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ARTICLE

Using the Dynamic Behavior of Macrocyclic Monomers with a Bis(hindered amino)disulfide Linker for the Preparation of End-functionalized Polymers

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Polymer topology transformations based on dynamic covalent chemistry (DCC) have attracted broad interest as the macroscopic properties of polymers can be freely changed in response to the polymer topology even after their synthesis. However, controlling the primary structures that accompany the topology transformation via DCC remains challenging. Herein, a method is presented that allows controlling functional end groups and molecular weight in DCC-based polymers using a combination of macrocyclic monomers and bifunctional acyclic compounds that contain bis(2,2,6,6-tetramethylpiperidin-1-yl)disulfide (BiTEMPS) moieties. The BiTEMPS moieties are stable at room temperature, but exchange disulfide bonds above 80 °C. Specifically, end-functionalized polymers were synthesized by simply heating a mixture of a macrocyclic compound with one BiTEMPS moiety and bifunctional acyclic BiTEMPS compounds as sources of repeat units and terminal groups, respectively. In the present method, various end-functionalized polymers including A-B-A type triblock copolymers with roughly controlled molecular weight were prepared by changing the chemical structures of the bifunctional BiTEMPS compounds and their feed ratio relative to the cyclic monomers.

Introduction

The chemical structures of polymers are characterized not only by the chemical structures and number of repeat units, but also by the chemical structures of the end groups. The structures of the end groups of polymer chains significantly affect the physical properties of the polymeric materials, even though the number of terminal moieties is minuscule relative to that of the repeat units.[1–7] Over the last few decades, a vast body of research has been dedicated to the generation of precision polymerization systems that allow controlling the primary structure of polymers.[8–14] On the other hand, dynamic covalent chemistry (DCC),[15–23] which refers to reversible chemical reactions under conditions of equilibrium control, has also been employed to control the primary structure in polymers. As the formation of products occurs under thermodynamic control, the distribution of DCC-based products depends on their relative stability. In the synthesis of DCC-based polymers, the polymerization of macrocyclic monomers in the presence of acyclic compounds that act as chain-transfer agents, has been used to regulate primary structures, i.e., molecular weight and terminal structures.

For example, Grubbs *et al.* have reported the DCC-based synthesis of end-functionalized polymers by treating 1,4-cyclooctadiene (cyclic monomer) with functionalized acyclic alkenes in the presence of Grubbs catalyst.[24–27] Yokozawa *et al.* have developed a synthetic system for the generation of polyesters that controls the molecular weight and polymer end groups by using a combination of macrocyclic oligomers with ester and alkene moieties, and acyclic alkenes with functional groups in the presence of Grubbs catalyst.[28,29] The same group has also developed a system based on a combination of macrocyclic oligomers with ester linkages and acyclic esters with functional groups via base-catalyzed transesterifications.[30]

Although these reports demonstrate the possibility of controlling the primary structure of polymers via DCC, the number of linkages and repeat units applicable to DCC remain limited. Especially the synthesis of macrocyclic monomers with a specific number of dynamic covalent bonds in the cyclic topology remains quite challenging. If a series of macrocyclic monomers with well-defined structure was available and the molar ratio could be adjusted accurately in feed, it seems feasible that the applicability of DCC in polymer chemistry could be expanded.

Recently, we have developed a simple and efficient method for the preparation of structurally defined macrocycles with one DCC unit, i.e., the linker bis(2,2,6,6-tetramethylpiperidin-1-yl)disulfide (BiTEMPS) (**Figure 1a**).[31,32] Since the radicals generated from BiTEMPS upon heating are highly tolerant toward a variety of chemical species, including oxygen and

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olefins, BiTEMPS can be applied to the synthesis of various macrocyclic monomers from the corresponding linear polymers. Furthermore, the cyclization can be induced by simple heating, i.e., catalysts and/or additives are not required.

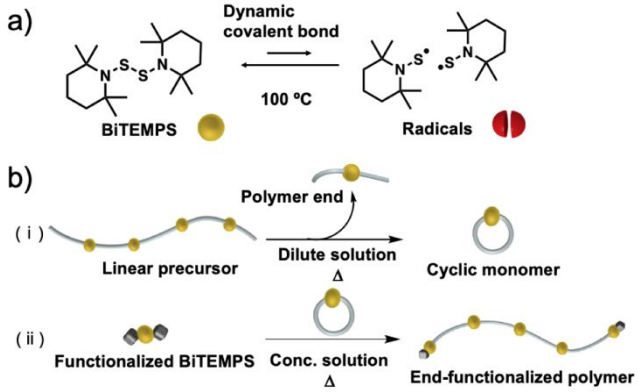


Figure 1. (a) Characteristic dissociation of BiTEMPS and (b) conceptual illustration of this study: i) synthesis of cyclic monomers with one BiTEMPS unit and ii) synthesis of BiTEMPS-based end-functionalized polymers.

Herein, we present a new method for controlling the primary structure of DCC-based polymers, i.e., controlling the functional end groups, the molecular weight, and the main-chain structure of DCC-based polymers by using macrocyclic monomers with one BiTEMPS unit. The polymers with the controlled primary structure were synthesized using the following sequence: (i) an entropy-driven transformation of the linear precursors with BiTEMPS in each repeat unit, induced by diluting and heating in order to isolate the macrocyclic monomers, followed by (ii) mixing the macrocyclic monomers with the functionalized BiTEMPS reagents and heating under high-concentration conditions (**Figure 1b**). The specific advantages of the present method are: 1) the possibility to control the molecular weight of the DCC-based polymer by accurately controlling the stoichiometry using isolated pure macrocyclic compounds with only one dynamic covalent bond; 2) the procedural simplicity, i.e., a reaction, in which macrocyclic monomers work as a source of the repeat units and the acyclic functionalized BiTEMPS reagent works as a source of the functional end group, is induced simply by heating under high-concentration conditions in air, whereby catalysts and/or additives are not required.

