Direct Transformation of Living Anionic Polymerization into RAFT-Based Polymerization

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Supporting Information

ABSTRACT: A method of direct switching from anionic polymerization into RAFT-based polymerization was developed. The transformation involved in situ addition of living carbanionic species, end-capped with DPE, toward CS2 and subsequent reaction with alkyl bromides, resulting in macro-RAFT agents (macro-CTAs). The macro-CTAs were used to mediate RAFT polymerization of (functional) vinyl monomers. These processes were performed in a continuous way without isolation of the intermediate. Diblock or ABA-type triblock copolymers, composed of polydiene segment and functional acrylate (2-hydroxyethyl acrylate, HEA) or acrylamide (N-isopropylacrylamide, NIPAM), were synthesized by RAFT polymerization mediated by PI macro-CTAs. The successful preparation of block copolymers was demonstrated by the self-assembly of amphiphilic diblock copolymer Pi-b-PNIPAM in water (selective solvent for PNIPAM) or heptane (selective solvent for PI). The obtained block copolymers are cleavable into homopolymer components due to the presence of the thiocarbonylthio moieties at their joint points. The block copolymers are also “clickable” as a whole onto Au nanoparticles through Au–sulfur complexation.

INTRODUCTION

Living polymerizations play a central role in the synthesis of polymers with well-defined structures such as block, star, and dendrimer-like polymers.1 Anionic polymerization is a classic, truly living system suitable for styrene, diene, (meth)acrylates, and cyclic monomers but intolerant of monomers with active hydrogen, vinyl acetate, and vinyl ethers. Controlled “living” radical polymerizations based on reversible deactivation reactions are applicable for, in principle, all monomers that can be polymerized by radical polymerization. There is, however, a rather rigorous selectivity between monomers and mediating agents. For instance, in the radical polymerization mediated by the reversible addition–fragmentation chain transfer (RAFT) process, the selection of RAFT agents for a specific monomer should take into account the stabilizing effect of the Z-group and the leaving ability of the R-group of the RAFT agent.2 In many synthetic studies, it is necessary to combine two different polymerizations in order to make block copolymers that cannot be obtained using a single mechanism. The publications in this area have been reviewed extensively.3,4

In the following, we will focus on combination of RAFT-based polymerization and other systems. There are generally two approaches, i.e., the system using a dual initiator, or infifer5,56 and the system employing end-group transformation. On one hand, inifers composed of thiocarbonylthio and alkyl halides,7–10 alkoxymine11 hydroxyl12–17 carboxyl18 and acyclic olefin19 groups have been proved very useful for combining RAFT and atom transfer radical polymerization (ATRP), nitroxide-mediated radical polymerization (NMRP), ring-opening polymerization (ROP), cationic polymerization, and ring-opening metathesis polymerization (ROMP), respectively. On the other hand, end-group transformation approach can be performed without a dual functional initiator precursor. The propagating center of the first block is converted into a functionality that is capable of initiating the polymerization of the second monomer. Thus, block copolymers are synthesized from an intermediate denoted as macroinitiator or macrochain-transfer agent (macro-CTA). For this purpose, the terminal halides of ATRP products were subject to nucleophilic attack by thiocarbonylthio salts to form macro-CTAs that could further mediate RAFT polymerizations.20–22 End-group modification of products prepared from ATRP, NMP, and cobalt-mediated polymerization with di(thiobenzoyl) disulfide afforded similar macro-RAFT agents.23–25 A mechanistic switch from RAFT to ROP was achieved using either a unique radical-induced hydroxylation process26 or insertion reaction of a single molecule of hydroxyethylene cinnamate.27 An inverse process that switched from ROP to RAFT was accomplished using esterification of hydroxyl terminus into thiocarbonylthio moiety.28 Switching from cationic into RAFT polymerizations was also reported for the synthesis of block copolymers containing segment of isobutylene or cyclic monomers, such as cyclic thiourea and oxazoline.29–31 A very special case was the direct transformation of the propagating radical center of RAFT polymerization into cationic center by in situ addition of a Lewis acid catalyst.32 This approach facilitated the synthesis of (meth)acrylates–vinyl ether block copolymers.

