

# Postpolymerization Modification of Poly(dihydropyrimidin-2(1H)-thione)s via the Thiourea–Haloalkane Reaction to Prepare Functional Polymers

Yuan Zhao,<sup>†</sup> Haibo Wu,<sup>†,‡</sup> Yuanyi Zhang,<sup>†</sup> Xing Wang,<sup>§</sup> Bin Yang,<sup>†</sup> Qingdong Zhang,<sup>†</sup> Xu Ren,<sup>†</sup> Changkui Fu,<sup>†</sup> Yen Wei,<sup>†</sup> Zhiming Wang,<sup>‡</sup> Yurong Wang,<sup>‡</sup> and Lei Tao<sup>\*,†</sup>

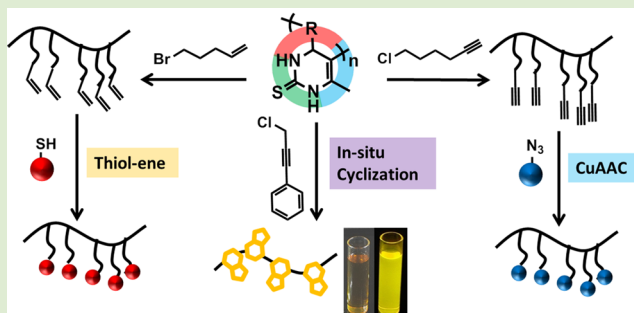
<sup>†</sup>The Key Laboratory of Bioorganic Phosphorus Chemistry & Chemical Biology (Ministry of Education), Department of Chemistry, Tsinghua University, Beijing 100084, P. R. China

<sup>‡</sup>School of Petrochemical Engineering, Changzhou University, Changzhou, Jiangsu 213164, P. R. China

<sup>§</sup>The State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing 100029, P. R. China

## S Supporting Information

**ABSTRACT:** A highly reactive thiourea-contained polycondensate, poly(dihydropyrimidin-2(1H)-thione) (poly(DHPMT)) has been facilely synthesized via the Biginelli polycondensation using thiourea and a difunctional compound containing benzaldehyde and  $\beta$ -keto ester groups as monomers. The thiourea moiety in the polymer structure has similar reactivity as the thiourea, thus the poly(DHPMT) is an excellent polymer precursor for preparing new functional polymers through the postpolymerization modification (PPM) strategy. After simple reaction with functional haloalkanes, the parent poly(DHPMT) could be almost completely converted (>99%) to daughter polymers containing alkene or alkyne side groups. Then, the daughter polymers have been further transferred to granddaughter polymers through another PPM via thiol–ene or Cu(I)-catalyzed azide–alkyne cycloaddition (CuAAC) reactions. Besides, when 3-phenylpropargyl chloride was used as the reactant, a bright yellow fluorescent polymer could be simply achieved due to the in situ formed conjugated heterocycle in the polymer structure, further demonstrating the diversity of the functional polymers through PPM. Considering the easily available monomers, simple polycondensation, and the excellent reactivity of the thiourea moiety in the polymer structure, this thiourea-contained Biginelli polycondensate might be a versatile platform for new functional polymer preparation.



Since the middle of the twentieth century, the concept of a macromolecule has been formally accepted, and many strategies have been successfully developed to prepare polymers with designed functions. Among them, postpolymerization modification (PPM) might be one of the most important to prepare new functional polymers by modifying the reactive chain ends or side chains of polymer precursors.<sup>1–5</sup> The history of PPM could actually date back to 1840 when Hancock and Ludersdorf independently reported the first PPM by treating natural rubber with sulfur to produce a tough and elastic material.<sup>6,7</sup> Until now, some large-scale manufactured polymers, such as poly(vinyl alcohol) (PVA), chitosan, some functional resins, etc., are still produced through the PPM strategy. However, traditional modification reactions normally have low efficiency and are easily hampered by the steric hindrance of giant polymer chains, leading to polymers with undefined structure and properties. PPM has therefore been overshadowed by other strategies to synthesize clearly structured polymers.<sup>8–11</sup>

