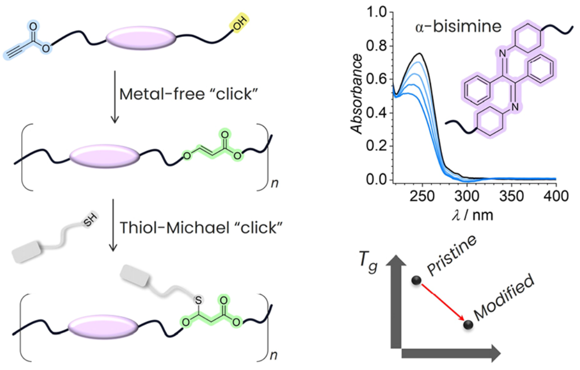
Access to Main-Chain Photoswitching Polymers via Hydroxyl-yne Click Polymerization

Linh Duy Thai, Jochen A. Kammerer, Patrick Théato, Hatice Mutlu,* and Christopher Barner-Kowollik*

ABSTRACT: Main-chain stimuli-responsive polymers synthesized via polymerization techniques that do not rely on metal-based catalysis are highly desirable for economic reasons and to avoid metal–polymer interactions. Herein, we introduce a metal-free head-to-tail organobase-catalyzed hydroxyl-yne click polymerization of an AB-type monomer to realize photoswitchable polymers featuring α-bismines as main-chain repeating units. The prepared main-chain α-bisimine-based polymers show excellent photoswitching in solution. We further post-functionalize the obtained polymers with various thiol compounds via thiol-Michael reactions to significantly lower the glass transition temperature (T_g), likely to be beneficial for the photoswitching process in the solid state. Thus, the herein introduced polymerization technique not only provides metal-free access to main-chain stimuli-responsive polymers, but also allows for the flexible post-modification of the obtained polymers to generate advanced macromolecular architectures with tunable properties.



The specific properties of adaptable polymeric materials in response to light[1], pH,[2] or temperature[3] are contingent on the inclusion of stimuli-sensitive moieties into the constituting polymer chains. The significance of adaptable soft-matter materials is demonstrated through their countless applications across many fields of science and industry.[4]

From a synthetic point of view, reversible deactivation radical polymerization (RDRP) techniques are routinely employed to synthesize polymers bearing pendant active stimuli-responsive moieties.[5] However, access to main-chain linear polymers via these pathways has proven challenging, despite recent innovative solutions, including radical ring-opening polymerization.[6] The insertion of such main-chain elements is of critical importance for specific applications, where large morphological changes are required.[7] In contrast, step-growth polymerization[8] provides an access route to main-chain functional polymers, even though one has to contend with high dispersities ($Đ > 2$) as a disadvantage. Nevertheless, other key features, e.g., a good control over the sequence order and scalability, strongly compensate for these disadvantages.[9]

We have previously demonstrated the feasibility of head-to-tail Acyclic Diene METathesis (ADMET) polymerization for the realization of responsive polymers having photoswitching moieties as main-chain active groups.[2,10] Macromolecular structures obtained via ADMET were further post-modified based on the formation of the internal acrylate bonds in their polymer backbone.[10a] However, the use of costly Hoveyda-Grubbs second generation (HG-II) catalysts potentially limits the application scope of this technique. Further issues entail the challenging removal of the Ru-based catalyst as well as the affinity of some chemical scaffolds, e.g., imines, hydrazones, toward complexation with such metal centers.[11] Therefore, alternative methods that enable efficient and environmentally friendly main-chain polymer synthesis (with well-defined structures and attractive properties) and post-polymerization modification are critically required.

Among various types of photoresponsive polymers, main-chain photoswitching polymers are highly attractive for many advanced applications, such as photoactuators,[12] energy storage,[13] and photopatterning,[14] due to the pronounced structural and morphological change induced by the clean, efficient, and reversible photoswitching (mostly via photo-isomerization) of the installed photoswitches.[15]

Herein, we introduce a metal-free (head-to-tail) hydroxyl-yne click polymerization[16] to synthesize main-chain α-bisimine polymers. Our approach is powerful as hydroxyl-yne ligation is a click reaction, reaching full conversion within minutes to hours.[17] To our best knowledge, it is the first time that hydroxyl-yne polymerization is reported in a head-to-tail fashion in the current report. The resulting main-chain