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There was a desire to combine anionic and RAFT polymerizations to prepare block copolymers of diene or ethylene oxide (EO) and functional vinyl monomers. A number of papers reported the transformation of hydroxyl or amino terminus of PEO, an anionic polymerization product, either commercially available or homemade, into thiocarbonylthio moieties through esterification using carboxyl- or acid chloride-functionalized thiocarbonylthio compounds,33−40 addition of dithiobenzoic acid to the double bond after attachment of a single maleic acid,41 or amidation using succinimidy ester-functionalized dithioesters.38,39 Besides, sequential conversion of −OH into allyl halides and then diioethers or xanthates was also achieved through various organic reactions.33−47 Polymers of vinyl monomers prepared by anionic polymerization, such as (hydrogenated) polydienes and polystyrene functionalized with hydroxyl termini, were used as macro-CTA precursors in block copolymerization with N,N-dimethylacrylamide (DMA), N-isopropylacrylamide (NIPAM), glucose-functionalized methacrylamide, and vinylpyridines, etc.38−40 All these transformation processes involved two or more steps of reactions at the chain ends.

In the present work, we report a direct method to convert the propagating center of anionic polymerization into thiocarbonylthio moiety that facilitates continuous synthesis of block copolymers. The conversion of the living anionic species into thiocarbonylthio moiety may be as high as 95%. Amphiphilic block copolymers of isoprene and NIPAM or 2-hydroxyethyl acrylate (HEA) are prepared using the direct transformation method. In these products, the thiocarbonylthio moiety is located in the middle of the two block chains. Therefore, the diblock copolymers are cleavable by nucleophilic reaction and clickable onto Au nanoparticle surfaces via sulfur−Au complexation.

**EXPERIMENTAL SECTION**

**Materials.** Styrene (Shanghai Linfeng, 99%), isoprene (TCI, 99%), 1,1-diphenylethylene (DPE) (Alfa Aesar, 98%), benzyl bromide (Sinopharm Chemical Reagent Co., 99%), 1-phenylthiohydroxymethyl (Aldrich, 97%), N,N,N,N′-tetramethylethylenediamine (TMEDA) (J&K, 99%), diethyliyl glycol dimethyl ether (DEGDME) (J&K, 99%), and 12-crown-4 ether (TCI, 97%) were distilled over CaH2 and stored at −10 °C. Styrene and isoprene were distilled over di-n-butylmagnesium (Bu2Mg) (Aldrich, 1.0 M in heptane) before use. N-isopropylacrylamide (NIPAM) (Shanghai Wujin, 99%) was recrystallized twice from hexane prior to use. 2-Hydroxyethyl acrylate (HEA) (Shanghai Dibai, 98%) was distilled under vacuum. 2,2′-Azobisisobutyronitrile (AIBN) (Shanghai Fourth Factory of Chemicals, 99%) was recrystallized twice from methanol. Carbon disulfide (CS2) (Sinopharm Chemical Reagent Co., 99%) was purified by vigorously shaking with KMnO4 (0.4 wt % based on CS2) followed by filtration and distillation to collect a colorless fraction. n-Butyllithium (n-BuLi) (Aldrich, 2.5 M solution in cyclohexane/heptane) was used as received. sec-Butyllithium (s-BuLi) (Aldrich, 1.3 M solution in cyclohexane) was titrated before use. Lithium naphthalenide was prepared according to the literature,51 and the concentration was 1.05 M. Tetrahydronorafuran (THF) (Shanghai Feida, 99.5%) was distilled from 1,1-diphenylethylthiol (DPHLLi, adduct of s-BuLi and DPE) on the vacuum line before use. All other reagents were used as received unless otherwise indicated.

