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Combining Enzymatic Monomer Transformation with Photoinduced Electron Transfer – Reversible Addition–Fragmentation Chain Transfer for the Synthesis of Complex Multiblock Copolymers

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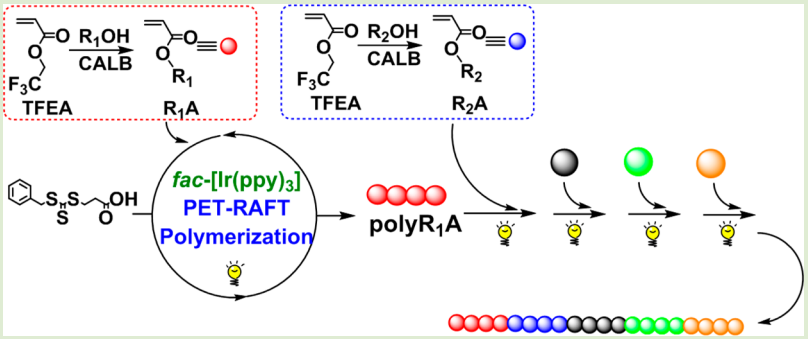
Supporting Information



ABSTRACT: A novel and facile method, involving enzymatic monomer synthesis and a photocontrolled polymerization technique, has been successfully employed for the preparation of high-order multiblock copolymers. New acrylate monomers were synthesized via enzymatic transacylation between an activated monomer, i.e., 2,2,2-trifluoroethyl acrylate (TFEA), and various functional alcohols. These synthesized monomers were successfully polymerized without further purification via photoinduced electron transfer–reversible addition–fragmentation chain transfer (PET-RAFT) polymerization under low energy blue LED light (4.8 W) in the presence of an iridium-based photoredox catalyst (*fac*-[Ir(ppy)$_3$]). In this condition, PET-RAFT allows us to achieve high monomer conversion (∼100%) with excellent integrity of the end group (>80%). Different multiblock (co)polymers, including poly(hexyl acrylate) pentablock homopolymer, poly(methyl acylate-*b*-ethyl acrylate-*b*-*n*-propyl acrylate-*b*-*n*-butyl acrylate-*b*-*n*-pentyl acrylate) pentablock copolymer, and poly(3-oxobutyl acrylate-*b*-methyl acrylate-*b*-3-(trimethylsilyl)prop-2-yn-1-yl acrylate) triblock copolymer containing functional groups were rapidly prepared via sequential addition of monomers without purification steps.

Modern synthetic methods demand high efficiency in terms of minimization of the number of synthesis and purification steps.[1,2] In organic chemistry, researchers try to combine a series of reactions in one synthetic operation to prepare sophisticated molecules.[3,4] Recently, such synthetic strategies have also been introduced into the synthesis of complex macromolecules.[5−10] For instance, Haddleton and co-workers have conducted simultaneous copper-catalyzed "click" reaction and atom transfer radical polymerization (ATRP) to prepare glycopolymers in one-pot polymerization.[11] Sawamoto et al. also combined living radical polymerization and transesterification to prepare copolymers with perfect control of monomer sequence.[12−14] However, these approaches require several purification steps for the synthesis of functional monomer and macromolecules, limiting the development of these creative methodologies. Thus, more elegant synthetic strategies toward complex macromolecular architectures, such as high-order multiblock copolymer with different functionalities, are still challenging. To overcome this challenge, organic chemists have developed enzymatic reaction due to their ability to catalyze specific reactions;[15,16] for instance, Lipase B from *Candida antarctica* (CALB) has proved to be an effective catalyst for the transacylation reaction between esters and nucleophile compounds, such as alcohols.[15] We have recently combined monomer transformation via enzymatic transacylation with controlled radical polymerization techniques, including ATRP and reversible addition–fragmentation chain transfer (RAFT) polymerization for the preparation of well-defined functional copolymers.[17−20]

With the requirement to achieve controlled polymerization in mild conditions and regulated by external stimuli, light-