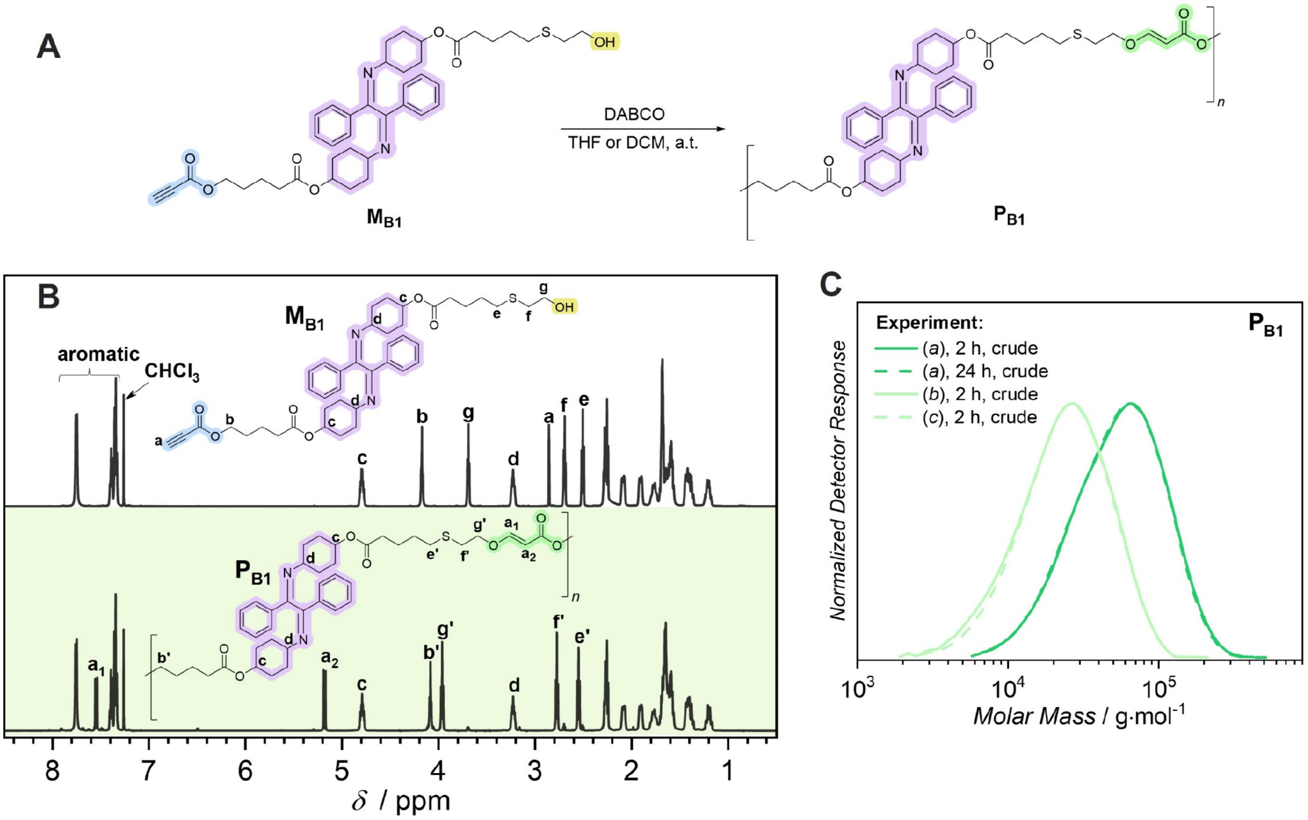


Figure 1. (A) Monomer design ($\mathbf{M_{B1}}$) and overall reaction scheme for the head-to-tail hydroxyl-yne polymerization. (B) Stacked ^{1}H NMR spectra (600 MHz, 32 scans, in $CDCl_3$) of monomer $\mathbf{M_{B1}}$ and the resulting polymer ($\mathbf{P_{B1}}$). The resonance assignment was assisted by ^{1}H and COSY NMR spectroscopy (refer to Supporting Information, Section 7). (C) Size exclusion chromatography (SEC) traces recorded in dimethylacetamide (DMAc) for polymer $\mathbf{P_{B1}}$, generated under different conditions (refer to Table 1 for the detailed experimental parameters). The number-averaged molar mass (M_n) was determined on the basis of poly(methyl methacrylate) (PMMA) calibration standards. The M_n for the synthesized polymer ($\mathbf{P_{B1}}$) is in the range of 18500−42500 g·mol^{-1}.

polymers exhibit excellent photoswitchabilty in solution. Our careful monomer design enables the post-modification of the polymer via a thiol-Michael click reaction, effectively grafting side chains to the polymer backbone to lower the resulting glass transition temperature (T_g), likely to benefit the solid state photoswitching efficiency.[10b] In short, we introduce a metal-free click polymerization as a potent method to integrate stimuli-responsive components, i.e., photoswitches, as main-chain repeating units as well as to construct graft polymers via post-polymerization modification with tunable properties.

We commence by discussing the design of the α-bisimine-based monomer for the head-to-tail hydroxyl-yne polymerization. The primary alcohol and the activated alkyne groups are placed at opposing ends of the monomer, making it an AB-type monomer (Figure 1A). In comparison to the head-to-tail (AB-type) ADMET monomer featuring an α-bisimine we have previously reported,[10b] the structure of the former contains one C−S bond generated by the thiol-halide substitution reaction. Depending on the length of the functional thiol used as well as the alkyl halide, the spacing or density of the chromophore can readily be adjusted.

Polymerization of the hydroxyl-yne monomer is induced upon addition of DABCO (1,4-diazabicyclo[2.2.2]octane) (20 mol %) at ambient temperature.[17] The influence of solvent and monomer concentration on the number-averaged molar mass (M_n) of the resulting polymers was studied. Accordingly, we selected dichloromethane (DCM) and tetrahydrofuran (THF) as solvents, and the molar concentration was set to either 0.4 or 0.8 M (refer to Table 1). Surprisingly, a lower concentration of monomer (0.4 M) in DCM solvent gave the best result in terms of M_n (M_n = 42500 g mol^{-1}, Figure 1C and Table 1), a value that is more than twice as high as that for main-chain α-bisimine polymers synthesized via head-to-tail ADMET polymerization.[10b] For other step-growth polymerization techniques, e.g., polycondensation, a highly concentrated solution of monomers, and long reaction times are generally required for preventing termination due to cyclization and to enable high conversion. Here, the hydroxyl-yne reaction as an X-yne click reaction[16,18] has a very high driving force, rapidly taking place and achieving very high conversions (>99%) within 2 h in a small-scale synthesis (100−200 mg). Prolonged

Table 1. Experiment Parameters for the Synthesis of Polymer $\mathbf{P_{B1}}$

experiment[a]	solvent	[$\mathbf{M_{B1}}$] (M)	M_n (g·mol^{-1})[b]	M_p (g·mol^{-1})[b]	$Đ$[b]
a	DCM	0.4	42500	69000	1.6
b	DCM	0.8	18500	27000	1.6
c	THF	0.4	19000	27000	1.6

[a] The polymerization was performed at ambient temperature for 2 h on a 100 mg scale. In all experiments, 20 mol % of the organic base (DABCO) was used. [b] DMAc-SEC on the basis of PMMA calibration standards, M_p denotes the peak molar mass and $Đ$ stands for dispersity.