With the recent development of modern efficient modular reactions, such as the click reactions<sup>12–19</sup> and highly efficient multicomponent reactions (MCRs),<sup>20–34</sup> functional groups can be effectively introduced into the polymer chain once the polymer precursor containing corresponding reactive modules are obtained.<sup>1,35,36</sup> Thus, the PPM strategy has regained attention, and a series of elegant polymers with clear structure have been successfully prepared through this “old” method.<sup>35–39</sup> By now, how to synthesize highly reactive polymer precursors and how to choose efficient modification reactions for subsequent PPM have been recognized as the two determinants for the future development of PPM.

Recently, our group studied in detail the tricomponent Biginelli reaction and introduced this old reaction (>120 years) into polymer chemistry.<sup>40,41</sup> The Biginelli-type polycondensate, poly(dihydropyrimidin-2(1H)-one) (poly(DHPM)), has also

Received: June 30, 2015

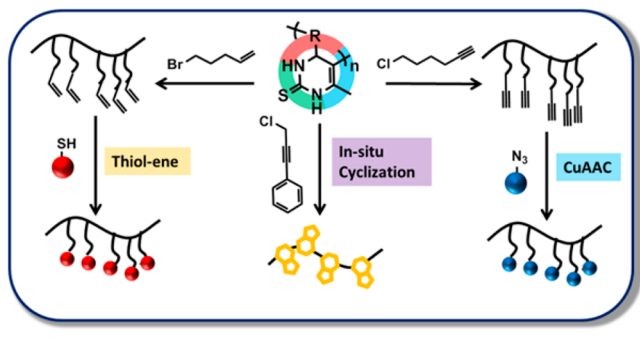
Accepted: July 23, 2015

Published: July 27, 2015

been successfully prepared in a large scale using an easily available difunctional monomer (AB monomer) containing benzaldehyde and  $\beta$ -keto ester groups in the presence of urea. The DHPM group which used to be studied as pharmaceuticals showed interesting metal bonding ability in the polymer structure, indicating the mutual reinforced relation between functional groups and the polymer chain.<sup>42</sup> By deeper investigation of that multicomponent polymerization, we realized the unreactive poly(DHPM) can be easily upgraded to a reactive polymer precursor by implanting the highly reactive thiourea group in the Biginelli ring.

Thiourea is an excellent nucleophile like thiol but more stable and not smelly, and the thiourea–haloalkane is a well-known efficient reaction in organic chemistry. However, the thiourea–haloalkane reaction has been rarely employed in polymer chemistry for PPM. Herein, we reported the preparation of a thiourea-containing polymer through the Biginelli polycondensation and its descendants through PPM via the efficient thiourea–haloalkane reaction. By simply using thiourea as the reactant, a Biginelli polycondensate, poly-(dihydropyrimidin-2(1H)-thione) (poly(DHPMT)), could be facily prepared and further modified to generate a series of derivative polymers via the efficient substitution reaction between the thiourea group and haloalkanes (Scheme 1).