**Measurement.** High-performance liquid chromatography (HPLC) was performed on an instrument composed of a Waters 515 pump, a C-18 column (Symmetry Shield RP-18, 5.0 μm, 4.6 × 250 mm), a Waters 486 UV detector, and a Waters 410 RI detector. Gel permeation chromatography (GPC) was performed on a Waters system equipped with three TSK-GEL H-type columns (particle size: 5.0 μm, Mw ranges: 0−1000, 0−2 × 104, and 0−4 × 105 g/mol) and a TSK-GEL guard column, a Waters 515 pump, a Waters 2414 RI detector, and a Waters 2487 UV detector, using THF and THF with 0.25% tetrabutylammonium bromide as the eluents for PI CTA and PI-b-NIPAM, respectively, at a flow rate of 1 mL/min at 40 °C. For PI-b-PHEA block copolymers, DMF with 0.2% LiBr served as the eluent at a flow rate of 1 mL/min at 80 °C for GPC characterization. Two TSK-GEL H-type columns (particle size: 7.5 μm, Mw ranges: 0−5000 and 0−9 × 105 g/mol) and a TSK-GEL guard column were calibrated by polystyrene standards (Mn, range: 682−1.4 × 104 g/mol). The absolute molecular weights (Mn) were measured by employing GPC-MALS equipped with a Waters 515 pump, a multilangle (14°−15°) laser light scattering (MALS) detector (Wyatt Technology, DAWN HELLOS) with the He−Ne light wavelength at 658.0 nm, and a RI detector (λ = 658 nm, Wyatt Technology, OptilabEX). THF was used as the eluent at 35 °C at a flow rate of 1 mL/min. The refractive index increment dn/dc was measured off-line by OptilabEX at 25 °C. 1H and 13C NMR spectra in CDCl3, THF-d8, or DMSO-d6 were collected on a Bruker 500 MHz spectrometer using tetramethylsilane (TMS) as the internal standard. Spectrophotometer Lambda 35 (PerkinElmer) was used for UV−vis measurements. The IR spectrum was recorded on a Magna-550 FTIR instrument (KBr cast). Thermogravimetric analysis (TGA, TA Q5000) was conducted under nitrogen atmosphere from ambient temperature to 700 °C at a heating rate of 20 °C/min. Transmission electron microscopy (TEM) images were recorded on a Tecnai G2 20 Twin TEM (FEI). The specimens for TEM observations were prepared by depositing a drop of the sample onto a carbon-coated copper grid.

**Model Reaction.** DPE (1.02 g, 5.67 mmol) was dissolved in dry THF (30 mL) under a N2 atmosphere, and the solution was cooled to ca. −80 °C. s-BuLi (5 mL, 5.65 mmol) was added using a syringe. After 15 min, Cs2 (0.44 g, 5.80 mmol) was added, and the system was stirred for another 20 min at ca. −80 °C. After addition of benzyl bromide (0.98 g, 5.73 mmol) using a syringe, the reaction mixture was slowly warmed up to room temperature and stirred for 30 min. Then, the mixture was concentrated by rotary evaporation, and an orange oil was obtained. Characterizations were performed without further purification. Purity by HPLC = 99%. Yield: 2.76 g (97.9%). 1H NMR (DMSO-d6): δ (ppm) = 0.43 (d, 3H, CH3−CH); 0.57 (t, 3H, CH3−CH2); 0.81 (m, 2H, CH3); 1.13 (s, 1H, CH−CH2); 2.62 (g, 1H, CH−CH2); 2.69 (g, 1H, CH−CH2); 4.36 (s, 2H, CH2−Ph); 7.16−7.46 (m, 15H, ArH). 13C NMR (DMSO-d6): δ (ppm) = 11.53 (CH−CH2); 20.57 (CH3−CH2); 30.66 (CH3−CH); 31.25 (15C, 1C); 41.87 (CH2−Ph); 49.00 (CH−CH2); 72.14 (C−Ph); 127.36−130.25 (15C, o, m, p-Ar); 135.15 (1C, phenyl attached to methylene), 143.26 (2C, phenyl attached to tertiary carbon), 245.59 (C=C=O). FT-IR: ν (cm−1) = 1097 and 1238 (C=C=O). UV−vis (MAX): THF: 230 and 325 nm.