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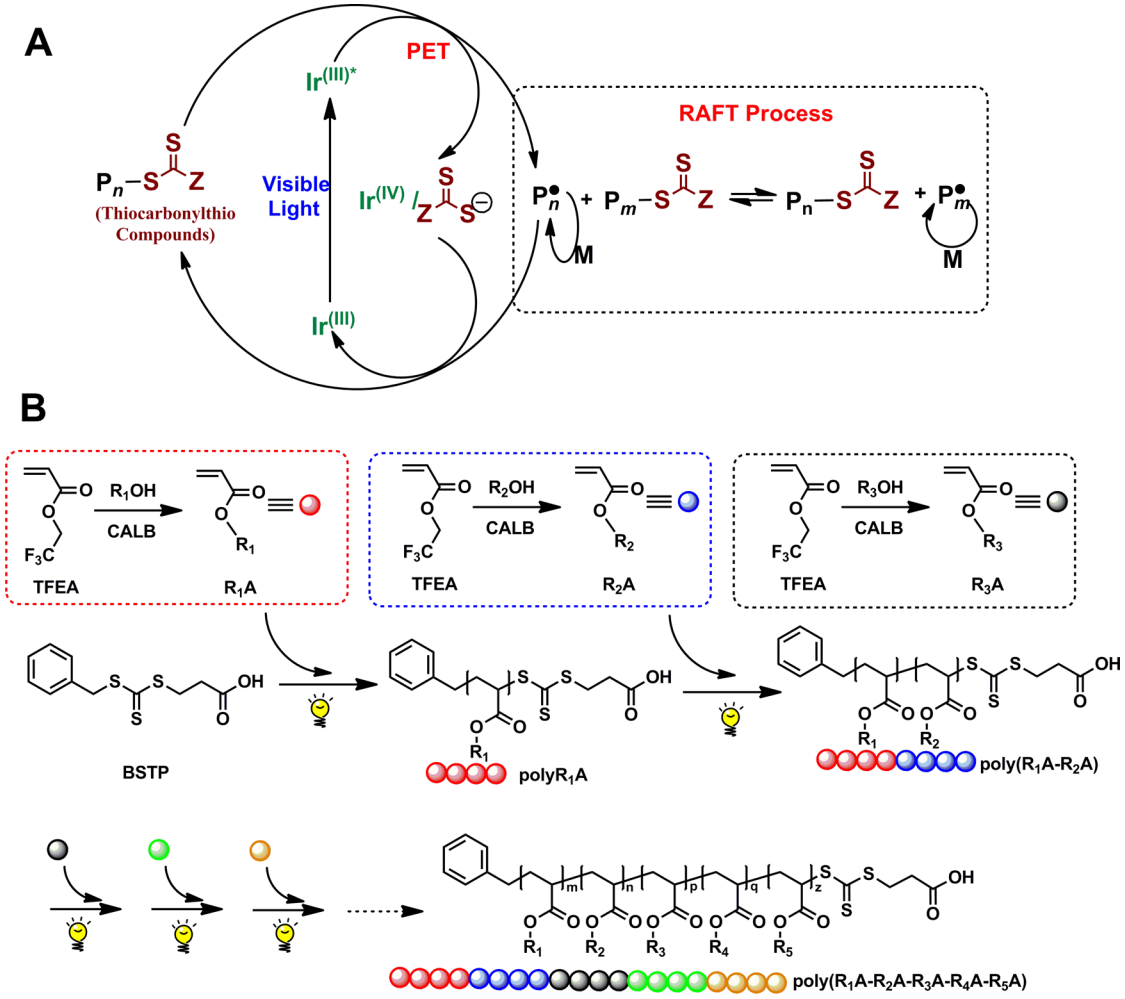
Scheme 1. (A) PET-RAFT Mechanism and (B) Synthesis of Well-Defined Multiblock Copolymers via a Combination of Enzymatic Monomer Transformation and PET-RAFT Polymerization