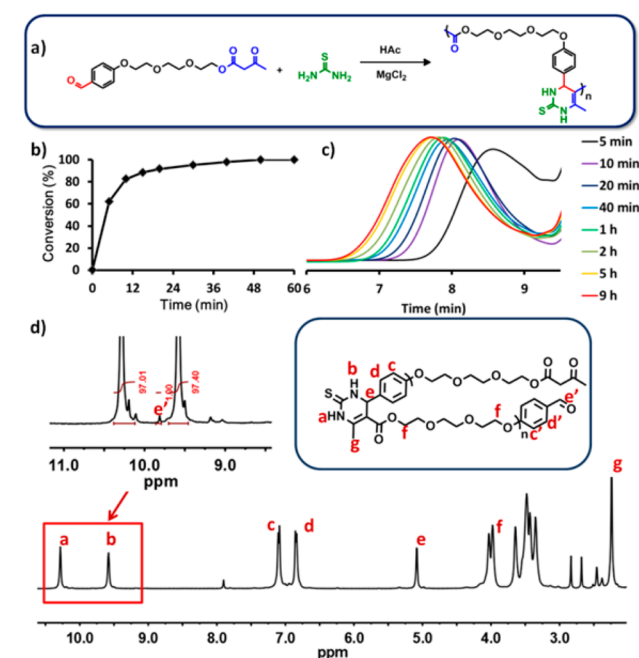
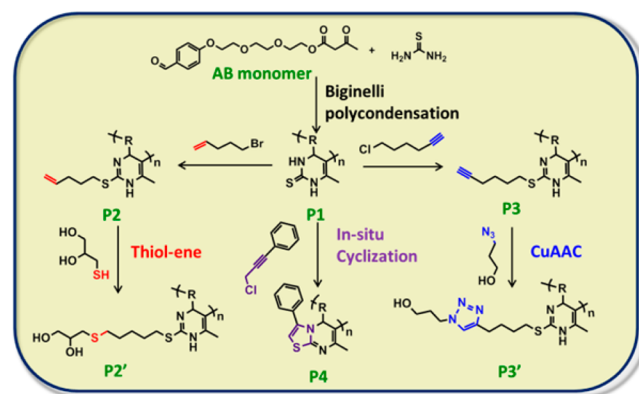
### Scheme 1. Postpolymerization Modifications of Poly(DHPMT) and Its Derivatives



The alkene or alkyne groups could thus be easily incorporated into the polymer for the following thiol–ene reaction or CuAAC click reaction, respectively. Moreover, by reacting directly with 3-phenylpropargyl chloride, a fluorescent polymer containing a new conjugated heterocycle in the polymer chain could be facily prepared (Scheme 2). Considering the simple preparation and the excellent reactivity for subsequent PPM, the thiourea-containing poly(DHPMT) might be an excellent precursor to prepare multipurpose functional polymers, revealing the new vitality of “old” efficient reactions when people look at them from the perspective of PPM.

The preparation of poly(DHPMT) (P1) (Figure 1a) was carried out as in our previous report, and the reaction ratio was designed as  $[\text{AB monomer}]/[\text{thiourea}]/[\text{MgCl}_2] = 1/2/0.1$ . The excess thiourea was used for faster polymerization. The monomer conversion was detected by  $^1\text{H}$  NMR. By comparing the integral ratio of the aldehyde group protons with the newly formed methine protons in DHPMT ( $\sim 5.04\text{--}5.14$  ppm), a time-dependent increase of monomer conversion has been observed (Figure 1b and Figure S1). Oligomers rapidly formed in the first 10 min, while the conversion was about 80%. Afterward, the conversion reached approximately 100% in 50

### Scheme 2. Preparation of New Functional Polymers through Successive PPM via the Thiourea–Haloalkane and Other Efficient Reactions



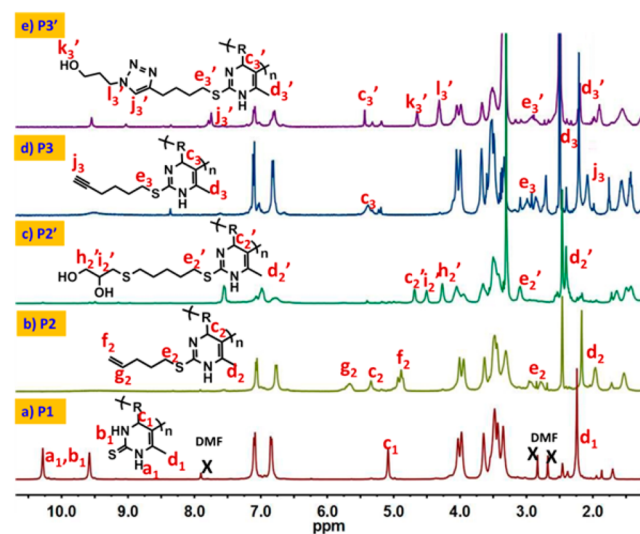
**Figure 1.** Biginelli polycondensation of AB monomer and thiourea. (a) Reaction conditions:  $[\text{AB monomer}]/[\text{thiourea}]/[\text{magnesium chloride}] = 1/2/0.1$ , acetic acid as solvent,  $100\text{ }^\circ\text{C}$ . (b) The conversions of the Biginelli reaction. (c) GPC tracking the condensation polymerization. (d)  $^1\text{H}$  NMR spectrum ( $\text{DMSO-}d_6$ , 400 MHz) of the final polymer (P1).