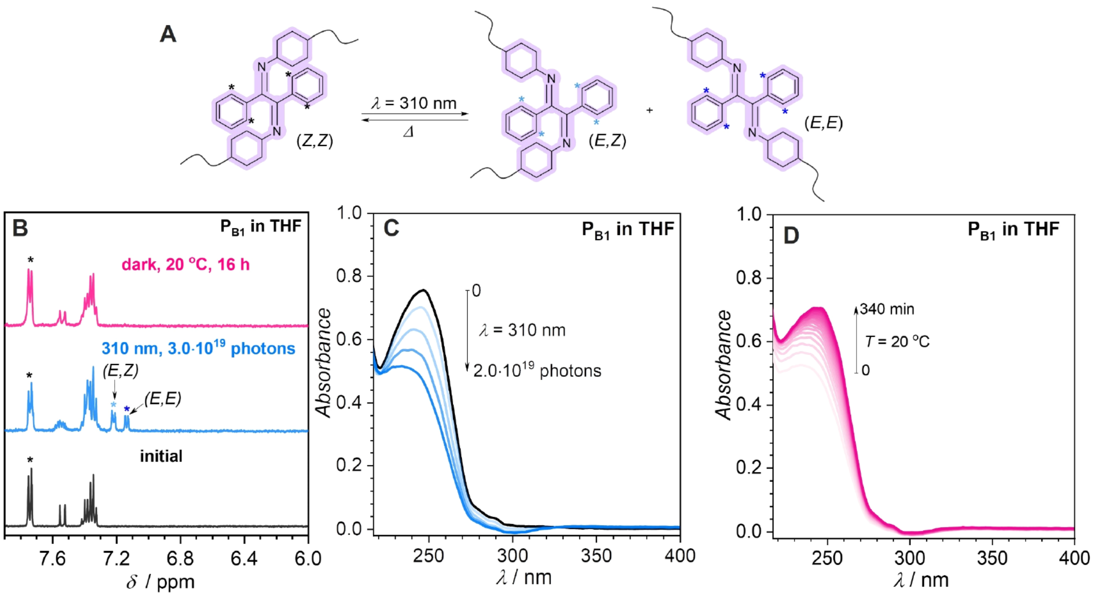


Figure 2. Solution isomerization of the α-bisimine core in the main-chain polymer $\mathbf{P_{B1}}$. (A) Overall scheme for forward and thermal back isomerization. (B) Zoom-in between 7.9 ppm and 6.0 ppm of the exemplary ^{1}H NMR spectra (400 MHz, 32 scans, CD_2Cl_2) of $\mathbf{P_{B1}}$ in solution (0.5 $g \cdot L^{-1}$ or 7.0×10^{-4} $mol \cdot L^{-1}$) before and after 310 nm irradiation. The resonances marked with an (*) correspond to the protons shown in (A) in the (*Z*,*Z*), (*E*,*Z*), (*E*,*E*) forms. UV−vis spectra of $\mathbf{P_{B1}}$ polymer solution (2.3×10^{-5} $mol \cdot L^{-1}$) were recorded after exposure to a specific number of photons at 310 nm irradiation (C) and thermal back isomerization at 20 °C in THF (D). It should be noted that prior to irradiation, THF was passed through a short basic aluminum oxide column to remove peroxides, which can potentially cause undesirable side reactions upon UV exposure.

reaction times (24 h) do not enhance the M_n (Figure 1C). We speculate that a lower concentration (0.4 M in our case) may help solubilize the growing polymer chains more efficiently during the polymerization. In fact, Tang et al. also reported an optimal hydroxyl-yne polymerization of stimuli-inactive monomers in 0.4 M solution at ambient temperature.[17] Furthermore, the head-to-tail design of our monomer eliminated the impact of a nonideal stoichiometry.

The selective reaction between the hydroxy and the alkyne groups to form vinyl ether ester bonds (i.e., ether acrylate) is evidenced by the ^{1}H NMR spectra recorded for the resulting polymer (Figure 1B). The resonances at 7.54 and 5.18 ppm are associated with the acrylate protons, in line with literature.[17,19] Furthermore, an inspection of the NMR spectrum indicates no evidence of transesterification.

More importantly, there was no impact on the α-bisimine core, as revealed by the stacked NMR spectra in Figure 1B. Thus, the technique features excellent control over the sequence of the α-bisimine photoswitches within the polymer chain.