Experimental

Materials

All reagents and solvents were purchased from Sigma-Aldrich, FUJIFILM Wako Pure Chemical Corporation, Tokyo Chemical Industry, and Kanto Chemical, and used as received, unless otherwise noted. **BiTEMPS-diol,**[31] **BiTEMPS-diacrylate**[32] and **BiTEMPS** containing macrocyclic monomers[32] were synthesized according to previously published methods.

Measurements

^{1}H and ^{13}C NMR spectra were recorded on a Bruker AVANCE III HD500 spectrometer. The LED method for DOSY measurement was used. Pulse program: ledbpgp2s, Diffusion time: 40 ms, Diffusion gradient length: 2000 µs, Maximum gradient strength: 51 g/cm.[33] IR spectra were recorded on a JEOL FT/IR-4100 Fourier transform infrared spectrometer as thin films with KBr. Gel permeation chromatography (GPC) measurements were carried out at 40 °C on TOSOH HLC-8320 SEC system equipped with a guard column (TOSOH TSK guard column Super H-L), three columns (TOSOH TSK gel SuperH 6000, 4000, and 2500), a differential refractive index detector, and a UV-vis detector. Tetrahydrofuran (THF) was used as the eluent at a flow rate of 0.6 mL/min. Polystyrene (PS) standards (M_n = 4430–3142000; M_w/M_n = 1.03–1.08) were used to calibrate the GPC system. In experiments involving anthracene, GPC measurements were carried out at 40 °C on Jasco ChromNAV Lite system equipped with a guard column (TOSOH TSK guard column Super H-L), three columns (TOSOH TSK gel SuperH 6000, 4000, and 2500), a differential refractive index detector, and a UV-vis detector. Tetrahydrofuran (THF) was used as the eluent at a flow rate of 0.6 mL/min.

Synthesis of *c*-PBT(Bu)[32]

BiTEMPS-diacrylate[32] (1.89 g, 2.86 mmol), and 1,4-butanedithiol (335 µL, 2.86 mmol) were dissolved in THF (10.0 mL). Then dimethylphenylphosphine (DMPP) (50.0 µL, 350 µmol) was added to this solution and the mixture was stirred for 3 h at room temperature. The reaction mixture was poured into 500 mL of a poor solvent (hexane) to obtain **Linear polymer-1** as a white solid (2.13 g, 95.3%, M_n =12,000, PDI = 1.60).

In a 500 mL flask 1,4-dioxane (250 mL) was added to **Linear polymer-1** (2.50 g, M_n = 12,000, M_w/M_n = 1.60) under air. The mixture was allowed to stir at 100 °C for 24 hours. After the reaction, solvent was removed by freeze drying. Further purification was carried out by silica gel column chromatography with dichloromethane/hexane mixture (9/1 = v/v) and recrystallization from dichloromethane/hexane to afford ***c*-PBT(Bu)** (807 mg, 32.3%) as colorless crystal.

Synthesis of *c*-PBT(Ph) [32]

Linear polymer-2 (2.29 g, 94.3%, M_n =7,500, PDI = 1.94) which is a precursor of **PBT(Ph)** was synthesized under similar condition as above with **BiTEMPS-diacrylate** (2.00 g, 3.04 mmol), 1,4-benzenedithiol (428 mg, 3.03 mmol), and dimethylphenylphosphine (10 µL, 70 µmol).

In a 100 mL flask, 1,4-dioxane (180 mL) was added to **Linear polymer-2** (1.80 g, M_n = 7,500, M_w/M_n = 1.94) under air. The mixture was allowed to stir at 100 °C for 20 hours. After reaction, solvent was removed by freeze drying to obtain ***c*-PBT(Ph)** as white powder. Purification of **PBT(Ph)** was carried out using column chromatography on silica gel (dichloromethane/ethyl acetate, 95/5, v/v) to afford ***c*-PBT(Ph)** as a white solid (782 mg, yield 43.4%).

Synthesis of BiTEMPS-dialkyne

In a 20 mL flask in an ice bath, propargyl bromide (532 mg, 22.2 mmol) was added to a solution of **BiTEMPS-diol**[31] (1.00 g, 2.66 mmol) and sodium hydride (533 mg, 13.3 mmol) in dry DMAc

(2.50 mL). The solution was stirred at room temperature overnight. The resulting solution was poured into water and extracted with ethyl acetate. The combined organic layer was washed with water and brine, dried over Na_2SO_4, and concentrated under reduced pressure. Further purification was carried out by flash column chromatography with hexane/ethyl acetate mixture (9/1, v/v) and recrystallized from cyclohexane to afford **BiTEMPS-dialkyne** as yellow solid (1.13 g, 93.8%). ^{1}H NMR (500 MHz, $CDCl_3$): δ/ppm 4.19 (d, *J* = 2.4 Hz, 4H, -CC*H*$_2$O-), 3.95 (m, 2H, -C(CH$_3$)$_2$CH$_2$*CH*<), 2.42 (t, *J* = 2.4 Hz, 2H, C*H*C-), 2.00-1.96 (m, 4H, -C(CH$_3$)$_2$*CH*$_2$CH<), 1.44-1.40 (16H, -C(*CH*$_3$)$_2$CH$_2$CH<, -C(CH$_3$)$_2$*CH*$_2$CH<), 1.19 (s, 12H, -C(*CH*$_3$)$_2$CH$_2$CH<); ^{13}C NMR (125 MHz, $CDCl_3$): δ/ppm 80.09, 74.08, 70.10, 59.52, 55.11, 46.04, 34.93, 26.93; FT-IR (KBr, cm^{-1}): 3426, 3308, 3293, 2977, 2932, 2855, 2371, 1458, 1379, 1362, 1320, 1295, 1267, 1238, 1191, 1173, 1085, 1054, 1007, 986, 913, 891, 665, 634, 619, 526, 484; FAB-MS (m/z): calcd for $C_{24}H_{40}N_2O_2S_2$, 452.2531; found, 452.2526.