mediated polymerization has attracted great interest due to the smart control in both space and time.[21−28] In 2012, Hawker and co-workers used an Ir-based photoredox catalyst and ATRP initiator, i.e., ethyl α-bromophenylacetate, to synthesize well-defined polymers, fulfilling controlled radical polymerization regulated by visible light.[29] Inspired by the seminal work of Hawker[29] and Stephenson,[30] we had applied this technique for the postmodification of polymer using visible light.[31] More recently, our group developed a new photocontrolled polymerization, namely, photoinduced electron transfer−reversible addition−fragmentation chain transfer (PET-RAFT) polymerization.[25] This polymerization technique is based on the ability of $Ir^{(III)}$ (*fac*-[$Ir(ppy)_3$]) under visible light to generate an excited $Ir^{(III)}$* species which is capable of reducing thiocarbonylthio compounds and produce a radical ($P^{\bullet}$) through photoinduced electron transfer (PET)[32] (Scheme 1A). The generated radical ($P^{\bullet}$) has the capacity to initiate the RAFT process or to react with $Ir^{(IV)}$ to regenerate the chain transfer agent (also dormant chains) and $Ir^{(III)}$ species that restarts the cycle. The PET-RAFT technique was successfully employed for the polymerization of various families of monomers, including (meth)acrylate, (meth)acylamide, vinyl acetate, etc., with an excellent control over molecular weight and molecular weight distribution.

We envisioned a combination of enzymatic monomer transformation with visible-light-mediated polymerization to prepare high-order multiblock copolymers. The concept included two steps. In the first step, functional monomers were prepared via transacylation of 2,2,2-trifluoroethylacrylate (TFEA) with various alcohols in the presence of CALB. Subsequently, the monomers were polymerized via PET-RAFT without further purification at full monomer conversion. Successive chain extensions using monomers prepared by enzymatic reaction have allowed the synthesis of pentablock copolymers without the laborious purification procedure.

First, 2,2,2-trifluoroethyl acrylate (TFEA) was reacted with various alcohols via an enzymatic transacylation to yield new functional monomers (Scheme 1B). The TFEA monomer was chosen as the building block because trifluoroethyl (TFE) is a good leaving group due to the strong electron-withdrawing effect of the $-CF_3$ group, which allows us to achieve a high yield of transacylation (>95%). The transacylation reaction was performed at 40 °C using an equimolar of TFEA and alcohol in the presence of immobilized CALB. As shown in Figure 1, TFEAs were reacted and converted into new monomers. The enzymatic reaction proceeded rapidly in the first 3 h (conversion ∼85%). However, an additional 9 h was required to reach very high conversion (95−99%) due to the low concentration of substrates (Figure 1 and SI, Figure S1). The

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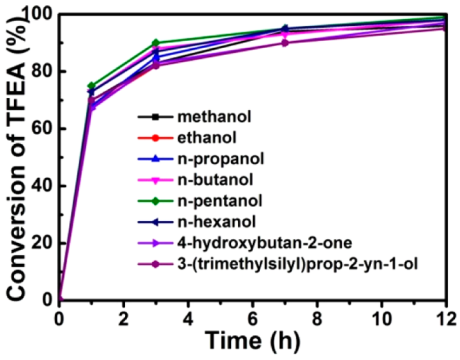

Figure 1. Kinetic study of monomer transformation via enzymatic transacylation of the equimolar equivalent of 2,2,2-trifluoroethyl acrylate (TFEA) and various alcohols in the presence of CALB at 40 °C.

