be the side reaction that diverts the stoichiometry. As tertiary amines have been reported as an efficient end-capping reagent for poly(2-oxazoline)s,^[40,41] the limited chain growth obtained was most likely a consequence of quaternary salt of monomers and oligomers and thus stops the chain growth and affects the stoichiometry, which is also responsible for the sharp tailing peak at the 10 min region, as the THF GPC solvent includes TEA that could react with oligomers and form the quaternary salt structure. It was also noticeable that if dithiol and TEA were mixed first and PFBB was then added

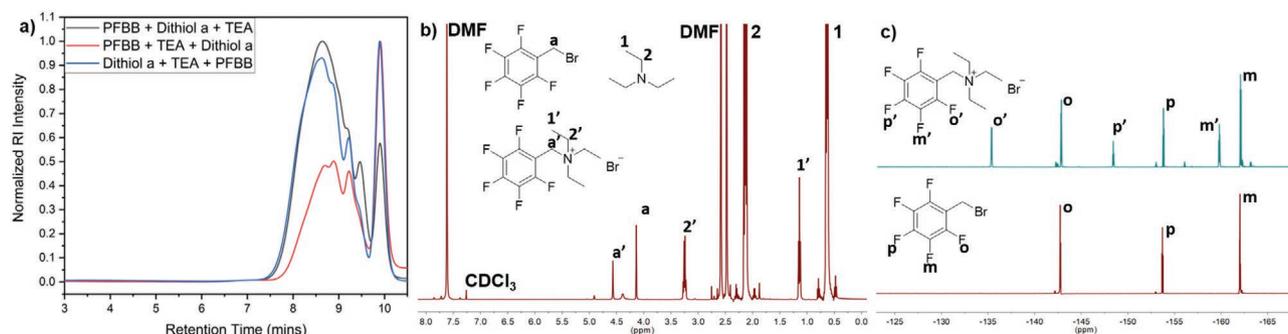


Figure 4. a) GPC (THF eluent) traces of polymer of PFBB-dithiol a via different addition order b) ^1H NMR of PFBB and TEA mixture in DMF. c) ^{19}F NMR comparison of PFBB and TEA mixture in DMF with PFBB in DMF, where a secondary pentafluoro pattern was observed.

slowly, gelation of reaction system was observed in seconds, suggesting that potential side reactions on meta-fluorine is possible if the base amount is substantial.

To diminish possible side reactions caused by the base, increase the extent of reaction, and obtain longer polymer chains, the effect of different bases and their stoichiometry were investigated. As ring structures of 1,5,7-Triazabicyclo[4.4.0]dec-5-ene (TBD) and DBU were more bulky than TEA and it has been reported that both TBD and DBU can be utilized as organocatalysts for para-fluoro-thiol click reaction,^[16,39] TEA, DBU, and TBD were selected to initiate the step growth polymerization of PFBB and dithiol a. By screening 2.05, 1.05, and 0.05 equivalent of the base, the contribution of the base to the reaction and its impact on the degree of polymerization were investigated. The obtained results are presented in Table 1 and GPC traces are shown in Figure 5. Based on the M_n given by the GPC and the molar mass of polymer repeating unit, theoretical extent of reaction ξ was calculated following Carothers equation and shown in Table 1.

The polymerization reactions, which were carried out with 0.05 equiv. of the respective base (P3, P6, P9) show, that only

very low molecular weight polymers are formed, regardless of the base strength. These results underpin the non-catalytic nature of the base in this reaction. It is assumed, that the base is removed from the reaction mixture by scavenging the formed HF and HBr, reducing its concentration in the reaction solution. Therefore, the stoichiometric ratio of the base was increased, yielding the highest molecular weights, when 2.05 equiv. were used. The obtained results for P1, P4, and P7 demonstrate further the effect of base strength on molecular weight. When using the stronger base TBD (P7), the highest number average molecular weight was obtained (9.7 kg mol^{-1}). The increased average molecular weight is thought to result from the easing of thiol groups deprotonate into thiolate anions with a stronger base while the increased dispersity is presumably due to kinetic quenching from polymer precipitation as reported in previous literature^[39] It should be noted that fast reactions may also decrease the possibility of producing cyclic polymers, which is indicated as the low molecular weight tail that lowers down the number average molar mass in the GPC trace. It is also possible that as already shown in Figure 1, both click reactions are quite efficient, thus, after a short period of

Table 1. Investigations on the type of base, stoichiometry, and solvent effect on step growth polymerization of PFBB and dithiol a.