Synthesis of BiTEMPS-dianthracene

In a 20 mL flask in an ice bath, the mixture of 9-chloromethyl anthracene (1.50 g, 6.62 mmol) and dry DMAc (4.00 mL) was added to a solution of **BiTEMPS-diol** (503 mg, 1.34 mmol) and sodium hydride (264 mg, 6.60 mmol) in dry DMAc (2.00 mL). The solution was stirred at room temperature overnight. The resulting solution was poured into water and extracted with ethyl acetate. The combined organic layer was washed with water and brine, dried over Na_2SO_4, and concentrated under reduced pressure. Purification was carried out by flash column chromatography to afford **BiTEMPS-dianthracene** as yellow solid (626 mg, 63%). ^{1}H NMR (500 MHz, $CDCl_3$): δ/ppm 8.45 (s, 2H, aromatic), 8.35 (d, *J* = 8.8 Hz, 4H, aromatic), 8.01 (d, *J* = 8.3 Hz, 4H, aromatic), 7.55 (m, 4H, aromatic), 7.47 (m, 4H, aromatic), 5.49 (s, 4H, -C*H*$_2$O-), 3.95 (m, 2H, –C(CH$_3$)$_2$CH$_2$*CH*<), 2.13–2.11 (m, 4H, –C(CH$_3$)$_2$*CH*$_2$CH<), 1.52-1.44 (16H, –C(*CH*$_3$)$_2$CH$_2$CH<, –C(CH$_3$)$_2$*CH*$_2$CH<), 1.18 (s, 12H, –C(*CH*$_3$)$_2$CH$_2$CH<); ^{13}C NMR (125 MHz, $CDCl_3$): δ/ppm 131.64, 131.5, 129.18, 128.48, 126.35, 125.06, 124.35, 70.93, 62.38, 59.70, 46.73, 35.11, 27.11; FT-IR (KBr, cm^{-1}): 3422, 3048, 2967, 2931, 2886, 1624, 1460, 1377, 1363, 1344, 1237, 1173, 1118, 1075, 1038, 1005, 988, 967, 943, 909, 879, 838, 786, 727, 525; FAB-MS (m/z): calcd for $C_{48}H_{56}N_2O_2S_2$, 756.3783; found, 756.3794.

Synthesis of PBT(Bu)-dialkyne

In a 20 mL test tube, 1,4-dioxane (0.5 mL) was added to the mixture of ***c*-PBT(Bu)** (200 mg, 256 μmol) and **BiTEMPS-dialkyne** (11.6 mg, 25.6 μmol). Then, it was stirred at 100 °C for 24 hours. After the reaction, the reaction mixture was poured into 50 mL of methanol to afford **PBT(Bu)-dialkyne** (171 mg, 80.8%).

Synthesis of PBT(Bu+Ph)-dialkyne

In a 20 mL test tube, 1,4-dioxane (0.5 mL) was added to the mixture of ***c*-PBT(Bu)** (50.0 mg, 64.0 μmol), ***c*-PBT(Ph)** (51.3 mg, 64.0 μmol), and **BiTEMPS-dialkyne** (5.80 mg, 12.8 μmol). Then, it was stirred at 100 °C for 6 hours. After the reaction, the reaction mixture was poured into 50 mL of methanol to afford **PBT(Bu+Ph)-dialkyne** (72.3 mg, 67.5%).