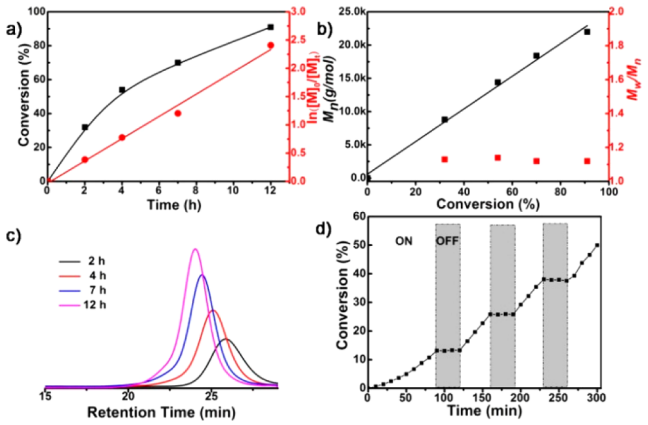

Figure 2. Photoinduced electron transfer−reversible addition−fragmentation chain transfer (PET-RAFT) polymerization of *n*-hexyl acrylate (HA) synthesized by enzymatic transacylation of TFEA in the presence of *n*-hexanol, using BSTP as a chain transfer agent and *fac*-[Ir(ppy)$_3$] as photoredox catalyst: (a) conversion and $\ln[M]_0/[M_t]$ versus exposure time; (b) M_n and M_w/M_n versus monomer conversion; (c) GPC traces of polymers at different time of exposure; and (d) "on/off" experiment by online Fourier transform near infrared monitoring monomer conversions.

enzymatic reactions are selective and afford high yield in comparison with conventional chemical reactions, which allows us to remove the purification steps. In this communication, we polymerized monomers synthesized via enzymatic reaction without further purification to yield complex multiblock copolymers, except the removal of enzyme by simple centrifugation before polymerization.

Visible-light-mediated polymerization has emerged as a novel and facile polymerization technique and garnered recently much attention due to its unique abilities to be switched between "ON" and "OFF" states.[21,22,24,25] We decided to investigate our PET-RAFT polymerization technique, as a model polymerization, for the control of *n*-hexyl acrylate (HA), which was prepared by enzymatic transacylation of TFEA with *n*-hexanol. 3-Benzylsulfanylthiocarbonylsulfanyl propionic acid (BSTP) and *fac*-[Ir(ppy)$_3$] were used as the chain transfer agent (CTA) and photoredox catalyst (*fac*-[Ir(ppy)$_3$]), respectively. The targeted degree of polymerization (DP) and the ratio of catalyst to monomer were fixed to 200 and 5 ppm, respectively. The polymerizations were performed in dimethyl sulfoxide (DMSO) at room temperature (25 °C) under blue LED light (4.8 W, λ_{max} = 435 nm). As shown in Figure 2, the polymerization proceeded smoothly, reaching 92% conversion in 12 h (Figure 2a). The plot of $\ln([M]_0/[M]_t)$ increased linearly versus exposure time, which suggests a controlled/"living" polymerization process. The plot of $M_{n,GPC}$ versus monomer conversion gave also a linear relationship (Figure 2a and 2b). The molecular weight distributions during polymerization remained as narrow as 1.12 (Figure 2b and 2c). The kinetic study by online Fourier transform near infrared spectroscopy showed that the polymerization exhibited excellent temporally controllable character when exposed to an alternating light "on" and "off". When the light was turned "off", no polymerization was observed, while once the light was turned "on", the polymerization proceeded as expected (Figure 2d).