Name	Base type	Base eq.	Solvent	Conc. [M]	$M_{n, \text{GPC}} [\text{kg mol}^{-1}]$	$M_{w, \text{GPC}} [\text{kg mol}^{-1}]$	D	Conv. [%]
P1	TEA	2.05	DMF	1.00	4.2	8.0	1.93	90
P2	TEA	1.05	DMF	1.00	3.0	5.6	1.92	86
P3	TEA	0.05	DMF	1.00	n. d.	n. d.	n. d.	n. d.
P4	DBU	2.05	DMF	1.00	4.5	10.4	2.33	91
P5	DBU	1.05	DMF	1.00	3.6	7.6	2.08	88
P6	DBU	0.05	DMF	1.00	n. d.	n. d.	n. d.	n. d.
P7	TBD	2.05	DMF	1.00	9.7	40.1	4.31	95
P8	TBD	1.05	DMF	1.00	4.7	10.1	2.15	91
P9	TBD	0.05	DMF	1.00	n. d.	n. d.	n. d.	n. d.
P10	TBD	2.05	DMF	0.66	7.0	18.8	2.70	94
P11	TBD	2.05	THF	1.00	2.3	5.2	2.24	82
P12	TBD	2.05	CHCl_3	1.00	n. d.	n. d.	n. d.	n. d.
P13	TBD	2.05	THF/DMF	0.66	4.7	14.6	3.10	91
P14	TBD	2.05	CHCl_3/DMF	0.66	4.4	17.0	3.81	90

Abbreviations: TEA: triethyl amine, DBU: 1,8-diazabicyclo [5.4.0]undec-7-ene, TBD: 1,5,7-Triazabicyclo- [4.4.0]dec-5-ene, n.d.: not determined as very low oligomeric products formed. Conversion was based on change of integration of para-fluoro peak in ^{19}F NMR which represents the consumption of para-fluorine.