We subsequently explored the solution isomerization of the α-bisimine core in THF. THF is an ideal solvent for the solution photoisomerization of the α-bisimine photoswitch due to the excellent solubility of the constituting polymer in THF and its low UV cutoff wavelength. We use a monochromatic wavelength of 310 nm at a laser power of 6.0−6.2 mW and initially traced the photoisomerization via UV−vis spectroscopy. As shown in Figure 2C, the gradual decrease of the peak absorption corresponding to the (*Z*,*Z*)-isomer upon 310 nm irradiation with different doses of photons indicated the photoisomerization to the (*Z*,*E*)- and (*E*,*E*)-form. Full recovery of the (*Z*,*Z*)-isomers was reached after approximately 6 h by thermal reversion at 20 °C (Figure 2D).

We subsequently employed ^{1}H NMR spectroscopy to study the isomerization kinetics of the macromolecular photoswitches in depth. We calculated the ratio of the isomers from the integral values of the resonance peaks associated with the respective isomers (i.e., (*Z*,*Z*), (*E*,*Z*), and (*E*,*E*)) after depositing a defined number of photons (up to 3.0×10^{19} photons at 310 nm). An exemplary ^{1}H NMR spectrum is shown in Figure 2B. In accordance with the UV−vis measurements, the NMR data show a full thermal back-switching process after 16 h at 20 °C when the resonances of the (*E*,*Z*) and (*E*,*E*) completely disappeared and those of the initial (*Z*,*Z*) isomer recovered (Figure 2B). Figure 3B displays the kinetic curves for the forward isomerization. To simplify the calculation of the rate coefficient ($k_{f,310}$), we assumed the direct conversion of the (*Z*,*Z*)-isomer to both (*E*,*Z*) and (*E*,*E*) isomers in the forward isomerization. Accordingly, we employed a first order kinetic model for the analysis of the data. While this model describes the experimental data reasonably well ($k_{f,310} = 1.3 \times 10^{-4}$ s^{-1}, $R^2 = 0.9752$; Figure 3D), the second-order kinetics provided a slightly better fit ($k_{f,310} = 0.23$ M^{-1} s^{-1}, $R^2 = 0.9856$, Figure 3F), which implies that a more complex process of the isomerization of the α-bisimine photoswitch might be operational. For the thermal reversion, the post-310 nm irradiated sample was kept in the dark at 20 °C, and the ^{1}H NMR spectra were recorded at 10 min intervals. The kinetic traces of the back-isomerization were subsequently plotted (Figure 4A). We fitted the traces with first-order kinetics, and the results clearly pointed to the direct reversion of (*E*,*Z*)- and (*E*,*E*)- isomers to the (*Z*,*Z*)-isomer (associated with the rate coefficients of k_{b1} and k_{b2}, respectively) rather than a sequential mechanism (i.e., (*E*,*E*) to (*E*,*Z*) to (*Z*,*Z*)).

We subsequently explored whether there is any significant difference in the photoisomerization behavior of the main-chain α-bisimine core of polymers synthesized from hydroxyl-yne versus those previously obtained via the metal-based ADMET polymerization route. Thus, we conducted an

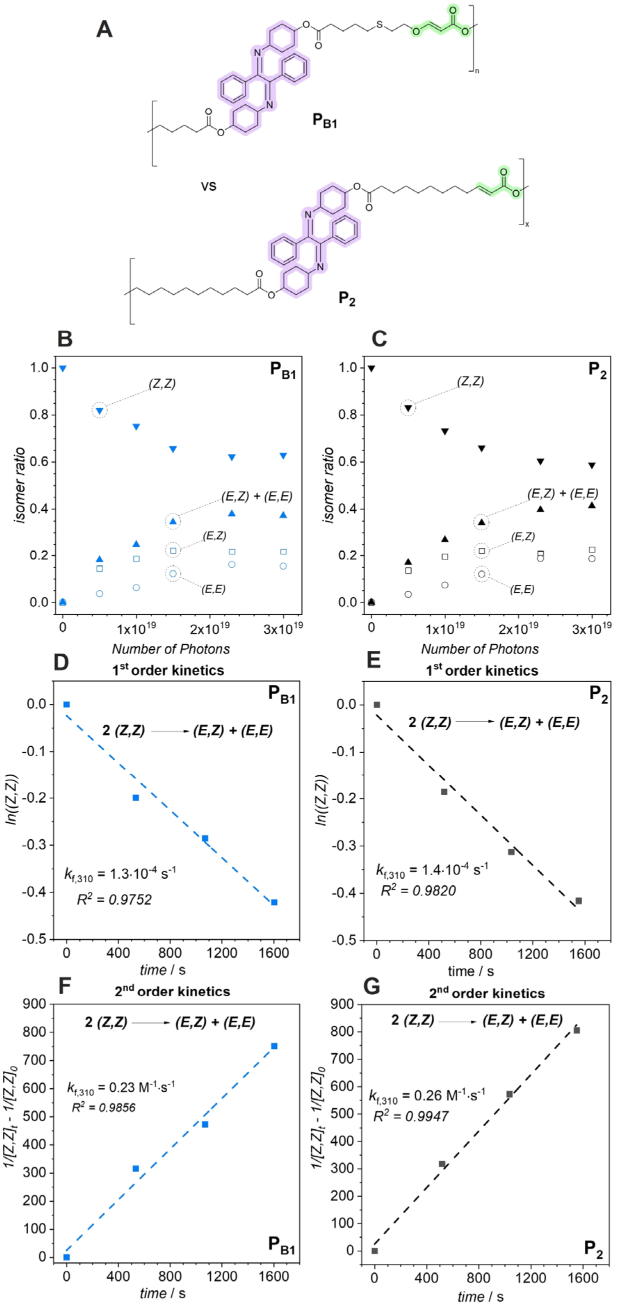


Figure 3. (A) Structural comparison of $\mathbf{P_{B1}}$ synthesized via head-to-tail hydroxyl-yne and $\mathbf{P_2}$ synthesized via head-to-tail ADMET polymerization. Kinetic traces for the forward isomerization at 310 nm irradiation (P = 6.0−6.2 mW, up to 3.0 × 10^{19} photons) for $\mathbf{P_{B1}}$ (B) and $\mathbf{P_2}$ (C). The ratio of isomers was determined by ^{1}H NMR spectroscopy. First-order kinetic model for the forward isomerization of $\mathbf{P_{B1}}$ (D) and $\mathbf{P_2}$ (E). Second-order kinetic analysis for the forward isomerization of $\mathbf{P_{B1}}$ (F) and $\mathbf{P_2}$ (G). The number of photons (N_p) was converted to time via eq S1.