**Transformation of Anionic Living Center into Macro-CTAs, PI-cSSR (R = Phenylethyl).** Isoprene (5 mL, 3.41 g, 50.1 mmol) was dissolved in THF (30 mL) under a N2 atmosphere to form a solution, to which s-BuLi (2.2 mL, 2.22 mmol) was injected to initiate the polymerization. After the reaction was stirred at 0 °C for 20 min, an aliquot of the solution was taken and terminated for GPC analysis. The reaction mixture was cooled to ca. −80 °C. DPE (0.41 g, 2.28 mmol) was injected, and the reaction stood for 15 min; then Cs2 (0.17 g, 2.24 mmol) was injected, and the reaction stood for another 30 min. An equimolar amount of 1-phenylethyl bromide (0.41 g, 2.22 mmol) was added using a syringe, and the reaction mixture was stirred for 5 h at 50 °C. An orange-colored solution was obtained which was used directly, or after simple concentration by evaporation, for the subsequent RAFT polymerizations either in solution or in bulk. For analysis, an aliquot of solution was concentrated, and the viscous residue was precipitated in methanol thrice and dried under vacuum. In the case of experiments using chelating agents, a double molar equivalent of ligands such as TMEDA, 12-crown-4 ether, or DEGDME was added before addition of phenylethyl bromide. PI-cSSR (R = phenylethyl, the subscript denotes the degree of polymerization (DP) of PI segment calculated from Mw/NMw = 1.08; Mw/NMw = 1500 g/mol. The procedure for synthesis of telechelic bifunctional macro-CTA, R SSCS-PI-cSSR (R = phenylethyl, DP from Mw/MNw = 1.08) was similar to...
that for PI16-CSSR (R = phenylethyl), except that lithium naphthalenide was used to initiate the polymerization of isoprene. \(M_{n,GPC} = 4400 \text{ g/mol}, M_{w}/M_n = 1.05, M_{w,SEC} = 3500 \text{ g/mol.}\)

**RAFT Polymerization of Styrene Mediated by PI16-CSSR (R = Phenylethyl).** The PI-based macro-RAFT agent obtained in the above process, PI16-CSSR (R = phenylethyl) (0.4 g, 0.19 mmol, \(M_{n,GPC} = 2100 \text{ g/mol}), and AIBN (15.6 mg, 0.1 mmol) were dissolved in styrene \((6.5 \text{ mL, } 59.2 \text{ g, } 0.69 \text{ mmol})\) (molar ratio of AIBN/PI16-CSSR/styrene = 1/2/600). The reaction mixture was degassed by three cycles of freeze–pump–thaw, backfilled with nitrogen, and then heated at 70 °C for a predetermined period. Samples were taken at various reaction times via syringe for analysis. After 12 h, the reaction was quenched into liquid nitrogen to stop the polymerization. \(M_{n,GPC} = 18000 \text{ g/mol}, M_{w}/M_n = 1.21, M_{w,NMR} = 20200 \text{ g/mol, conversion} = 58.4\%.

**RAFT Polymerization of NIPAM Mediated by PI16-CSSR (R = Phenylethyl).** PI16-CSSR (R = phenylethyl) (0.2 g, 0.1 mmol, \(M_{n,GPC} = 2100 \text{ g/mol}), AIBN (8.2 mg, 0.05 mmol), and NIPAM (3.39 g, 30 mmol) were dissolved in THF (15 mL) (molar ratio of AIBN/PI16-CSSR/NIPAM = 1/2/600). The reaction mixture was degassed by three cycles of freeze–pump–thaw, backfilled with nitrogen, and then heated at 70 °C for a predetermined period. Samples were taken at various reaction times via syringe for analysis. After 75 min, the reaction was quenched into liquid nitrogen to stop the polymerization. \(M_{n,GPC} = 24800 \text{ g/mol}, M_{w}/M_n = 1.45, M_{w,NMR} = 13300 \text{ g/mol}, \text{ conversion} = 50\%.