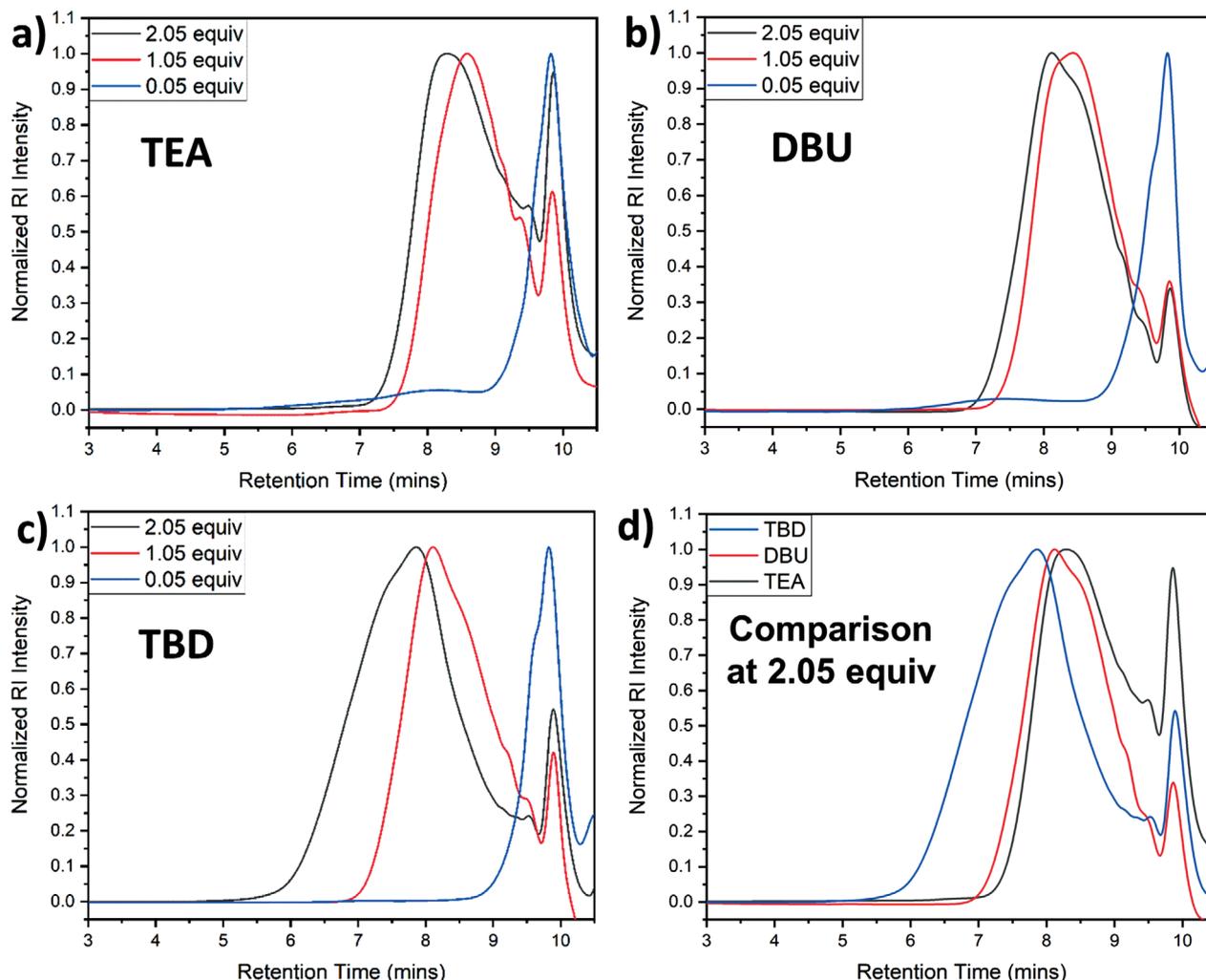


Figure 5. GPC traces of step-growth polymerization of PFBB and dithiol a with different amounts of a) TEA b) DBU, c) TBD, and d) comparison of TEA, DBU, and TBD using 2.05 equiv. of the respective base.

time, the polymer concentration is high, which allows more long chain coupling, resulting rapid increase of molecular weight, while for stronger base not only the click reaction but also the chain-chain coupling is more efficient.

The effect of solvent was investigated with DMF, THF, and CHCl_3 , as PFTR click reactions require aprotic polar solvent environment, while the dithiol compounds show poor solubility under such conditions. Furthermore, the formation of a dimer precursor by utilizing PFTR-unfavored solvent^[26] like CHCl_3 and a subsequent solvent system change were explored to drive the polymerization. The obtained results are summarized in Table 1 and the corresponding GPC traces are displayed in Figure 6. When CHCl_3 was employed in the polymerization (P12), the absence of higher molecular weight species was observed in the GPC traces. However, conducting the reaction in DMF (P10) and THF (P11) resulted in the formation of polymers with moderate molecular weights of 7.0 and 2.3 kg mol^{-1} , respectively. The low molecular weight, which was observed for the reaction in THF was thought to result from the low solvent polarity and the observed precipitation of a yellow gel

during the reaction. The gelation indicated the possibility of side reactions with meta- or ortho-fluorine atoms and hence cross-linking. The step growth polymerization was shown to proceed in solvent mixtures of CHCl_3 /DMF and THF/ DMF at a concentration of 0.66 M concentration (P13, P14). However, the obtained molecular weights were lower, when compared to the polymerization reactions at the same concentration, which were conducted in solely DMF (P10).

It was also shown that in CHCl_3 /DMF mixtures, the polymerization rate is decreased dramatically, yielding high molecular weight species in 24–48 h, while also forming an insoluble gel. The increase in molecular weight at later stages of the polymerization was thought to result from the different reaction kinetics of thiol-bromo and PFTR reaction in CHCl_3 . Therefore, thiol-bromo reactions occur rapidly, which leaves para-fluorine group to react with thiol after the addition of DMF, and the suggested base end-capping reaction cannot interfere with the growth of the polymer chain, thus plenty of long-chain coupling was allowed in an elongated period of time which yielded broad dispersed polymer with high molecular weight species.