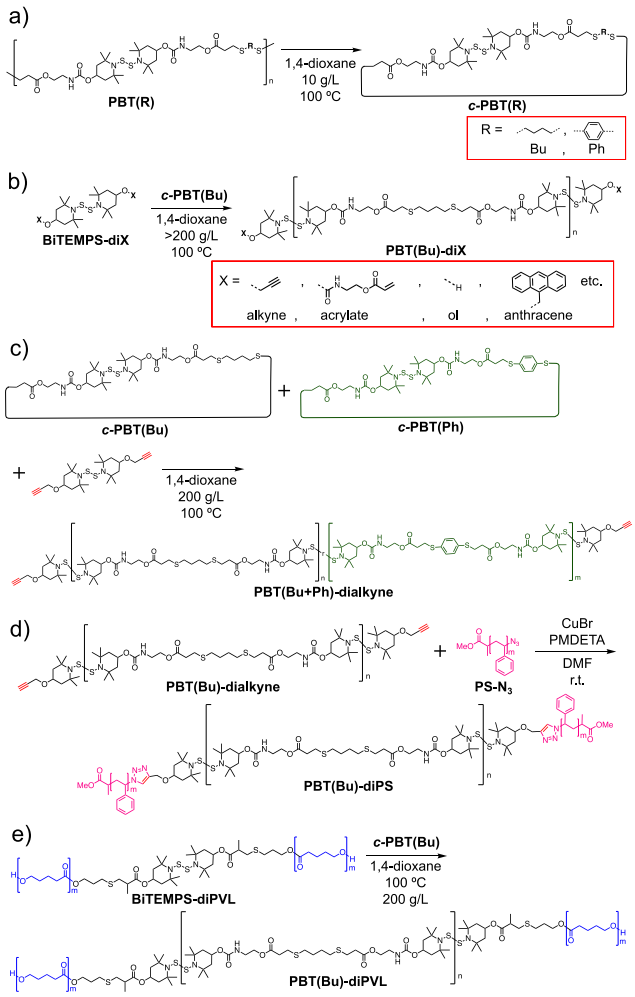
Synthesis of PBT(Bu)-diPS

In a 50 mL flask, a solution of **PBT(Bu)-dialkyne** (M_n = 7600 g/mol, M_w/M_n = 1.60, 50.0 mg, 6.60 μmol), PS-N_3 (M_n = 7500 g/mol, M_w/M_n = 1.12, 128 mg, 16.5 μmol), Cu(I)Br (2.08 mg, 12.5 μmol) and DMF (3 mL) was prepared. After the mixture was bubbled with nitrogen for 15 minutes, PMDETA (10.0 μL, 14.6 μmol) was added and stirred at room temperature for 24 hours. The reaction was quenched via exposure to air and diluted with THF. The solution was filtered through a column filled with neutral alumina in order to remove the copper complex. After evaporation and precipitating into hexane, the resulting precipitated polymer was collected by filtration. Further purification was carried out by preparative HPLC (eluent, chloroform) and dried under vacuum to obtain **PBT(Bu)-diPS** (67.0 mg, 44%).

Synthesis of PBT(Bu)-diPVL

In a 20 mL test tube, 1,4-dioxane (0.5 mL) was added to ***c*-PBT(Bu)** (100 mg, 128 μmol) and **BiTEMPS-diPVL** (M_n = 7300 g/mol, M_w/M_n = 1.15, 214 mg, 25.6 μmol)(ESI 1.9-1.11). Then, it was stirred at 100 °C for 6 hours. After the reaction, the solvent was removed by freeze drying. The reaction mixture was poured into 100 mL of methanol to afford **PBT(Bu)-diPVL** (M_n = 11000 g/mol, M_w/M_n = 1.22, 258 mg, 82.1%).

Results and discussion



Scheme 1. (a) Synthetic route to two macrocyclic monomers; (b) synthetic route to end-functionalized polymers; (c) synthetic route to end-functionalized random copolymers; (d), (e) synthetic route to tri-block copolymers.

Firstly, we synthesized two macrocyclic monomers and a series of acyclic BiTEMPS derivatives with functional groups. The two macrocyclic monomers were prepared by a previously reported method.[32] BiTEMPS-containing polymers (**PBT(R)**) were heated under relatively dilute conditions (10 g/L) to obtain ***c*-PBT(Bu)** and ***c*-PBT(Ph)** (**Scheme 1a**). A series of BiTEMPS derivatives with functional groups, i.e., **BiTEMPS-diol**,[31] **BiTMEPS-dialkyne**, **BiTEMPS-diacrylate**,[32] and **BiTEMPS-dianthracene**, were prepared. A BiTEMPS derivative with two hydroxy groups (**BiTMEPS-diol**) was used as the starting material that was converted into BiTEMPS-dialkyne and BiTEMPS-dianthracene by Williamson ether synthesis, as well as into BiTEMPS-diacrylate by a reaction with the corresponding isocyanate with the acrylate. The chemical structures of these compounds were confirmed by ^{1}H and ^{13}C NMR as well as FT-IR spectroscopy in combination with fast atom bombardment mass spectrometry (FAB-MS) (Experimental parts, **Figures S1** and **S2**).

With the resulting compounds in hand, i.e., two macrocyclic monomers, which work as a source of the repeat unit in the main chain, and functionalized BiTEMPS derivatives, which work as a source of polymer-ends, we attempted the synthesis of DCC-based linear polymers with functional groups at the polymer chain ends. Initially, we chose **BiTEMPS-dialkyne** as a source of the polymer termini to heat with macrocyclic monomer ***c*-PBT(Bu)**.

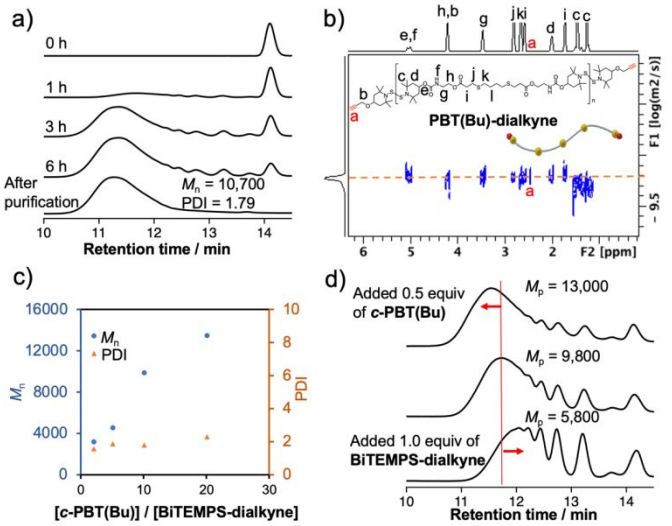


Figure 2.(a) Change in the GPC profiles of the polymerization of ***c*-PBT(Bu)** in the presence of **BiTEMPS-dialkyne** (calibration: PS standards; eluent: THF; flow rate: 0.6 mL/min; RI detector). (b) DOSY NMR spectrum of **PBT(Bu)-dialkyne** (500 MHz, 25 °C, $CDCl_3$). (c) Molecular weight and molecular-weight distribution of the polymer relative to the feed ratio. (d) Change in GPC profiles when 0.5 equiv. of ***c*-PBT(Bu)** or 1 equiv. of **BiTEMPS-dialkyne** were added during the polymerization.