**RAFT Polymerization of HEA Mediated by PI16-CSSR (R = Phenylethyl).** PI16-CSSR (R = phenylethyl) (0.2 g, 0.1 mmol, \(M_{n,GPC} = 2100 \text{ g/mol}), AIBN (8.2 mg, 0.05 mmol), and HEA (3.2 mL, 3.55 g, 30.6 mmol) were dissolved in a mixture solvent of dioxane/methanol \((4/1, v/v)\) (molar ratio of AIBN/PI16-CSSR/HEA = 1/2/600). The reaction mixture was degassed by three cycles of freeze–pump–thaw, backfilled with nitrogen, and then heated at 70 °C for predetermined period. Samples were taken at various reaction times via syringe for analysis. After 3 h, the reaction was quenched into liquid nitrogen to stop the polymerization. \(M_{n,GPC} = 26000 \text{ g/mol}, M_{w}/M_n = 1.36, \text{ conversion} = 33.6\%.

**Cleavage of Block Copolymers.** PI25y-b-PS68 diblock copolymer \((0.1 \text{ g, } M_{n,GPC} = 21000 \text{ g/mol) was mixed with s-BuLi (1 mL, 1.01 \text{ mmol) in THF (20 mL) under a N2 atmosphere. The mixture was stirred at room temperature for 3 h, quenched with methanol, then concentrated, and precipitated in methanol. The collected powder was dried under vacuum. \(M_{n,GPC} = 10000 \text{ g/mol}, M_{w}/M_n = 1.20.)

**Self-Assembly of PI25y-b-PNIPAM99 in Selective Solvents.** PI25y-b-PNIPAM99 diblock copolymer was purified by washing with \(n\)-hexane twice \((\approx 150 \text{ mL x 2})\) to remove the residual PI-based macro-CTA. Then the purified product \((10 \text{ mg, } M_{n,GPC} = 47000 \text{ g/mol, PDI = 1.39})\) was dissolved in THF (1 mL), and the solution was stirred for 24 h; then deionized water (9 mL) or heptane (9 mL) was added dropwise using syringe pump under vigorous stirring within 3 h. After stirring overnight, the blue opalescent suspension was dialyzed against deionized water or heptane for 3 days using a dialysis bag with a 14 kDa cutoff molecular weight.

**“Click” Reaction between Diblock Copolymers and Au Nanoparticles (AuNPs).** Citrate-stabilized AuNPs were synthesized by reduction of HAuCl4·4H2O \((50 \text{ mg, } 0.12 \text{ mmol})\) using sodium citrate \((0.20 \text{ g, } 0.68 \text{ mmol})\) in aqueous solution \((500 \text{ mL})\). The average particle size determined by TEM was 22.8 nm in diameter. The aqueous dispersion with a wine red color was concentrated by centrifugation \((12000 \text{ rpm, } 30 \text{ min})\) and then mixed with a THF solution of PI25y-b-PS68 diblock copolymer \((0.2 \text{ g, } M_{n,GPC} = 21000 \text{ g/mol, 10 wt %). After vigorous stirring for 24 h at ambient temperature, the mixture was centrifuged \((12000 \text{ rpm, } 30 \text{ min})\), and the solid was collected, followed by eight cycles of washing with THF \((10 \text{ mL x 8})\) and centrifugation to remove the free copolymers in solution. The purified AuNPs grafted with copolymer, PI25y-g-AuNPs-g-PS68 were vacuum-dried overnight. Polymer content (by TGA) = 26%.

### RESULTS AND DISCUSSION

The transformation of anionic living center into thiocarboxanyloxy moiety is achieved through nucleophilic addition of anionic species toward carbon disulfide and subsequent reaction of the resulting dithiocarboxylates with alkyl bromides. It was reported that the nucleophilic reaction of CS2 and carbanion may proceed via both C-addition and S-addition (thiophilic addition) modes depending on reaction conditions and molecular structures. We achieved selective C-addition with the aid of 1,1-diphenylethylene (DPE) to modify the activity of the carbanion. This is demonstrated by a small molecular model reaction among sec-butyllithium (s-BuLi), DPE, CS2, and benzyl bromide, as discussed in the following section.