After the preliminary study of PET-RAFT polymerization of HA, we decided to use this methodology to synthesize multiblock copolymers. To achieve multiblock copolymers via sequential addition of monomer without purification, the polymerization should reach "full" monomer conversion after every chain extension cycle with high end-group fidelity.[33−38] A model multiblock pentablock P(HA-*b*-HA-*b*-HA-*b*-HA-*b*-HA) homopolymer was synthesized by sequential addition of HA with each block of targeted molecular weight of 4680 g/mol (DP = 30). We first employed 5 ppm Ir photoredox catalyst to prepare the multiblock polymer. Although the chain extensions were successful (SI, Figure S2), the monomer conversions were close to 60% after 24 h of reaction for the third chain extension. To overcome this problem, the amount of photoredox catalyst Ir(ppy)$_3$ was increased to 10 ppm to ensure full monomer conversion after each chain extension cycle during a reasonable time. The polymerization was kept under blue LED light for 24 or 48 h (24 h for the first three blocks and 48 h for the fourth and fifth block). For the synthesis of each block, the polymerization was stopped by covering with aluminum foil (light "off"), and an aliquot was withdrawn for ^{1}H NMR and GPC analysis. High overall monomer conversions (85%−98%) for all blocks were achieved (SI, Figure S4). The monomer conversions slightly decreased for the fourth and fifth block with 93% and 85%, respectively, which was attributed to high viscosity of the polymerization solution. The trithiocarbonate end group has a characteristic absorption at λ_{max} = 305 nm in UV−vis spectra (SI, Figure S3). Using this characteristic signal and the extension coefficient of trithiocarbonate (ε = 14 500 mol^{-1} L^{-1} cm^{-1}), we calculated the end-group fidelity after five chain extensions to be close to 90%. In addition, the presence of a trithiocarbonate end group in the pentablock P(HA-*b*-HA-*b*-HA-*b*-HA-*b*-HA) homopolymer was confirmed by GPC analysis using RI and UV detectors (λ_{max} = 305 nm, SI, Figure S5). Both GPC traces were in good agreement, which confirms the presence of trithiocarbonate in the polymer chains. Finally, NMR was invoked to determine the end-group fidelity using the characteristic peaks of the phenyl group (a) and −CH$_2$− (b) adjacent to the thiocarbonylthio group. The ^{1}H NMR spectrum of the purified pentablock P(HA-*b*-HA-*b*-HA-*b*-HA-*b*-HA) homopolymer reveals a high end-group fidelity greater than 90%, calculated using the following equation: $f(\%) = [I^{3.4\ ppm}/2]/[I^{7.25-7.12\ ppm}/3] \times 100$ (Figure 3a), in accord with UV−vis results. The GPC analysis of the polymers showed monomodal distributions with a significant shift to lower retention time after each chain extension (Figure 3b). The molecular weight increased linearly with the number of chain

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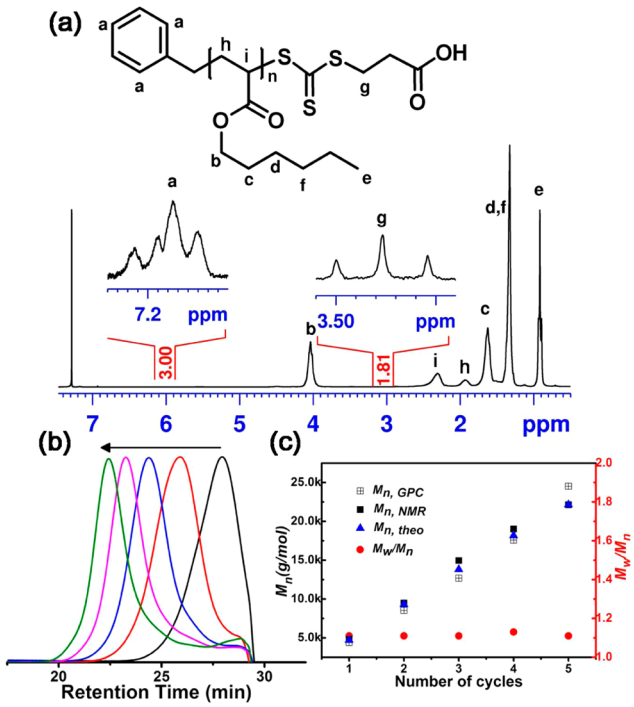

Figure 3. Synthesis of poly(HA-*b*-HA-*b*-HA-*b*-HA-*b*-HA) pentablock homopolymer via a combination of enzymatic monomer transformations and successive chain extensions using PET-RAFT polymerization. (a) ^{1}H NMR spectrum (recorded in $CDCl_3$) of the purified P(HA-*b*-HA-*b*-HA-*b*-HA-*b*-HA) pentablock homopolymer prepared after five chain extensions. (b) GPC traces of block copolymers (black line) poly(HA), (red line) poly(HA-*b*-HA), (blue line) poly(HA-*b*-HA-*b*-HA), (pink line) poly(HA-*b*-HA-*b*-HA-*b*-HA), and (green line) poly(HA-*b*-HA-*b*-HA-*b*-HA-*b*-HA). (c) Evolution of molecular weight (M_n) determined by GPC and NMR analyses, and M_w/M_n versus number of chain extension cycles.