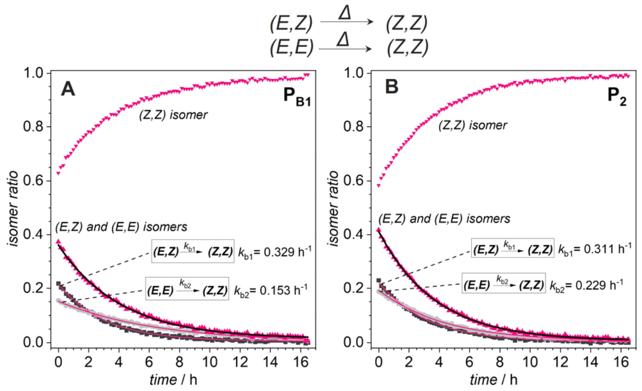


Figure 4. Thermal reversion of $\mathbf{P_{B1}}$ (A) and $\mathbf{P_2}$ (B) at 20 °C in THF. The ratio of isomers was calculated via ^{1}H NMR spectroscopy. The first-order kinetic model was used to derive the rate coefficients.

isomerization kinetics study of the ADMET-derived polymer $\mathbf{P_2}$, and a structural comparison is shown in Figure 3A.[10b] We used identical irradiation conditions, i.e., irradiation wavelength (λ = 310 nm), laser power (6.0−6.2 mW), solvent (THF), and temperature (25 °C for forward and 20 °C for thermal back isomerization). The first-order kinetic coefficient of the ADMET polymer $\mathbf{P_2}$ differs only insignificantly by 10^{-5}s^{-1} from the herein introduced hydroxyl-yne click polymer $\mathbf{P_{B1}}$ (Figure 3D,E and F,G and Figure 4A,B), within the error margin of the experiment, and we conclude that the polymerization technique does not affect the performance of the α-bisimine photoswitch. Further, the presence of a heteroatom (i.e., S) in polymer $\mathbf{P_{B1}}$ does not appear to significantly affect the kinetics of the isomerization.

We further inspected the possibility of post-polymerization modification of polymer $\mathbf{P_{B1}}$. Previously, we post-modified the photoswitching polymers synthesized from ADMET polymerization via thiol-Michael click reaction between the internal arylate groups in the polymer backbone and alkyl thiols.[10b] Such structural modification resulted in the reduction of T_g of the post-modified polymers and, most importantly, led to an increased photoswitching efficiency in the solid state.[10b] Thus, we designed our new monomer and the synthesis route in such a way that the obtained polymer $\mathbf{P_{B1}}$ also contained ether acrylate bonds that are suitable for a post-polymerization modification, and its thermal properties can be adjusted by thiol-Michael click reactions. We conducted the thiol-Michael reactions catalyzed by an *N*-heterocyclic carbene (NHC) catalyst[19a] between $\mathbf{P_{B1}}$ and different types of thiol compounds (Figure 5A; details on the reaction condition are provided in the SI, section 3). For linear aliphatic thiols, full conversion was achieved, whereas for thiols containing bulky groups, such as adamantane and *tert*-butyloxycarbonyl (Boc), the conversion was lower or zero (Figures 5A and S12−S21). ^{1}H NMR spectra clearly evidence the successful and selective reactions. The Resonances of the related protons shown in Figure 5A, i.e., protons $\mathbf{a_3}$ (δ = 4.87 ppm), $\mathbf{a_4}$ (δ = 2.73 and 2.87 ppm), and $\mathbf{g'}$ (δ = 3.55 and 3.84 ppm) are in agreement with values reported in literature[19a] (refer to Figures 5B and S12−S21). There was no shift of the resonances in the aromatic region associated with the α-bisimine core, indicating that photoswitching remains unaffected by the post-modification. We subsequently measured the T_g of the parent and the post-modified polymers (polymer $\mathbf{P_{B1\text{-}TMS}}$ is highly prone to hydrolysis and thus was excluded). Compared to the parent polymer ($\mathbf{P_{B1}}$), all post-modified polymers displayed lower T_g (Figure 5C). The polymer $\mathbf{P_{B1-C12}}$ modified with a C12-alkyl thiol had the lowest T_g (−9.2 °C), followed by polymer $\mathbf{P_{B1-C2Boc}}$ with the bulky Boc group (17.8 °C). Our results unambiguously show that hydroxyl-yne click polymerization is a potent method to install active moieties into the main-chain, and the resulting polymers can be manipulated chemically in a facile and effective manner.