**Model Reaction.** The reaction between s-BuLi and DPE, followed by nucleophilic addition toward CS2, and then nucleophilic replacement on benzyl bromide were performed at low temperature in a continuous way without isolation of the intermediates (except for analysis), as shown in Scheme 1. All reactants were fed in a stoichiometric ratio. The obtained orange-colored oil was directly analyzed after simple evaporation concentration.

**Scheme 1. Model Reactions Converting Anionic Species into Thiocarboxanyloxy Moiety**

Figure 1 shows the HPLC, FTIR, and NMR results of the product. The content of the main product is 99% as detected by UV detector at double wavelengths connected to HPLC. The reaction is found to be quantitative in a short reaction time with only one peak observed in HPLC diagram (Figure 1a). In the FTIR spectrum (Figure 1b), the strong absorption at 1097 cm⁻¹ is assignable to C=S stretch vibration. In the ¹H NMR spectrum (Figure 1c), the chemical shifts of methyl protons derived from the sec-butyl group, methylene protons from DPE, and benzyl methylene protons from benzyl bromide are at 0.5, 2.7, and 4.3 ppm, respectively. The integration ratio, 3:1:1, agrees well with the anticipated structure. The ¹³C NMR spectrum (Figure 1d) shows a signal at δ = 245.6 ppm for the thiocarboxyl group. These results demonstrate that the reaction of CS2 with DPE-modified carbanion occurs exclusively in C-addition mode and is nearly quantitative. However, measurement of molecular weight by mass spectrometry failed, possibly due to the susceptibility of the thiocarboxanyloxy moiety to MS conditions.

**Synthesis of Mono- and Difunctional Macro-CTAs.** The procedure for synthesis of PI- and PS-based macro-CTAs is very similar to that of model reaction, as shown in Scheme 2. The polymerization medium can be either cyclohexane or THF in order to adjust the content of 1,4-microstructure of PI segment. Nonetheless, the end-capping with DPE and the subsequent addition to CS2 must be taken in THF or mixture of cyclohexane/THF \((v/v: 1 / 3)\). It is also important to use crown ether as chelating agent to promote the reaction between the intermediate dithiocarboxylic anion and alkyl bromides.

The three-step end-group transformation is conducted in a continuous process. Figure 2 shows the results of PI-based macro-CTA synthesis, using 1-phenylethyl bromide as the
precursor for the leaving group. The three-step reaction causes only a slight shift in GPC elution curves while keeping a narrow distribution (Figure 2a). The obtained macro-CTA is orange in color, showing a maximum absorption at around 329 nm in the UV/vis spectrum (Figure 2b), which is typical for dithioesters. The $^1$H NMR spectrum in Figure 2c shows signals at $\delta = 7.0$–7.5 ppm for aromatic protons derived from DPE moiety and phenylethyl leaving group. The methyl protons derived from the initiator $s$-BuLi show signals at around 0.75 ppm. The content of 1,4-microstructure is 90% as estimated from NMR. In addition, the $^{13}$C NMR spectrum in Figure 2d shows a clear signal at $\delta = 244.3$ ppm attributable to C=S in the terminus.

Unfortunately, no mass spectrum was acquired for PI macro-CTAs under various MALDI-TOF conditions due to instability of thiocarbonylthio moiety. Two key factors determine the efficiency of the end-group transformation: the end-capping with DPE in the presence of THF and the nucleophilic reaction of dithiocarboxylates with alkyl bromides with the aid of 12-crown-4 ether as the chelating agent. Without DPE end-capping, coupling products were always observed, no matter how CS$_2$ was added, e.g., in one-batch or slow addition or titration (Supporting Information). The coupling products may be formed via dimerization of dithiocarboxylate functionalized PI through Yates’ process.$^{61}$ The presence of crown ether in the reaction of the intermediate dithiocarboxylic anion and alkyl bromides guarantees 95% and 93% end-group functionality, respectively, for PS- and PI-based macro-CTA. Without crown ether the conversion of anionic species into thiocarbonylthio moiety is as low as 74% (determined by NMR), as shown in Table 1. This difference may be ascribed to the increasing nucleophilicity of dithiocarboxylic anion after the counterion, Li$^+$, was chelated.
by crown ether. Other additives, such as TMEDA and DEGDME, only slightly increase the transformation efficiency to ∼78%. In the case of benzyl bromide, TMEDA caused prompt precipitation due to quaternization reaction.