min, and the viscosity of the polymerization system increased continuously. The GPC analyses indicated the gradually increased molecular weight of the polymer (Figure 1c), and the polycondensation almost finished in 5 h to generate a polymer with quite high molecular weight. The polycondensation was quenched after 9 h when the molecular weight only slightly increased after extended polymerization time ( $M_{n\text{GPC}} \sim 23\ 100$ ,  $\text{PDI} \sim 1.45$ ). By simple precipitation in water and then ultrasonic washing with water and diethyl ether for three times followed by filtration, the final polymer could be easily obtained. From the  $^1\text{H}$  NMR spectrum of the purified polymer (Figure 1d), the characteristic PhCH peak (5.08 ppm) and two NH peaks of the Biginelli cyclization product (9.58 ppm, 10.28 ppm) could be clearly identified. The integral ratio between the methine PhCH peak and NH groups ( $I_{5.08}/I_{9.58}/I_{10.28}$ ) is 1/1/1,

suggesting the efficient and thorough Biginelli polycondensation. The degree of polymerization (DP) was calculated through the integral ratio between the aldehyde residue at the polymer chain end (9.82 ppm) and the amide group in the DHPMT (9.58 ppm) as approximately 97, and the molecular weight is therefore calculated as about  $M_{nNMR} \sim 36\,700$  g/mol.

Many literatures have revealed that after the Biginelli reaction the thiourea moieties in the Biginelli ring have similar reactivity as the thiourea which can dynamically transform under base conditions to the isothiourea isomer for nucleophilic substitution reaction.<sup>43–45</sup> Therefore, in current research, several experiments have been designed to evaluate the reactivity of P1.

First, P1 was treated with 5-bromo-1-pentene (S/Br = 1/1.2) in the presence of potassium carbonate and sodium iodide. From the <sup>1</sup>H NMR spectrum (Figure 2b) of obtained polymer



**Figure 2.** <sup>1</sup>H NMR spectra (DMSO-*d*<sub>6</sub>, 400 MHz) of three polymers (P1, P2, P2', P3, P3', bottom to top).

(P2), the sulfamide protons (9.58 ppm, 10.28 ppm) completely disappeared, while the methine and methyl protons in the P1 (PhCHN, 5.08 ppm; CH<sub>3</sub>, 2.24 ppm) shifted in the P2 to 5.34 and 2.17 ppm, respectively. The new signals of the vinyl group (4.89 ppm, 5.67 ppm) could be clearly identified, and the integral ratio of  $I_{5.67}/I_{2.17}$  is 0.33 (theoretical value: 0.33), suggesting all the thiourea moieties in P1 have been successfully transferred to the thioether and the vinyl group has been intactly introduced into the polymer chain after the PPM process. Subsequently, the daughter polymer (P2) underwent another PPM via an UV assistant thiol–ene reaction to generate the granddaughter polymer (P2'). Typically, 3-mercaptopropanediol has been chosen as the thiol source to react with the vinyl group in P2. From the <sup>1</sup>H NMR spectrum of the obtained polymer (P2'), the characteristic vinyl protons in P2 nearly disappeared, and the methine protons in P2 (PhCHN, 5.34 ppm) have been found to shift (4.69 ppm), indicating the almost complete PPM of P2 (Figure 2c). The GPC analyses suggested that P2 ( $M_{nGPC} \sim 29\,000$ , PDI  $\sim 1.44$ ) and P2' ( $M_{nGPC} \sim 33\,000$ , PDI  $\sim 1.74$ ) have increased molecular weight after PPM, further confirming the successful PPM of P1 and P2 (Figure S2). It is interesting that the PDI of P2' became broader than that of P2, which might be attributed to the changed polymer polarity after PPM, leading to changed