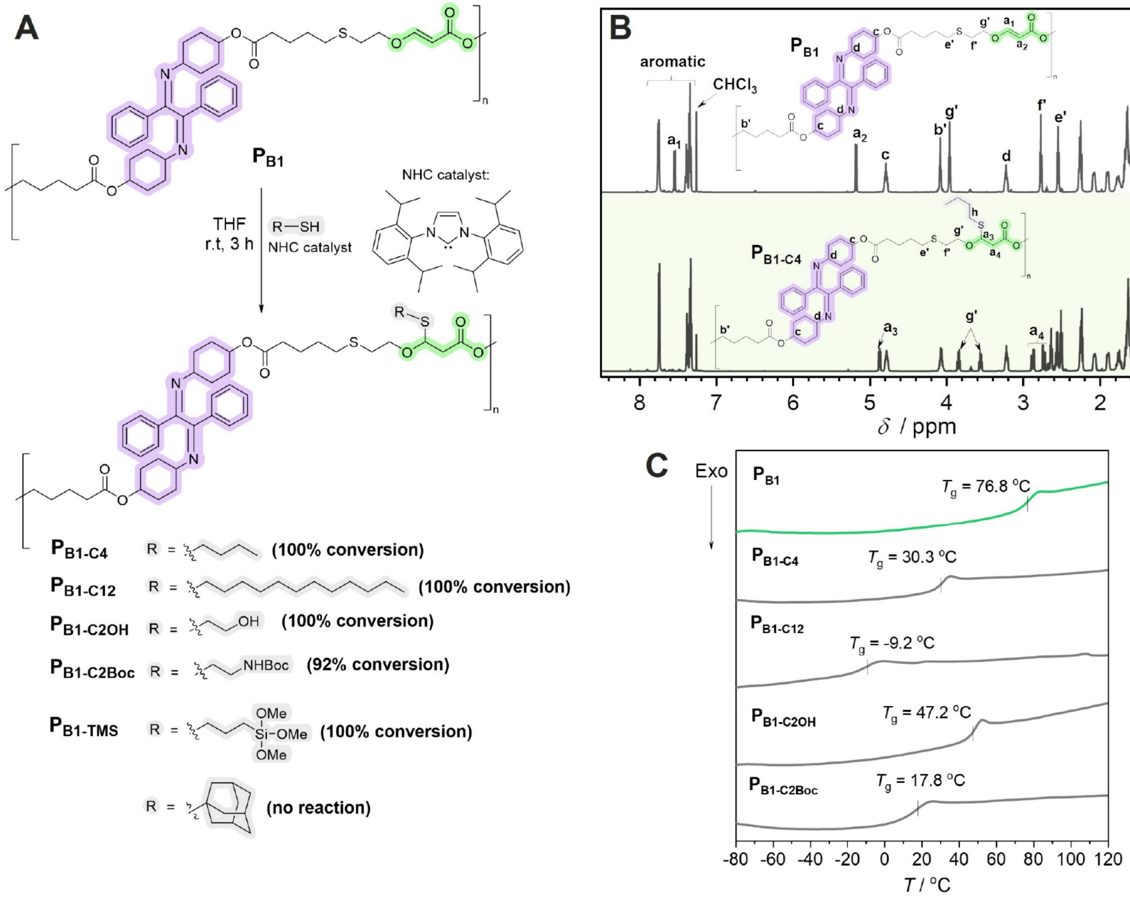


Figure 5. (A) General scheme for the post-polymerization modification of $\mathbf{P_{B1}}$ via thiol-Michael reaction. Details of the reaction conditions are provided in the SI, section 3. (B) Exemplary ^{1}H NMR spectrum (600 MHz, 32 scans, $CDCl_3$) of a post-modified polymer ($\mathbf{P_{B1-C4}}$). The resonance assignment was assisted by 1D and 2D (COSY) NMR spectroscopy (SI, section 7). The spectra for other compounds can be found in SI, section 7. (C) Stacked DSC thermograms of the parent polymer ($\mathbf{P_{B1}}$) and the post-modified polymers. Conditions: 3 cycles of heating and cooling from −90 to 120 °C at 20 °C·min^{-1} in a nitrogen atmosphere. The plotted DSC curves are taken from the second heating cycle.

We demonstrate the utilization of a hydroxyl-yne click reaction to polymerize head-to-tail stimuli-responsive monomers on the example of the α-bisimine photoswitch. The polymer displays reversible photoswitching with the kinetic traces agreeing with other α-bisimine main-chain polymers derived from ADMET polymerization, rendering the photoswitching efficiency independent of the synthetic route. Furthermore, we used facile thiol-Michael chemistry to efficiently modify the parent polymer and effectively lower the glass transition temperature (T_g), the relevant factor to increase the solid-state photoswitching efficiency, as we have previously demonstrated.[10b] By combining the two orthogonal reactions for the synthesis and post-polymerization modification, we obtained a metal-free α-bisimine main-chain polymer with a relatively higher molar mass (up to M_n = 42500 g·mol^{-1}) and tunable thermal properties. We believe that our synthetic approach can be generalized and applied to various stimuli-responsive molecules to access responsive macromolecular structures with tunable properties beyond tuning of glass transition temperatures.