Dilithium species Li−PI−Li was prepared from anionic polymerization of isoprene initiated by lithium naphthalenide in THF. However, the end-group functionality cannot be determined by NMR due to the lack of distinct proton in the initiator fragment. The successful synthesis of bifunctional macro-CTA is indicated by a clear shift of monomodal peak of GPC diagrams before and after the chain extension of the second block (Supporting Information).

### Synthesis of Block Copolymers.

PI-based macro-CTAs were used to mediate radical polymerizations of styrene, NIPAM, and HEA to prepare block copolymers. These reactions were carried out either in bulk (for styrene) or in solution (for NIPAM and HEA). The RAFT polymerizations of these monomers generally exhibit living character although the Z-groups of macro-CTAs are attached to a polymer chain. Nonetheless, different behaviors are observed for different monomers and RAFT agents.

The results of styrene RAFT polymerizations mediated by PI-CSSR (R = phenylethyl) are presented in Figure 3 and Supporting Information, respectively. Figure 3 shows a linear kinetics for the system mediated by PI16-CSSR (R = phenylethyl), indicating a stationary concentration of the propagating radicals which is caused by a dynamic balance between radical generation and termination after the main equilibrium of the RAFT process has been built. GPC curves gradually shift to high molecular weight region with increasing monomer conversions (Figure 3a). The molecular weight distributions are narrow, with the polydispersity indices (PDIs) being around 1.2 (Figure 3c). It is noted, however, that benzyl as the leaving group leads to a slow consumption of macro-CTA (Supporting Information), whereas phenylethyl results in a fast depletion of the initial RAFT agent. This difference is clear by inspecting the evolution of GPC peak intensities of the macro-CTA precursors in the two systems.

<table>
<thead>
<tr>
<th>Table 1. Macro-CTAs Synthesized from Living Anionic Species</th>
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<tr>
<td>sample</td>
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<tr>
<td>PS$_{10}$-CSSR (R = phenylethyl)$^{cd}$</td>
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<tr>
<td>PI$_{10}$-CSSR (R = phenylethyl)$^d$</td>
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<tr>
<td>RSSC-PI$_{41}$-CSSR (R = phenylethyl)</td>
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$^{a}$Determined by $^1$H NMR. For example, for PI-based macro-CTA, M$_n$NMR = $\left(\frac{68 \times A_1/2}{A_2/6}\right) + 57 \times A_3 + 180 \times A_4 + 76 \times A_5 + M_R$, where $A_1$ and $A_2$ are the areas of the vinyl protons of PI and the methyl protons from initiator (s-BuLi), respectively. $M_R$ is the mass of leaving group. $^{b}$f (%) (functionality) is determined by $^1$H NMR. For PI-based macro-CTA, f (%) = $\frac{A_3/15}{A_2/6} \times 100\%$, where $A_3$ is the area of the aromatic protons (∼C$_6$H$_5$) at 7.0−7.5 ppm; for PS-based macro-CTA, f (%) = $\frac{A_3/15}{A_2/6} \times 100\%$, where $A_4$ is the area of the methine proton in R group (∼CH(CH$_3$)-Ph) at 4.86 ppm. $^c$12-crown-4-ether was added as the chelating agent, other systems were conducted without any chelating agent. $^d$Solvent for polymerization is cyclohexane.

![Figure 3. Kinetic results of styrene RAFT polymerization mediated by PI$_{16}$-CSSR (R = phenylethyl): (a) GPC traces of samples taken during the polymerization; (b) reaction kinetics; (c) dependence of molar mass (g/mol) on monomer conversion.](image-url)
In a similar way, ABA-type triblock copolymer of styrene and isoprene, PS₁₃₃-b-PI₄₁-b-PS₁₃₃ (SIS), was prepared from RSSC-PI₄₁-CSSR (R = phenylethyl) mediated RAFT polymerization of styrene. A product of SIS with molar mass $M_{n,GPC} = 17,600$ g/mol and PDI = 1.16 was obtained (Supporting Information).