interaction between the polymer and GPC column and the wider PDI. The granddaughter polymer P2' has lower glass transition ( $T_{gp2'} \sim 35.7$  °C) than the daughter polymer ( $T_{gp2} \sim 52.3$  °C), and the daughter polymer P2 has lower glass transition ( $T_{gp2} \sim 52.3$  °C) than the parent polymer P1 ( $T_{gp1} \sim 98.5$  °C), which are attributed to the continued introduction of flexible chains into the polymer structure, indicating the PPM is an efficient strategy to get new functional polymers (Table 1 and Figure S9). Also, the P2 ( $\sim 216$  °C) and P2' ( $\sim 213$  °C) have lower decomposition temperature than P1 ( $\sim 243$  °C) (Table 1 and Figure S3).

**Table 1.** Physical Properties of Polymers before and after PPM

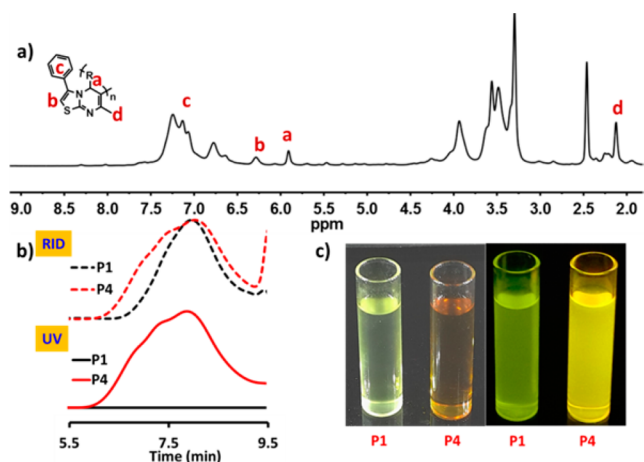
polymer	$M_{nGPC}$ (g/mol) <sup>a</sup>	PDI <sup>a</sup>	$T_g$ (°C) <sup>b</sup>	$T_{d1}$ (°C) <sup>c</sup>	$T_{d2}$ (°C) <sup>c</sup>
P1	23100	1.45	98.5	243	516
P2	29000	1.44	52.3	216	619
P2'	33000	1.74	35.7	213	517
P3	29200	1.45	47.6	214	525
P3'	44800	1.45	58.9	238	497
P4	27500	1.76	96.7	247	531

<sup>a</sup>Determined by GPC. <sup>b</sup>Determined by DSC. <sup>c</sup>Determined by TGA (Figures S3, S5, and S8).

Similarly, other functional groups have also been included through the PPM to get new functional polymers. For example, the alkynyl-contained polymer can be easily obtained by modification of P1 with 6-chloro-1-hexyne. From the <sup>1</sup>H NMR spectrum of purified daughter polymer (P3) (Figure 2d), the methine and the methyl protons (PhCHN, 5.08 ppm, CH<sub>3</sub>, 2.24 ppm) in P1 downfield shifted in P3 to 5.34 and 2.21 ppm, respectively. The signal of the alkynyl group (2.08 ppm) could be clearly observed, while the integral ratio of  $I_{2.08}/I_{2.21}$  is 0.32 (theoretical value: 0.33), suggesting the integrated alkynyl group under the reaction conditions and the successful PPM. Subsequently, the daughter polymer (P3) with the alkynyl group has been reacted with the azide compound via the CuAAC click reaction using 1-azido-3-propanol as the model molecule. The <sup>1</sup>H NMR spectrum of the further modified granddaughter polymer (P3') showed the complete disappearance of the alkynyl signal and a new proton signal (7.75 ppm) of the 1,2,3-triazole heterocycle, suggesting the highly efficient CuAAC reaction between the P3 and 1-azido-3-propanol (Figure 2e). The GPC traces of P3 ( $M_{nGPC} \sim 29\,200$ , PDI  $\sim 1.45$ ) and P3' ( $M_{nGPC} \sim 44\,800$ , PDI  $\sim 1.45$ ) showed the gradually increased molecule weight of modified polymers (Figure S4), further confirming the smooth PPMs of P1 and P3. For the same reason as mentioned above, P3 showed a lower  $T_g$  ( $\sim 47.6$  °C) and  $T_{d1}$  ( $\sim 214$  °C) than the original polymer P1 ( $T_{gp1} \sim 98.5$  °C,  $T_{d1P1} \sim 243$  °C). However, since a rigid 1,2,3-triazole heterocycle has been introduced into the polymer, P3' has a higher  $T_g$  ( $\sim 58.9$  °C) and  $T_{d1}$  ( $\sim 238$  °C) than that of P3 (Table 1, Figure S5, Figure S9).