AUTHOR INFORMATION

Corresponding Authors

Hatice Mutlu − *Institut de Science des Matériaux de Mulhouse, UMR 7361 CNRS/Université de Haute Alsace, Mulhouse Cedex 68057, France;* orcid.org/0000-0002-4683-0515; Email: hatice.mutlu@uha.fr

Christopher Barner-Kowollik − *School of Chemistry and Physics and Centre for Materials Science, Queensland University of Technology (QUT), Brisbane, QLD 4000, Australia; Institute of Nanotechnology (INT), Karlsruhe Institute of Technology (KIT), 76344 Eggenstein-Leopoldshafen, Germany;* orcid.org/0000-0002-6745-0570; Email: christopher.barnerkowollik@qut.edu.au

Authors

Linh Duy Thai − *School of Chemistry and Physics and Centre for Materials Science, Queensland University of Technology (QUT), Brisbane, QLD 4000, Australia; Institute of Nanotechnology (INT), Karlsruhe Institute of Technology (KIT), 76344 Eggenstein-Leopoldshafen, Germany;* orcid.org/0000-0003-2256-0423

Jochen A. Kammerer − *School of Chemistry and Physics and Centre for Materials Science, Queensland University of Technology (QUT), Brisbane, QLD 4000, Australia*

Patrick Théato − *Institute for Chemical Technology and Polymer Chemistry, Karlsruhe Institute of Technology (KIT), D-76131 Karlsruhe, Germany; Soft Matter Synthesis Laboratory, Institute for Biological Interfaces III, Karlsruhe Institute of Technology (KIT), D-76344 Eggenstein-Leopoldshafen, Germany;* orcid.org/0000-0002-4562-9254

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. CRediT: **Linh Duy Thai** conceptualization, data curation, investigation, writing-original draft; **Jochen A. Kammerer** writing-review & editing; **Patrick Théato** supervision, writing-review & editing; **Hatice Mutlu** conceptualization, supervision, writing-review & editing; **Christopher Barner-Kowollik** conceptualization, project administration, resources, supervision, writing-review & editing.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

C.B.-K. acknowledges the Australian Research Council (ARC) for funding in the context of a Laureate Fellowship, enabling his photochemical research program. The authors acknowledge funding for the project from QUT's Centre for Materials Science. H. M. acknowledges the University of Haute-Alsace for the financial support from the French National Research Agency with the reference "ANR-22-CPJ1-0077-01" and from the CNRS for the junior professorship contract. J.A.K. acknowledges the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) for his WBP fellowship 500289223. The Central Analytical Research Facility (CARF) at QUT is gratefully acknowledged. P.T. acknowledges support from the Helmholtz Association.

REFERENCES

(1) Bertrand, O.; Gohy, J.-F. Photo-responsive polymers: synthesis and applications. *Polym. Chem.* **2017**, *8* (1), 52−73.

(2) Thai, L. D.; Kammerer, J. A.; Mutlu, H.; Barner-Kowollik, C. Photo-and halochromism of spiropyran-based main-chain polymers. *Chemical Science* **2024**, *15*, 3687−3697.

(3) Jochum, F. D.; Theato, P. Temperature-and light-responsive smart polymer materials. *Chem. Soc. Rev.* **2013**, *42* (17), 7468−7483.

(4) Wei, M.; Gao, Y.; Li, X.; Serpe, M. J. Stimuli-responsive polymers and their applications. *Polym. Chem.* **2017**, *8* (1), 127−143.

(5) (a) Moad, G. RAFT polymerization to form stimuli-responsive polymers. *Polym. Chem.* **2017**, *8* (1), 177−219. (b) Zhang, C.; Ye, G.; Wang, W.; Ding, X.; Feng, Y.; Wang, R. Thermal, pH, and Photo Multistimuli Responsive Block Copolymer Self-Assembly Nanoparticles for Drug Delivery Using Visible-Light-Induced PET-RAFT. *ACS Applied Nano Materials* **2024**, *7* (1), 370−381. (c) Rajbanshi, A.; Hilton, E.; Dreiss, C. A.; Murnane, D.; Cook, M. T. Stimuli-Responsive Polymers for Engineered Emulsions. *Macromol. Rapid Commun.* **2024**, 2300723.

(6) (a) Prebihalo, E. A.; Luke, A. M.; Reddi, Y.; LaSalle, C. J.; Shah, V. M.; Cramer, C. J.; Reineke, T. M. Radical ring-opening polymerization of sustainably-derived thionoisochromanone. *Chemical Science* **2023**, *14* (21), 5689−5698. (b) Do, P. T.; Poad, B. L.; Frisch, H. Programming photodegradability into vinylic polymers via radical ring-opening polymerization. *Angew. Chem.* **2023**, *135* (6), No. e202213511. (c) Sbordone, F.; Veskova, J.; Richardson, B.; Do, P. T.; Micallef, A.; Frisch, H. Embedding peptides into synthetic polymers: radical ring-opening copolymerization of cyclic peptides. *J. Am. Chem. Soc.* **2023**, *145* (11), 6221−6229.

(7) Wang, V.; Kim, J.; Kim, J.; Lee, S. W.; Kim, K. T. On-demand shape transformation of polymer vesicles via site-specific isomerization of hydrazone photoswitches in monodisperse hydrophobic oligomers. *Polym. Chem.* **2021**, *12* (35), 5027−5036.

(8) Billiet, L.; Fournier, D.; Du Prez, F. Step-growth polymerization and 'click' chemistry: The oldest polymers rejuvenated. *Polymer* **2009**, *50* (16), 3877−3886.

(9) (a) Gerke, C.; Ebbesen, M. F.; Jansen, D.; Boden, S.; Freichel, T.; Hartmann, L. Sequence-controlled glycopolymers via step-growth polymerization of precision glycomacromolecules for lectin receptor clustering. *Biomacromolecules* **2017**, *18* (3), 787−796. (b) Collet, H.; Souaid, E.; Cottet, H.; Deratani, A.; Boiteau, L.; Dessalces, G.; Rossi, J. C.; Commeyras, A.; Pascal, R. An expeditious multigram-scale synthesis of lysine dendrigraft (DGL) polymers by aqueous N-carboxyanhydride polycondensation. *Chemistry−A European Journal* **2010**, *16* (7), 2309−2316.