extension cycles (Figure 3c). The molecular weight given by GPC and NMR was in good agreement with the theoretical values, calculated using the following equation: $M_{n,theo} = ([M]_0/[CTA]_0) \times \alpha \times MW^{Monomer} + MW^{BSTP}$, where $[M]_0$, $[CTA]_0$, α, $MW^{Monomer}$, MW^{BSTP} correspond to the initial monomer and CTA concentration, conversion of monomer, molar mass of monomer and BSTP, respectively. The molecular weight distributions remained as narrow as 1.10 even after five cycles, which indicates high end-group fidelity (Figure 3c). Such narrow molecular weight distribution was consistent with the high livingness of the polymer chain evidenced by ^{1}H NMR and UV−vis. The end-group fidelity was also calculated using GPC traces and a previously published method. After five chain extensions, we found that the end-group fidelity was greater than 85% (SI, Figure S6).

The catalyst concentration was increased to 15 ppm to achieve higher monomer conversion for the fourth and fifth chain extension. However, the increase in catalyst amount led to the loss of end group, as reflected by the appearance of low molecular weight tailings after the second and third chain extensions (SI, Figure S7).

Following the successful synthesis of the pentablock P(HA-*b*-HA-*b*-HA-*b*-HA-*b*-HA) polymer, we tried to test the versatility of our system for the synthesis of pentablock copolymers constituted of five different blocks based on a monomer sequence of methyl acrylate (MA), ethyl acrylate (EA), *n*-propyl acrylate (PA), *n*-butyl acrylate (BA), and *n*-pentyl acrylate (P′A). These monomers were prepared by enzymatic transacylation of TFEA with corresponding alcohols, including methanol, ethanol, *n*-propanol, *n*-butanol, and *n*-pentanol, respectively, and used directly without further purifications. The DP for each block was targeted to be 50. High monomer conversions for every chain extension, except for the last chain extension (#1: 97%; #2: 98%; #3: 92%; 4#: 89%; #5: 62%), were achieved using a molar ratio of [catalyst]:[monomer] equal to 10 ppm.

GPC traces for each chain extension shifted to low retention time with narrow molecular weight distributions (M_w/M_n ranging from 1.09 to 1.14) (Figure 4a and 4b). After five

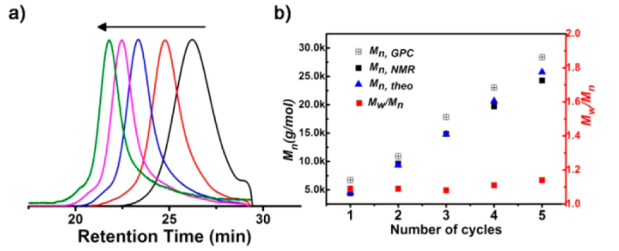

Figure 4. Synthesis of the pentablock poly(MA-*b*-EA-*b*-PA-*b*-BA-*b*-P′A) copolymer containing five different blocks using a combination of enzymatic monomer transformation and PET-RAFT polymerization. (a) GPC traces of (black line) poly(MA), (red line) poly(MA-*b*-EA), (blue line) poly(MA-*b*-EA-*b*-PA), (pink line) poly(MA-*b*-EA-*b*-PA-*b*-BA), and (green line) poly(MA-*b*-EA-*b*-PA-*b*-BA-*b*-P′A). (b) Molecular weights and molecular weight distributions versus number of chain extension cycles.

chain extension cycles, a pentablock poly(MA-*b*-EA-*b*-PA-*b*-BA-*b*-P′A) copolymer with a molecular weight of 28 390 g/mol (calculated by GPC) and M_w/M_n of 1.14 was successfully obtained. The molecular weight of the final pentablock copolymer was also determined by GPC equipped with a light scattering (LS) detector, which gave an absolute molecular weight of 25 950 g/mol, in accord with the theoretical molecular weight ($M_{n,theo}$ = 25 760 g/mol). Low molecular weight tailing can be observed, which indicates some loss of end group during the successive chain extension (SI, Figure S8). We were able to calculate the end-group fidelity to be ∼80% by the deconvolution of GPC traces. ^{1}H NMR analysis of the final pentablock copolymer revealed the end-group fidelity was close to 70% (SI, Figure S9). This result is also in good accord with our results calculated by UV−vis using the absorbance signal of trithiocarbonate at 305 nm.