The thiol group in the dihydropyrimidin-2(1H)-thione has been verified as an excellent reaction site for PPM. Moreover, the nucleophilic activity of the secondary amine in DHPMT could also be triggered during the thiourea–haloalkane reaction by suitable reactants, resulting in a new polymer with different main chain. For example, when 3-phenylpropargyl chloride reacted with the P1 through thiourea–haloalkane substitution, the in situ cyclization simultaneously occurred via the Michael addition between the amine group and alkynyl group, leading

to a new polymer (P4) containing a heterocycle in the polymer structure. From the  $^1\text{H}$  NMR spectrum, the characteristic peaks (SCH, 6.28 ppm; PhCH, 5.91 ppm;  $\text{CH}_3$ , 2.13 ppm) of newly formed thiazolo[3,2- $\alpha$ ]pyrimidine are clearly visible, while the integral ratio of  $I_{5.91}/I_{2.13}$  is 0.33 (theoretical value: 0.33), confirming the complete thiourea–haloalkane substitution and Michael addition reactions (Figure 3a). Although the daughter



**Figure 3.** PPM of P1 with 3-phenylpropargyl chloride. (a)  $^1\text{H}$  NMR spectrum ( $\text{DMSO}-d_6$ , 400 MHz) of the P4. (b) GPC curves via RID detector (dotted line) and UV detector at 400 nm (solid line) of the polymers before and after PPM. (c) The imaging of P1 and P4 solution in THF (2 mg/mL) under bright field (left) and blue light (right).

polymer (P4) has similar a  $T_g$  ( $\sim 96.7^\circ\text{C}$ ) and  $T_{d1}$  ( $\sim 247^\circ\text{C}$ ) with the parent polymer P1 ( $T_{gP1} \sim 98.5^\circ\text{C}$ ,  $T_{d1P1} \sim 243^\circ\text{C}$ ) (Table 1, Figure S8, Figure S9), it still has different properties due to the newly generated heterocycle. P4 has an absorption peak at 390 nm in the UV spectrum, while the absorption peak of P1 is 310 nm (Figure S6). Therefore, during the GPC analyses, P1 and P4 could be detected with an RID detector, while only P4 showed an obvious peak ( $M_{n\text{GPC}} \sim 27\,500$ , PDI  $\sim 1.76$ ) with an UV detector (400 nm) (Figure 3b). Meanwhile, the P4 has a longer emission wavelength (518 nm) than the P1 (480 nm) (Figure S7) resulting from the structure of thiazolo[3,2- $\alpha$ ]pyrimidine. Therefore, the P4 solution (THF, 2 mg/mL) showed bright yellow fluorescence under blue light, while the P1 solution (THF, 2 mg/mL) only showed yellow-green fluorescence (Figure 3c), further confirming the preparation of a new functional polymer by the PPM strategy.