(10) (a) Thai, L. D.; Guimaraes, T. R.; Spann, S.; Goldmann, A. S.; Golberg, D.; Mutlu, H.; Barner-Kowollik, C. Photoswitchable block copolymers based on main chain α-bisimines. *Polym. Chem.* **2022**, *13* (39), 5625−5635. (b) Thai, L. D.; Guimaraes, T. R.; Chambers, L. C.; Kammerer, J. A.; Golberg, D.; Mutlu, H.; Barner-Kowollik, C. Molecular photoswitching of main-chain α-bisimines in solid-state polymers. *J. Am. Chem. Soc.* **2023**, *145* (27), 14748−14755. (c) Thai, L. D.; Fanelli, J.; Munaweera, R.; O'Mara, M. L.; Barner-Kowollik, C.; Mutlu, H. Main-chain Macromolecular Hydrazone Photoswitches. *Angew. Chem., Int. Ed.* **2024**, *63* (4), No. e202315887.

(11) (a) Edwards, J. P.; Wolf, W. J.; Grubbs, R. H. The synthesis of cyclic polymers by olefin metathesis: Achievements and challenges. *J. Polym. Sci., Part A: Polym. Chem.* **2019**, *57* (3), 228−242. (b) Tatum, L. A.; Su, X.; Aprahamian, I. Simple hydrazone building blocks for complicated functional materials. *Acc. Chem. Res.* **2014**, *47* (7), 2141−2149. (c) Greb, L.; Mutlu, H.; Barner-Kowollik, C.; Lehn, J.-M. Photo-and metallo-responsive N-alkyl α-bisimines as orthogonally addressable main-chain functional groups in metathesis polymers. *J. Am. Chem. Soc.* **2016**, *138* (4), 1142−1145.

(12) (a) Chen, M.; Yao, B.; Kappl, M.; Liu, S.; Yuan, J.; Berger, R.; Zhang, F.; Butt, H. J.; Liu, Y.; Wu, S. Entangled azobenzene-containing polymers with photoinduced reversible solid-to-liquid transitions for healable and reprocessable photoactuators. *Adv. Funct. Mater.* **2020**, *30* (4), 1906752. (b) Ryabchun, A.; Li, Q.; Lancia, F.; Aprahamian, I.; Katsonis, N. Shape-persistent actuators from hydrazone photoswitches. *J. Am. Chem. Soc.* **2019**, *141* (3), 1196−1200.

(13) (a) Qiu, Q.; Yang, S.; Gerkman, M. A.; Fu, H.; Aprahamian, I.; Han, G. G. Photon energy storage in strained cyclic hydrazones: emerging molecular solar thermal energy storage compounds. *J. Am. Chem. Soc.* **2022**, *144* (28), 12627−12631. (b) Petersen, A. U.; Hofmann, A. I.; Fillols, M.; Manso, M.; Jevric, M.; Wang, Z.; Sumby, C. J.; Müller, C.; Moth-Poulsen, K. Solar energy storage by molecular norbornadiene−quadricyclane photoswitches: polymer film devices. *Advanced Science* **2019**, *6* (12), 1900367.

(14) Weis, P.; Wang, D.; Wu, S. Visible-light-responsive azopolymers with inhibited $\pi-\pi$ stacking enable fully reversible photopatterning. *Macromolecules* **2016**, *49* (17), 6368−6373.

(15) Goulet-Hanssens, A.; Eisenreich, F.; Hecht, S. Enlightening materials with photoswitches. *Adv. Mater.* **2020**, *32* (20), 1905966.

(16) Fu, X.; Qin, A.; Tang, B. Z. X-yne click polymerization. *Aggregate* **2023**, *4* (5), No. e350.

(17) Si, H.; Wang, K.; Song, B.; Qin, A.; Tang, B. Z. Organobase-catalysed hydroxyl−yne click polymerization. *Polym. Chem.* **2020**, *11* (14), 2568−2575.

(18) (a) Akar, E.; Luleburgaz, S.; Gunay, U. S.; Kumbaraci, V.; Tunca, U.; Durmaz, H. Amino-yne reaction: An exquisite method for

polymer-polymer conjugation and post-polymerization modification. *Eur. Polym. J.* **2023**, *199*, 112470. (b) Daglar, O.; Gunay, U. S.; Hizal, G.; Tunca, U.; Durmaz, H. Extremely rapid polythioether synthesis in the presence of TBD. *Macromolecules* **2019**, *52* (9), 3558−3572.

(19) (a) Song, B.; Lu, D.; Qin, A.; Tang, B. Z. Combining hydroxyl-yne and thiol-ene click reactions to facilely access sequence-defined macromolecules for high-density data storage. *J. Am. Chem. Soc.* **2022**, *144* (4), 1672−1680. (b) Jiang, Q.; Zhang, H.; Jiang, Q.; Zhang, S.; Guan, S.; Huang, W.; Xue, X.; Yang, H.; Jiang, L.; Jiang, B.; Komarneni, S. Hydroxyl−yne click polymerization: a facile strategy toward poly (vinyl amino ether ester) s with color-tunable luminescence. *Polym. Chem.* **2023**, *14* (11), 1232−1240.