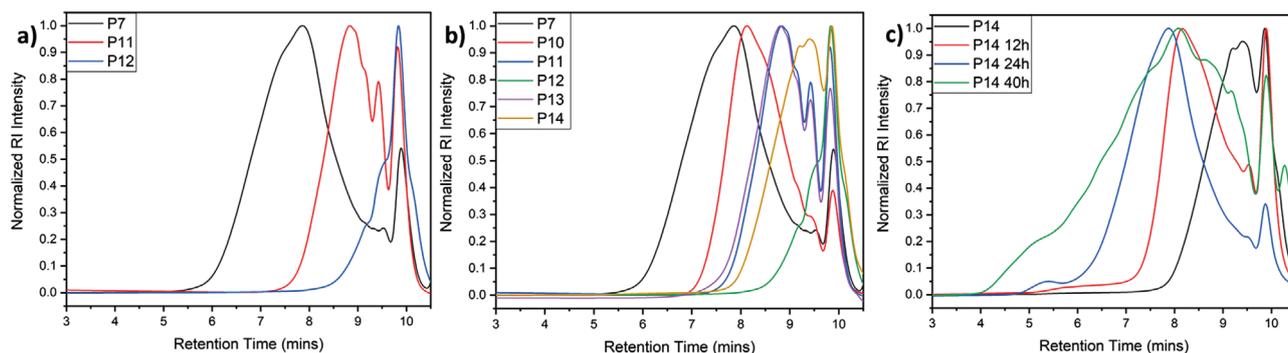


Figure 6. GPC traces for the investigation of solvent effects for step-growth polymerization of PFBB and dithiol a. a) Step-growth polymerization of PFBB and dithiol a in DMF (P7), THF (P11), and CHCl_3 (P12) respectively. b) Step-growth polymerization of PFBB and dithiol a in DMF (P7), THF (P11), CHCl_3 (P12), DMF with a concentration of 0.66 M (P10), addition of DMF to THF (P13, $c(\text{DMF}) = 0.66 \text{ M}$), and addition of DMF to CHCl_3 (P14, $c(\text{DMF}) = 0.66 \text{ M}$). c) GPC traces of P14 at 12 h, 24 h, and 40 h.

Based on the conducted screening results, using DMF as the solvent, 2.05 equiv of TBD mediating the step-growth polymerization at room temperature at 1.0 M concentration was employed as model conditions. Step-growth polymer of PFBB-dithiol b and PFBB dithiol c was then synthesized using the model conditions. In polymerization of PFBB and dithiol b TBD catalyzed results in slow chain growth that gives a polymer with molecular weight of lower than 3000 after 48 h, while DBU has performed best to produce a polymer with moderate molecular weight. Thus, step growth polymers of PFBB-dithiol a, PFBB-dithiol b, and PFBB dithiol c were synthesized using TBD and DBU catalyzed under previously mentioned model conditions and the MALDI-ToF analysis has shown the formation of desired polymer structure (Figures S7 and S8, Supporting Information). As fluorinated polymers are mainly termed as polymers possessing good thermal stability and hydrophobicity, thus, these two functionalities of three prepared polymers were characterized and discussed below. Based on the preparation of step growth polymers with dithiol a, b, and c, it is possible that other step growth polymers can also be synthesized via this approach based on the large library of commercially available dithiol candidates (Figure S9, Supporting Information) while some of the backbone can provide interesting properties including hydrophilicity from hydroxy groups, post-polymerization modification from double bonds, rigidity, and intermolecular forces from aromatic rings.

Thermal properties of obtained polymers were examined by TGA and DSC (Figure S10, Supporting Information). TGA traces of all three polymers have shown thermal resistance up to the temperature range of 310–350 °C, although weight loss was different among three polymers due to differences in aromatic content and elemental composition. The remaining weight of polymers of dithiol a was still high after the facile decomposition at 348 °C, the percentage weight loss of the decomposition corresponds to the degradation of thiol-ester function and decomposition of sulfur atoms in the polymer while until heated to 1000 °C, the remaining weight is still over 40%, owing to the high carbon content of this polymer. Similar weight loss pattern has been observed in the polymer of dithiol c. In the decomposition of polymer of dithiol b, the weight loss is more significant, 81% of weight loss was observed at 327 °C which might associate with the vaporization of the volatile ethylene glycol unit

after the decomposition of the thio-ester linkers. The thermal decomposition pattern of these three polymers indicates despite the thermal resistance to heating above 300 °C, the potential of obtaining better thermal stability by oxidation of thio-ester functions in these three polymers is possible. Analysis of DSC traces, which was taken from the second heating process, of three polymers shows good structure-property correspondence. Polymer of PFBB and dithiol a has the highest aromatic content and theoretically most rigid chain structure among three polymers, while the T_g obtained was 82 °C, the highest of three polymers. Polymer of PFBB with dithiol c has a short linear carbon chain in the backbone; the extra flexibility brings the T_g down to 35 °C while the polymer of PFBB with dithiol b has a long flexible polyethylene glycol segment that reduces the T_g to –25 °C.