A new multicomponent polycondensate, poly-(dihydropyrimidin-2(1H)-thione) (P1), has been successfully prepared through the Biginelli reaction. The P1 can be regarded as a highly reactive polymer precursor due to the thiourea moiety in the polymer structure. Benefiting from the highly efficient thiourea–haloalkane reaction, the P1 can be easily modified through the PPM strategy with various haloalkanes to incorporate new functional groups such as vinyl and alkynyl for further modification. In addition, a new heterocycle can be in situ generated in the polymer main chain by choosing suitable haloalkane to alter the polymer's optical properties, further confirming the PPM as a powerful tool to prepare new functional polymers.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsmacrolett.5b00428.

Detailed experimental procedures,  $^1\text{H}$  NMR spectrum during polycondensation, etc. (PDF)

## ■ AUTHOR INFORMATION

### Corresponding Author

\*E-mail: leitao@mail.tsinghua.edu.cn.

### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

This research was supported by the National Science Foundation of China (21104039, 21372033, and the Qing Lan Project).

## ■ REFERENCES

- Gauthier, M. A.; Gibson, M. I.; Klok, H. A. *Angew. Chem., Int. Ed.* **2009**, *48*, 48.
- Ono, R. J.; Liu, S. Q.; Venkataraman, S.; Chin, W.; Yang, Y. Y.; Hedrick, J. L. *Macromolecules* **2014**, *47*, 7725.
- Iha, R. K.; Wooley, K. L.; Nyström, A. M.; Burke, D. J.; Kade, M. J.; Hawker, C. J. *Chem. Rev.* **2009**, *109*, 5620.
- Hunt, J. N.; Feldman, K. E.; Lynd, N. A.; Deek, J.; Campos, L. M.; Spruell, J. M.; Hernandez, B. M.; Kramer, E. J.; Hawker, C. J. *Adv. Mater.* **2011**, *23*, 2327.
- Jo, H.; Theato, P. *Adv. Polym. Sci.* **2015**, DOI: 10.1007/12\_2015\_315.
- Cunningham, W. A. *J. Chem. Educ.* **1935**, *12*, 120.
- Günay, K. A.; Theato, P.; Klok, H.-A. *Functional Polymers by Post-Polymerization Modification: Concepts, Guidelines, and applications* **2013**, 1.
- Barbey, R.; Perrier, S. b. *ACS Macro Lett.* **2013**, *2*, 366.
- Perrier, S.; Takolpuckdee, P.; Mars, C. A. *Macromolecules* **2005**, *38*, 2033.
- Semsarilar, M.; Perrier, S. *Nat. Chem.* **2010**, *2*, 811.
- Golas, P. L.; Matyjaszewski, K. *Chem. Soc. Rev.* **2010**, *39*, 1338.
- Lowe, A. B. *Polym. Chem.* **2010**, *1*, 17.
- Roy, D.; Brooks, W. L.; Sumerlin, B. S. *Chem. Soc. Rev.* **2013**, *42*, 7214.
- Mukherjee, S.; Bapat, A. P.; Hill, M. R.; Sumerlin, B. S. *Polym. Chem.* **2014**, *5*, 6923.
- Robb, M. J.; Connal, L. A.; Lee, B. F.; Lynd, N. A.; Hawker, C. J. *Polym. Chem.* **2012**, *3*, 1618.
- Billiet, L.; Fournier, D.; Du Prez, F. *Polymer* **2009**, *50*, 3877.
- Reinicke, S.; Espeel, P.; Stamenović, M. M.; Du Prez, F. E. *ACS Macro Lett.* **2013**, *2*, 539.
- Yu, L.; Wang, L.-H.; Hu, Z.-T.; You, Y.-Z.; Wu, D.-C.; Hong, C.-Y. *Polym. Chem.* **2015**, *6*, 1527.
- Zhang, Z.; You, Y.-Z.; Wu, D.-C.; Hong, C.-Y. *Macromolecules* **2015**, *48*, 3414.
- Rudick, J. G. *J. Polym. Sci., Part A: Polym. Chem.* **2013**, *51*, 3985.
- Kakuchi, R. *Angew. Chem., Int. Ed.* **2014**, *53*, 46.
- Sehlinger, A.; Dannecker, P.-K.; Kreye, O.; Meier, M. A. *Macromolecules* **2014**, *47*, 2774.
- Yang, B.; Zhao, Y.; Wang, S.; Zhang, Y.; Fu, C.; Wei, Y.; Tao, L. *Macromolecules* **2014**, *47*, 5607.
- Yang, B.; Zhao, Y.; Ren, X.; Zhang, X.; Fu, C.; Zhang, Y.; Wei, Y.; Tao, L. *Polym. Chem.* **2015**, *6*, 509.
- Espeel, P.; Carrette, L. L.; Bury, K.; Capenberghs, S.; Martins, J. C.; Du Prez, F. E.; Madder, A. *Angew. Chem., Int. Ed.* **2013**, *52*, 13261.
- Espeel, P.; Du Prez, F. E. *Eur. Polym. J.* **2015**, *62*, 247.