It is well known that high polymerization concentrations are required for the synthesis of DCC-based linear polymers with high molecular weight.[17] Accordingly, we investigated the polymerization behavior of ***c*-PBT(Bu)** with **BiTEMPS-dialkyne** in 1,4-dioxane solutions with concentrations of 50 g/L, 100 g/L, 200 g/L, and 400 g/L (**Scheme 1b**). With increasing concentration, the polymerization proceeds faster. In order to obtain linear polymers with relatively high molecular weight, a monomer concentration of at least 200 g/L is required, and the reaction reaches completion after 6 h at 100 °C (**Figure S23**). The progress of the polymerization was monitored by GPC measurements (**Figure 2a**). After the reaction, the solution was added into methanol in order to remove residual macrocyclic monomers and acyclic BiTEMPS derivatives. All experimentally obtained ^{1}H NMR signals and their integrated values were consistent with the theoretical values calculated for the isolated polymer **PBT(Bu)-dialkyne** (**Figure S3**). DOSY NMR measurements were used to confirm the introduction of alkyne groups derived from **BiTEMPS-dialkyne**. We also checked that all the peaks that originate from the resulting polymer, including those of the termini, exhibit an almost single diffusion coefficient (**Figure 2b**). Moreover, we were able to obtain comparable results using various other functional groups such as hydroxy groups, acrylates, and anthracene moieties using

BiTEMPS-diol, **BiTEMPS-diacrylate**, and **BiTEMPS-dianthracene** as the acyclic components, respectively (**Figures S4–S12**).

Given that we demonstrated the synthesis of DCC-based polymers with functional groups at the polymer chain ends by adding functional BiTEMPS derivatives, we subsequently examined strategies to control the molecular weight of the resulting polymer. As the ratio between the source of the repeat unit (cyclic) and the terminal groups (acyclic) in the thermodynamic equilibrium is essential to determine the degree of polymerization, two approaches were investigated: 1) variations in the feed ratio and 2) addition of macrocyclic monomers or terminal groups during the polymerization. The former refers to changing the feed ratio between the macrocyclic monomer and the bifunctional BiTEMPS reagent. Accordingly, mixtures of molar ratios of 2/1, 5/1, 10/1, and 20/1 were treated for 6 h at 100 °C. As the macrocyclic compounds become the repeat unit of the polymer main chain, we were able to confirm that the molecular weight of the polymer increases upon increasing the mixing ratio between the macrocyclic monomer and the bifunctional BiTEMPS reagent (**Figure 2c**). The latter refers to adding further cyclic compounds or bifunctional BiTEMPS regent to the system during the polymerization. After 24 h of polymerization of ***c*-PBT(Bu)** / **BiTEMPS-dialkyne** = 5/1 at 100 °C, another 0.5 equivalents of ***c*-PBT(Bu)**, i.e., half amount of ***c*-PBT(Bu)** in feed, was added, and heating at 100 °C was continued for 6 h, which resulted in an increased M_p (**Figure 2d**, middle to top). On the other hand, upon adding 1 equivalent of **BiTEMPS-dialkyne**, i.e., same amount of **BiTEMPS-dialkyne** in feed, as a source of terminal groups, the M_p decreased (**Figure 2d**, middle to bottom). These results show that the molecular weight of the polymer can be tuned by the thermodynamic equilibrium ratio between the macrocyclic compounds and the reagents that determine the terminal structure.

In order to confirm whether functional groups were attached at the terminals, anthracene was introduced as a probe, as anthracene exhibits higher absorptivity than the components in the polymer chain, i.e., carbonyl groups and disulfide bonds. Given that **BiTEMPS-dianthracene** exhibits a higher UV absorption than ***c*-PBT(Bu)** at 375 nm, the insertion of anthracene into the polymer chain ends can be gauged by comparing the UV absorption (**Figures S25–S27**). Accordingly, we prepared the anthracene-terminated polymer (**PBT(Bu)-dianthracene**) by using **BiTEMPS-dianthracene** as a source of terminal groups, i.e., (***c*-PBT(Bu)/BiTEMPS-dianthracene** = 5/1; **Scheme 1b**). The UV absorption of **PBT(Bu)-dianthracene** was compared to that of **PBT(Bu)-dialkyne**, which was prepared in the same manner but using **BiTEMPS-dialkyne** instead of **BiTEMPS-dianthracene**. The 10-times larger peak intensity of **PBT(Bu)-dianthracene** relative to that of **PBT(Bu)-dialkyne** (**Figure S28**) in the GPC profiles detected by UV absorption at 375 nm, confirmed the introduction of anthracene into the resulting polymer. In addition, by assuming in first approximation that the UV absorption of groups other than anthracene is negligible, the abundance ratio of the terminal monomer after the reaction can be calculated from the GPC profiles at 375 nm, which exhibited good correlation to the residual ratio of the monomer calculated from the theoretical formula of the polymer (**Figure S29**, **Table S1**).

Subsequently, we applied this method to copolymerization reactions. It is known that copolymers are easily obtained by radical polymerization of two or more monomers, and that their properties depend on the monomers and their sequence. However, it should be noted that the reactivity of the monomers differs from that of the propagating radicals, which renders the preparation of copolymers via conventional free radical polymerization difficult. In contrast, the reactivity of the radicals generated from the two monomers in the present method is identical, i.e., both monomers cause the same radical exchange of BiTEMPS units (**Scheme 1c, Figure S24**). The progress of the copolymerization using equimolar amounts of ***c*-PBT(Bu)** and ***c*-PBT(Ph)** was monitored by GPC measurements (**Figure 3b**). The ^{1}H NMR spectrum of the obtained polymer, purified by reprecipitation in methanol, shows the all peaks derived from ***c*-PBT(Bu)** (k,l) and ***c*-PBT(Ph)** (m,n) as well as the alkyne peak (a) (**Figure S13**); the DOSY NMR spectrum (**Figure 3c**) exhibits a single diffusion coefficient, which confirms the copolymerization between ***c*-PBT(Bu)** and ***c*-PBT(Ph)** and the introduction of functional end groups in a one-pot synthesis.