Finally, spin-coated polymer films on quartz slides were made, to investigate the hydrophobicity of obtained polymers, and contact angle (CA) data was presented in Figure S11, Supporting Information. Given the high aromatic and fluorinated aromatic content in the polymer chain, the polymer of PFBB and dithiol a present a CA value of 90.2° which fits the anticipation. The polymer of PFBB and dithiol c also show a CA value of 78.8°, indicating moderate hydrophobicity that decreased compared to the polymer of PFBB and dithiol a due to the absence of aromatic segments. Polymer of PFBB and dithiol b was shown the least hydrophobic one with a CA value of 55.0°, which was expected as the presence of the ethylene glycol segment raises the hydrophilicity, although the polymer is still more hydrophobic than plain glass surface that has a CA value of 30.9°.

In conclusion, a new method for the synthesis of a series of fluorinated polymers using commercially available dithiol compounds and 2,3,4,5,6-pentafluoro benzyl bromides has been reported. The step-growth polymerization can proceed at room temperature while based on the nucleophilicity of dithiol compounds, the completion could be reached in 10 min. Stoichiometric amount of base activates the synthesis of a linear polymer and milder base allows formation of longer polymer chains. DMF acts as the optimum solvent for the polymerization, although a sequential addition of DMF into a CHCl_3 solvent system provides further polymer growth during elongated reaction time. Obtained polymers have a good thermal resistance up to 300 °C and hydrophobic character was measured by water contact angle measurements.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

click reactions, multi-block copolymers, para-fluoro thiol reaction, thiol-bromo reaction