The incorporation of functional groups to polymer chain relies on the synthesis of functional monomers, which often involves elaborate organic synthesis and subsequent purification steps, including column chromatography. We decided to test our methodology for the preparation of functional multiblock copolymers. Thus, we envisioned the synthesis of a triblock copolymer containing functional groups, such as ketones and alkynes. 4-Hydroxybutan-2-one and 3-(trimethylsilyl)prop-2-yn-1-ol were used as substrates for enzymatic monomer transformation, which produced 3-oxobutyl acrylate (OBA) and 3-(trimethylsilyl)prop-2-yn-1-yl acrylate (TMSPA), respectively. The triblock copolymer was synthesized with a monomer sequence of OBA, MA, and TMSPA using a concentration of 10 ppm and a polymerization time of 24 h for each chain extension. GPC analysis revealed a clear shift to higher molecular weight with iterative monomer addition (Figure

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5a). In addition, GPC analysis of the first two blocks showed monomodal molecular weight distributions of 1.12. When the

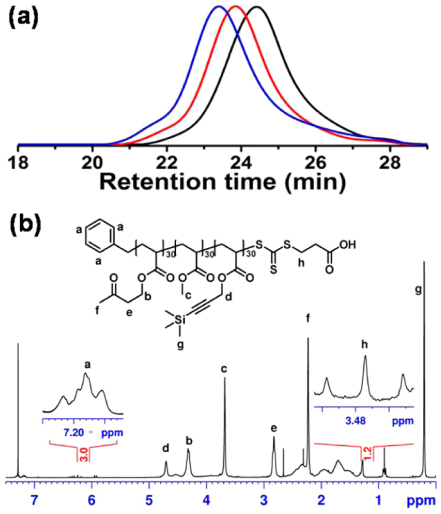

Figure 5. Synthesis of functional triblock P(OBA-*b*-MA-*b*-TMSPA) copolymer containing ketone and alkyne groups. (A) GPC traces of (black line) poly(OBA), (red line) poly(OBA-*b*-MA), and (blue line) poly(OBA-*b*-MA-*b*-TMSPA). (B) ^{1}H NMR spectrum of P(OBA-*b*-MA-*b*-TMSPA) triblock copolymer (recorded in $CDCl_3$).

third monomer TMSPA was added in the polymerization, a slight tailing at high retention time and at low retention time were observed, resulting in a broader molecular weight distribution (PDI = 1.24) (Figure 5a and Figure S10, SI), which was attributed to the high reactivity of TMSPA. The absolute molecular weight, determined by GPC using LS detector, of the functional triblock copolymer was close to 12 000 g/mol, which was relatively in accord with the theoretical value (M_n ~ 10 100 g/mol). ^{1}H NMR analysis of the purified triblock copolymer reveals that ~60% of end-group fidelity was retained (Figure 5b), while UV−vis shows ~70% of end-group fidelity (SI, Figure S3).

In summary, we have established a new and facile methodology to prepare multiblock copolymers using a combination of enzymatic transacylation reaction and photoinduced electron transfer−reversible addition−fragmentation chain transfer (PET-RAFT) polymerization. The purification steps at each chain extension were eliminated due to high end-group fidelity at high monomer conversion as well as the purification steps in the monomer synthesis. This approach has been successfully implemented for the synthesis of three different multiblock copolymers, i.e., a model poly(HA-*b*-HA-*b*-HA-*b*-HA-*b*-HA) and poly(MA-*b*-EA-*b*-PA-*b*-BA-*b*-P′A) comprising five different blocks and poly(OBA-*b*-MA-*b*-TMSPA) containing functional ketone and alkyne groups. Well-defined structures and narrow molecular weight distributions (1.10−1.24) were demonstrated by NMR and GPC analyses. This facile method provides an alternative method for the synthesis of polymers with multiple functionalities and complex architectures.

■ ASSOCIATED CONTENT

Supporting Information

Experimental details and Figures S1−S10. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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