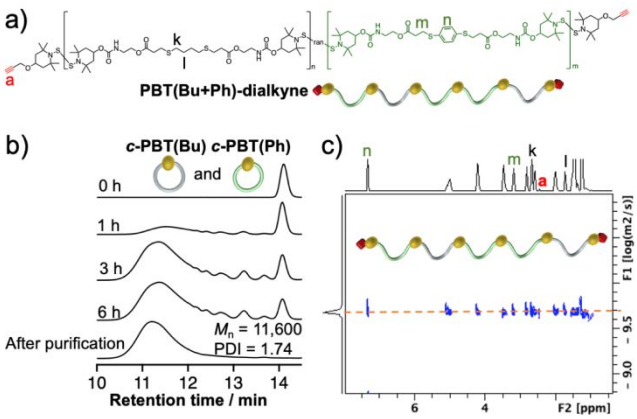


Figure 3.(a) Chemical structure of **PBT(Bu+Ph)-dialkyne**. (b) Change in the GPC profiles of the polymerization of ***c*-PBT(Bu)** and ***c*-PBT(Ph)** in the presence of **BiTEMPS-dialkyne** and after purification of **PBT(Bu+Ph)-dialkyne** (calibration: PS standards; eluent: THF; flow rate: 0.6 mL/min; RI detector). (c) DOSY NMR spectrum of **PBT(Bu+Ph)-dialkyne** (500 MHz, 25 °C, $CDCl_3$).

As an application and demonstration that telechelic polymers can be prepared by the present method, block copolymers were synthesized. The additional polymer chains were introduced into **PBT(Bu)-dialkyne** (M_p = 12,000; PDI = 1.60) via azide-alkyne cycloaddition (**Scheme 1d**). For that purpose, polystyrene with an azide group at one end (**PS-N_3**; M_p = 8,300; PDI = 1.11) was prepared. To achieve quantitative conversion, an excess of **PS-N_3** was used together with **PBT(Bu)-dialkyne**. The peak-top molecular weight shifted to higher molecular weight after the reaction. Further purification was carried out by preparative HPLC in order to obtain the corresponding block copolymer (**PBT(Bu)-diPS**; M_p = 22,000; PDI = 1.24) (**Figure 4b**). All signals and their integration values in the ^{1}H NMR spectrum are consistent with the theoretically expected values (**Figure S14**).

Moreover, we confirmed that all peaks exhibited a single diffusion coefficient in the DOSY NMR spectrum (**Figure 4a, c**), which demonstrates that the alkynes were quantitatively introduced at the terminal positions of the polymer, where they serve as an anchor point for the introduction of other polymer chains.

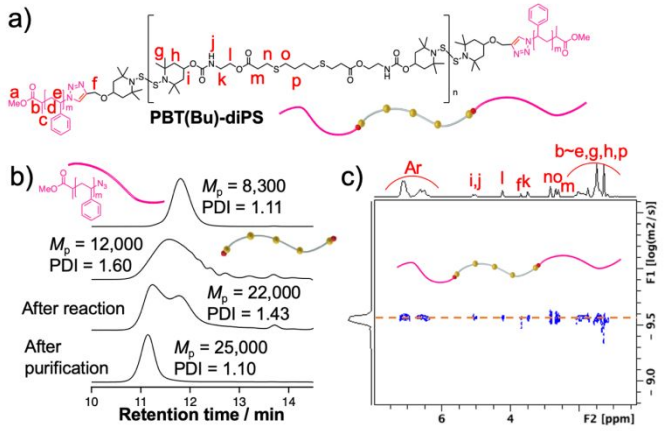


Figure 4. (a) Chemical structure of **PBT(Bu)-diPS**. (b) Change of the GPC profiles of azide-alkyne click reactions and GPC profile of **PBT(Bu)-diPS** (calibration: PS standards; eluent: THF; flow rate: 0.6 mL/min: RI detector). (c) DOSY NMR spectrum of **PBT(Bu)-diPS** (500 MHz, 25 °C, $CDCl_3$).

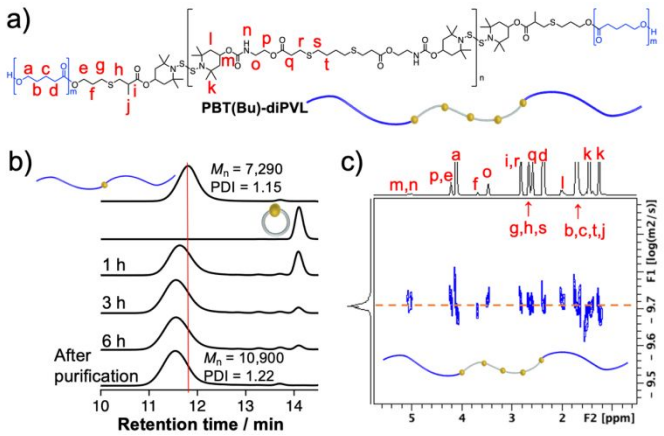


Figure 5.(a) Synthesis of **PBT(Bu)-diPVL**. (b) Change of the GPC profiles in the polymerization of ***c*-PBT(Bu)** in the presence of **BiTEMPS-diPVL**. (c) GPC profile of **PBT(Bu)-diPVL** (calibration: PS standard; eluent: THF; flow rate: 0.6 mL/min; RI detector).(d) ^{1}H DOSY NMR spectrum of **PBT(Bu)-diPVL** (500 MHz, 25 °C, $CDCl_3$).