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- [1] V. F. Cardoso, D. M. Correia, C. Ribeiro, M. M. Fernandes, S. Lanceros-Méndez, *Polymers* **2018**, *10*, 161.
- [2] S. Banerjee, *Handbook of Specialty Fluorinated Polymers: Preparation, Properties, and Applications*, Elsevier, New York **2015**.
- [3] T. Y. Inan, H. Doan, E. E. Unveren, E. Eker, *Int. J. Hydrogen Energy* **2010**, *35*, 12038.
- [4] S. Krishnan, Y. J. Kwark, C. K. Ober, *Chem. Rec.* **2004**, *4*, 315.
- [5] T. Matsuura, S. Ando, S. Matsui, S. Sasaki, F. Yamamoto, *Electron. Lett.* **1993**, *29*, 2107.
- [6] J. J. Reisinger, M. A. Hillmyer, *Prog. Polym. Sci.* **2002**, *27*, 971.
- [7] W. Yao, Y. Li, X. Huang, *Polymer* **2014**, *55*, 6197.
- [8] S. Agar, E. Baysak, G. Hizal, U. Tunca, H. Durmaz, *J. Polym. Sci., Part A: Polym. Chem.* **2018**, *56*, 1181.
- [9] M. V. del Blanco, V. Gomez, P. Fleckenstein, T. Keplinger, E. Cabane, *J. Polym. Sci., Part A: Polym. Chem.* **2019**, *57*, 885.
- [10] J. P. Kim, W. Y. Lee, J. W. Kang, S. K. Kwon, J. J. Kim, J. S. Lee, *Macromolecules* **2001**, *34*, 7817.
- [11] T. Yu, G. L. Wilkes, *J. Rheol.* **1996**, *40*, 1079.
- [12] L. Palangetic, N. K. Reddy, S. Srinivasan, R. E. Cohen, G. H. McKinley, C. Clasen, *Polymer* **2014**, *55*, 4920.
- [13] H. C. Kolb, M. G. Finn, K. B. Sharpless, *Angew. Chem., Int. Ed.* **2001**, *40*, 2004.
- [14] C. E. Hoyle, C. N. Bowman, *Angew. Chem., Int. Ed.* **2010**, *49*, 1540.
- [15] Y. Kohsaka, K. Hagiwara, K. Ito, *Polym. Chem.* **2017**, *8*, 976.
- [16] O. Daglar, U. S. Gunay, G. Hizal, U. Tunca, H. Durmaz, *Macromolecules* **2019**, *52*, 3558.
- [17] C. R. Becer, R. Hoogenboom, U. S. Schubert, *Angew. Chem. Int. Ed.* **2009**, *48*, 4900.
- [18] H. Mohapatra, J. Ayarza, E. C. Sanders, A. M. Scheuermann, P. J. Griffin, A. P. Esser-Kahn, *Angew. Chem., Int. Ed.* **2018**, *57*, 11208.
- [19] H. B. Song, A. Baranek, C. N. Bowman, *Polym. Chem.* **2016**, *7*, 603.
- [20] J. Dong, K. B. Sharpless, L. Kwisnek, J. S. Oakdale, V. V. Fokin, *Angew. Chem., Int. Ed.* **2014**, *53*, 9466.
- [21] B. Gao, L. Zhang, Q. Zheng, F. Zhou, L. M. Klivansky, J. Lu, Y. Liu, J. Dong, P. Wu, K. B. Sharpless, *Nat. Chem.* **2017**, *9*, 1083.
- [22] X. Xiao, F. Zhou, J. Jiang, H. Chen, L. Wang, D. Chen, Q. Xu, J. Lu, *Polym. Chem.* **2018**, *9*, 1040.
- [23] C. Yang, J. P. Flynn, J. Niu, *Angew. Chem., Int. Ed.* **2018**, *57*, 16194.
- [24] A. Mueller, T. Kowalewski, K. L. Wooley, *Macromolecules* **1998**, *31*, 776.
- [25] C. R. Becer, K. Babiuch, D. Pilz, S. Hornig, T. Heinze, M. Gottschaldt, U. S. Schubert, *Macromolecules* **2009**, *42*, 2387.
- [26] G. Delaittre, L. Barner, *Polym. Chem.* **2018**, *9*, 2679.
- [27] B. M. Rosen, G. Lligadas, C. Hahn, V. Percec, *J. Polym. Sci., Part A: Polym. Chem.* **2009**, *47*, 3940.
- [28] J. Xu, L. Tao, C. Boyer, A. B. Lowe, T. P. Davis, *Macromolecules* **2010**, *43*, 20.
- [29] Y. Zhang, G. Chen, Y. Lin, L. Zhao, W. Z. Yuan, P. Lu, C. K. W. Jim, Y. Zhang, B. Z. Tang, *Polym. Chem.* **2015**, *6*, 97.
- [30] V. P. Beyer, B. Cattoz, A. Strong, D. J. Phillips, A. Schwarz, C. Remzi Becer, *Polym. Chem.* **2019**, *10*, 4259.
- [31] J. M. Noy, A. K. Friedrich, K. Batten, M. N. Bhebe, N. Busatto, R. R. Batchelor, A. Kristanti, Y. Pei, P. J. Roth, *Macromolecules* **2017**, *50*, 7028.
- [32] J. M. Noy, Y. Li, W. Smolan, P. J. Roth, *Macromolecules* **2019**, *52*, 3083.
- [33] H. Turgut, A. C. Schmidt, P. Wadhvani, A. Welle, R. Müller, G. Delaittre, *Polym. Chem.* **2017**, *8*, 1288.
- [34] P. Boufflet, A. Casey, Y. Xia, P. N. Stavrinou, M. Heeney, *Chem. Sci.* **2017**, *8*, 2215.
- [35] E. Baysak, U. Tunca, G. Hizal, H. Durmaz, *J. Polym. Sci., Part A: Polym. Chem.* **2018**, *56*, 1853.
- [36] A. Wild, A. Winter, M. D. Hager, H. Görls, U. S. Schubert, *Macromol. Rapid Commun.* **2012**, *33*, 517.
- [37] N. Cakir, U. Tunca, G. Hizal, H. Durmaz, *Macromol. Chem. Phys.* **2016**, *217*, 636.
- [38] F. Cavalli, H. Mutlu, S. O. Steinmueller, L. Barner, *Polym. Chem.* **2017**, *8*, 3778.
- [39] N. H. Park, G. dos Passos Gomes, M. Fevre, G. O. Jones, I. V. Alabugin, J. L. Hedrick, *Nat. Commun.* **2017**, *8*, 166.
- [40] C. J. Waschinski, J. C. Tiller, *Biomacromolecules* **2005**, *6*, 235.
- [41] S. C. Lee, S. W. Kang, C. Kim, I. C. Kwon, S. Y. Jeong, *Polymer* **2000**, *41*, 7091.