- (27) Ntoukam, D. H. S.; Hervé, D.; Luinstra, G. A.; Theato, P. *J. Polym. Sci., Part A: Polym. Chem.* **2014**, *52*, 2841.
- (28) Seuyep N., D. H.; Denis, H.; Luinstra, G. A.; Theato, P. *Polym. Chem.* **2013**, *4*, 2724.
- (29) Kakuchi, R. *Adv. Polym. Sci.* **2015**, *269*, 1.
- (30) Kakuchi, R.; Theato, P. *ACS Macro Lett.* **2014**, *3*, 329.
- (31) Brändle, A.; Khan, A. *Polym. Chem.* **2012**, *3*, 3224.
- (32) Saha, A.; De, S.; Stuparu, M. C.; Khan, A. *J. Am. Chem. Soc.* **2012**, *134*, 17291.
- (33) Espeel, P.; Goethals, F.; Stamenović, M. M.; Petton, L.; Du Prez, F. E. *Polym. Chem.* **2012**, *3*, 1007.
- (34) Espeel, P.; Du Prez, F. E. *Adv. Polym. Sci.* **2015**, *269*, 105.
- (35) Nicolas, J.; Mantovani, G.; Haddleton, D. M. *Macromol. Rapid Commun.* **2007**, *28*, 1083.
- (36) Richards, S. J.; Jones, M. W.; Hunaban, M.; Haddleton, D. M.; Gibson, M. I. *Angew. Chem., Int. Ed.* **2012**, *51*, 7812.
- (37) Handa, N. V.; Serrano, A. V.; Robb, M. J.; Hawker, C. J. *J. Polym. Sci., Part A: Polym. Chem.* **2015**, *53*, 831.
- (38) Leibfarth, F. A.; Hawker, C. J. *J. Polym. Sci., Part A: Polym. Chem.* **2013**, *51*, 3769.
- (39) Slavin, S.; Burns, J.; Haddleton, D. M.; Becer, C. R. *Eur. Polym. J.* **2011**, *47*, 435.
- (40) Tao, L.; Zhu, C.; Wei, Y.; Zhao, Y. *Adv. Polym. Sci.* **2015**, *269*, 43.
- (41) Zhu, C.; Yang, B.; Zhao, Y.; Fu, C.; Tao, L.; Wei, Y. *Polym. Chem.* **2013**, *4*, 5395.
- (42) Zhao, Y.; Yu, Y.; Zhang, Y.; Yang, B.; Zhang, Q.; Wei, Y. *Polym. Chem.* **2015**, *9*, 4940.
- (43) Lengar, A.; Kappe, C. O. *Org. Lett.* **2004**, *6*, 771.
- (44) Singh, S.; Schober, A.; Gebinoga, M.; Groß, G. A. *Tetrahedron Lett.* **2009**, *50*, 1838.
- (45) Fatima, S.; Sharma, A.; Sharma, R.; Tripathi, R. P. *J. Heterocycl. Chem.* **2012**, *49*, 600.