Finally, we used a macromolecule as the source of the terminal groups, i.e., we attempted to insert repeat units that originate from cyclic monomers into macromolecular terminal groups. For that purpose, a macromolecule with one BiTEMPS unit at the center of the molecular chain (**BiTEMPS-diPVL**; M_n = 7,300; PDI = 1.15) was used as the terminal structure and heated under concentrated conditions with cyclic monomer ***c*-PBT(Bu)** to obtain the corresponding block copolymer (**PBT(Bu)-diPVL**; M_n = 10,900; PDI = 1.22) (**Scheme 1e**). As the reaction proceeded, the GPC peak of **BiTEMPS-diPVL** shifted to higher molecular weight, while the peak derived from the cyclic monomer decreased (**Figure 5b**). After the reaction, the polymer solution was added to methanol in order to remove low-molecular-weight fractions. In the ^{1}H NMR spectrum, all signals and their integrated values were consistent with the theoretically expected values (**Figure S19**). Moreover, all peaks exhibit a single diffusion coefficient in the DOSY NMR spectrum (**Figure 5a, c**). We also confirmed that the molecular weight in the middle of the triblock copolymer increased with increasing mixing ratio of the macrocyclic compounds (**Figures S20–S22**). Thus, we accomplished a one-pot synthesis of DCC-based tri-block copolymers under concomitant control of the molecular weight.

Conclusions

we have developed a polymerization method that allows controlling the primary structure of polymers by using macrocyclic monomers with one BiTEMPS unit, which works as dynamic covalent bond. Simple heating induces the polymerization reaction, i.e., catalysts and/or additives are not required. The one-pot synthesis of telechelic functional polymers, end-functionalized random copolymers, and ABA-type tri-block copolymers under control of the molecular weight were accomplished. As the structural options for the structure-defining cyclic monomers are virtually infinite, it should be possible to access a large variety of functional polymers that show the prominent properties.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

1 K. R. Huffman and D. J. Casey, *J. Polym. Sci., Polym. Chem. ed.* 1985, **23**, 1939–1954.

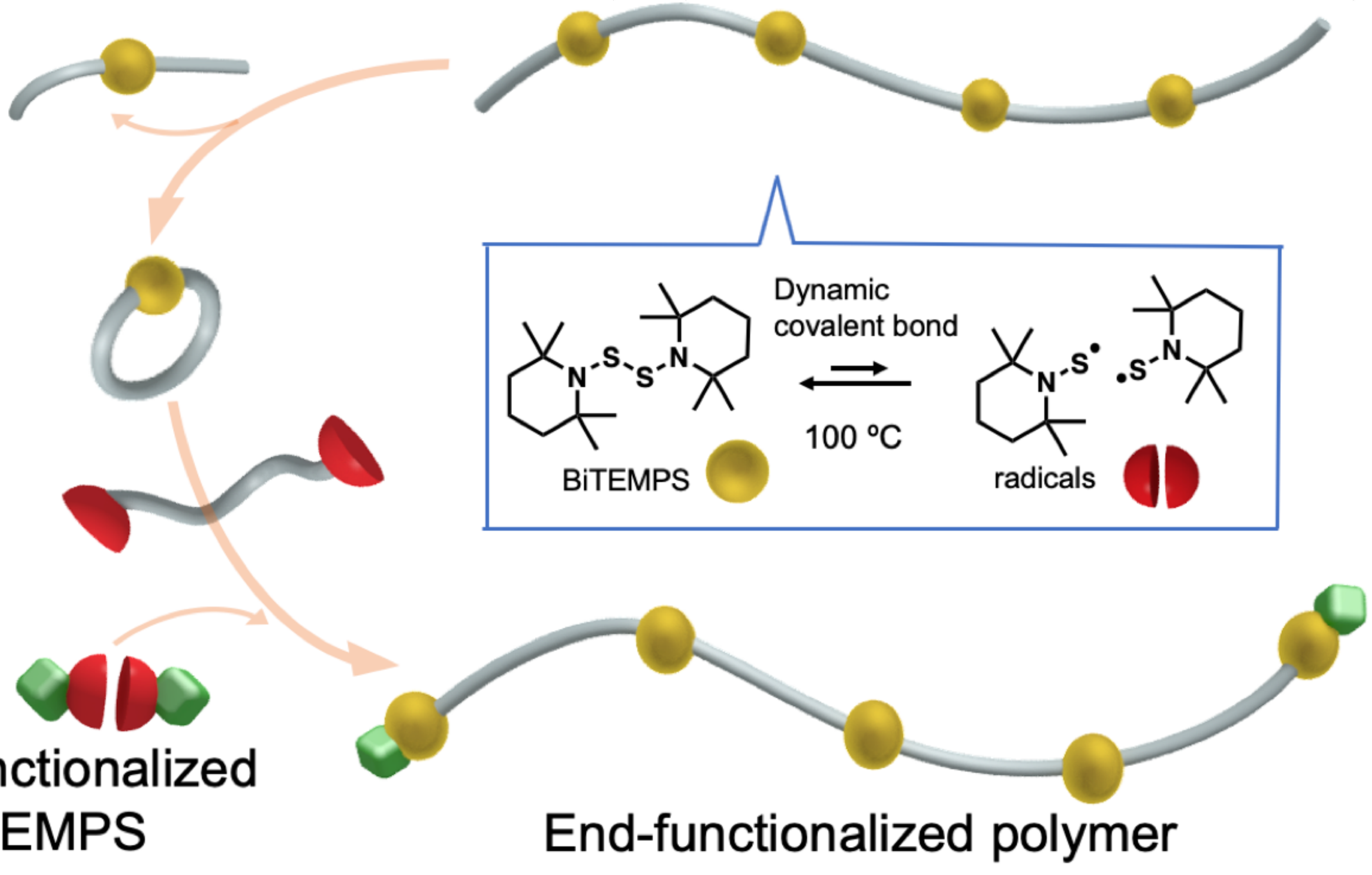
2 J. Sunshine, J. J. Green, K. P. Mahon, F. Yang, A. A. Eltoukhy, D. N. Nguyen, R. Langer and D. G. Anderson, *Adv. Mater.*, 2009, **21**, 4947–4951.

3 M. Kuemin, S. Schweizer, C. Ochsenfeld and H. Wennemers, *J. Am. Chem. Soc.*, 2009, **131**, 15474–15482.

4 Y. Kim, S. Cook, J. Kirkpatrick, J. Nelson, J. R. Durrant, D. D. C. Bradley, M. Giles, M. Heeney, R. Hamilton and I. McCulloch, *J. Phys. Chem. C*, 2007, **111**, 8137–8141.

5 J. Liu, T. Tanaka, K. Sivula, A. P. Alivisatos and J. M. J. Fréchet, *J. Am. Chem. Soc.*, 2004, **126**, 6550–6551.

6 B. J. B. Folmer, R. P. Sijbesma, R. M. Versteegen, J. A. J. Van Der Rijt and E. W. Meijer, *Adv. Mater.*, 2000, **12**, 874–878.
7 F. Ishiwari, G. Okabe, H. Ogiwara, T. Kajitani, M. Tokita, M. Takata and T. Fukushima, *J. Am. Chem. Soc.*, 2018, **140**, 13497–13502.
8 S. Perrier, *Macromolecules*, 2017, **50**, 7433–7447.
9 C. Fu, Z. Huang, C. J. Hawker, G. Moad, J. Xu and C. Boyer, *Polym. Chem.*, 2017, **8**, 4637–4643.
10 T. Yokozawa and Y. Ohta, *Chem. Rev.*, 2016, **116**, 1950–1958.
11 M. Ouchi, T. Terashima and M. Sawamoto, *Chem. Rev.*, 2009, **109**, 4963–5050.
12 S. Aoshima and S. Kanaoka, *Chem. Rev.*, 2009, **109**, 5245–5287.
13 N. Hadjichristidis, M. Pitsikalis, S. Pispas and H. Iatrou, *Chem. Rev.*, 2001, **101**, 3747–3792.
14 K. Matyjaszewski and J. Xia, *Chem. Rev.*, 2001, **101**, 2921–2990.
15 R. J. Wojtecki, M. A. Meador and S. J. Rowan, *Nat. Mater.*, 2011, **10**, 14–27.
16 A. Herrmann, *Chem. Soc. Rev.*, 2014, **43**, 1899–1933.
17 S. J. Rowan, S. J. Cantrill, G. R. L. Cousins, J. K. M. Sanders and J. F. Stoddart, *Angew. Chemie Int. Ed.*, 2002, **41**, 898–952.
18 P. Chakma and D. Konkolewicz, *Angew. Chemie - Int. Ed.*, 2019, **58**, 9682–9695.
19 S. P. Black, J. K. M. Sanders and A. R. Stefankiewicz, *Chem. Soc. Rev.*, 2014, **43**, 1861–1872.
20 J. M. Winne, L. Leibler and F. E. Du Prez, *Polym. Chem.*, 2019, **10**, 6091–6108.
21 A. P. Bapat, J. G. Ray, D. A. Savin and B. S. Sumerlin, *Macromolecules*, 2013, **46**, 2188–2198.
22 Y. Jin, Q. Wang, P. Taynton and W. Zhang, *Acc. Chem. Res.*, 2014, **47**, 1575–1586.
23 A. K. Chatterjee, T. L. Choi, D. P. Sanders and R. H. Grubbs, *J. Am. Chem. Soc.*, 2003, **125**, 11360–11370.
24 T. M. Trnka and R. H. Grubbs, *Acc. Chem. Res.*, 2001, **34**, 18–29.
25 X. Hou and K. Nomura, *J. Am. Chem. Soc.*, 2016, **138**, 11840–11849.
26 A. K. Diallo, X. Michel, S. Fouquay, G. Michaud, F. Simon, J. M. Brusson, J. F. Carpentier and S. M. Guillaume, *Macromolecules*, 2015, **48**, 7453–7465.
27 R. M. Thomas and R. H. Grubbs, *Macromolecules*, 2010, **43**, 3705–3709.
28 R. Okabayashi, Y. Ohta and T. Yokozawa, *Macromolecules*, 2017, **50**, 9589–9597.
29 R. Okabayashi, Y. Ohta and T. Yokozawa, *Macromolecules*, 2019, **52**, 1125–1133.
30 R. Okabayashi, Y. Ohta and T. Yokozawa, *Polym. Chem.*, 2019, **10**, 4973–4979.
31 A. Takahashi, R. Goseki and H. Otsuka, *Angew. Chem., Int. Ed.*, 2017, **56**, 2016–2021.
32 N. Tsurumi, R. Takashima, D. Aoki, S. Kuwata and H. Otsuka, *Angew. Chem., Int. Ed.*, 2020, **59**, 4269-4273.
33 D. Wu, A. Chen and C. S. Johnson, *J. Margn. Reson. A.*, 1995, **115**, 260–264.


Dynamic
covalent bond
100 °C
BiTEMPS
radicals
Functionalized
BiTEMPS
End-functionalized polymer