RAFT polymerizations of NIPAM are also performed using mono- and bifunctional macro-CTAs as the mediating agents, in which phenylethyl is the leaving group. In both systems, an induction period of $\sim 40$ min is observed, and GPC curves indicate a slow conversion of macro-CTAs, as shown in Figure 4 and the Supporting Information. The slow conversion is attributable to slow cross-initiation of NIPAM by the phenylethyl radical. For monofunctional macro-CTA-mediated system in Figure 4, a bimodal distribution is observed at the reaction time of 30 min due to the presence of residual initial macro-RAFT agent and possibly unfunctionalized polysisoprene precursor. After the induction period, the polymerization proceeds rather fast. The dependence of molecular weight on monomer conversion (Figure 4c) exhibits an abrupt increase in the initial period and then levels off in middle and later stages. Thus, the RAFT polymerization process of NIPAM is complicated by the slow initiation. This results in a relatively broader distribution of the final product (Figure 4c).

The system using bifunctional macro-CTA gives very similar results except that the final product is an ABA-type triblock copolymer, PNIPAM₁₁₃-b-PI₄₁-b-PNIPAM₁₁₃, with molar mass $M_{n,GPC} = 36,000$ g/mol and PDI = 1.37 (Supporting Information). Well-defined block copolymer containing PI and PNIPAM segments was previously synthesized by using single anionic mechanism, yet NIPAM needs to be protected.⁶²

RAFT polymerization of HEA mediated by PI-based macro-CTAs shows strict demands upon solvent selection. This is because HEA, like 2-hydroxyethyl methacrylate (HEMA),⁶³ tends to form gel during polymerization in some organic solvents. The cosolvent for PI and PHEA is quite limited. Thus, a mixture solvent of dioxane/methanol (4/1, v/v) is used for the synthesis of block copolymer, PI₂₀-b-PHEA₂₁₁, and PHEA₆₇-b-PI₂₀-b-PHEA₂₁₁. These products can be analyzed by GPC using DMF as eluent only for products with high contents of HEA units. As shown in Figure 5a, monomodal distributions with relatively low polydispersities are observed. Nevertheless, samples taken during the polymerization are not well soluble in DMF due to high content of PI fraction, which impedes GPC analysis.

In order to trace the reaction process by GPC, we used a polystyrene-based macro-CTA, PS₂₀-CSSR (R = phenylethyl), instead of PI counterparts, to mediate the RAFT polymerization of HEA. GPC measurement is performed using DMF as eluent with 0.2% LiBr as additive. As shown in Figure 5b, GPC curves shift to high molecular weight region during the polymerization, but slow initiation is again observed from the residual peak of the initial macro-RAFT agent and unfunctionalyzed PS precursor. The polymerization proceeds without occurrence of cross-linking reactions. Diblock copolymer product, PS₂₀-b-PHEA₉₂₂, with a relatively low polydispersity (PDI < 1.3) was obtained after purification by extraction with methanol. Characterizations of all block copolymers are summarized in Table 2. It should be pointed out that PDI values in Table 2 and Figures 3−5 were obtained from GPC integrations excluding the peaks of the residual macro-CTA precursors.

As a demonstration of amphiphilic block copolymer formation, we carried out the self-assembly of PI₇₅-b-PNIPAM₁₉₉ in water (selective solvent for PNIPAM) or heptane (selective solvent for PI) at room temperature (~10 °C). PI₇₅-b-PNIPAM₁₉₉ was purified by washing with n-hexane.
twice to remove the residual PI-based macro-CTA. The purified sample showed monomodal distribution of GPC diagram. Typically, PI13-b-PS68 was dissolved in THF, and then water was added to the solution using a syringe pump under vigorous stirring. During water addition the clear solution became turbid with precipitation. The obtained mixture was redispersed by mechanical shaking and collected for TEM measurement. As shown in Figure 6a, cylindrical micelles of microns in length are observed, which may be composed of PI as the core and PNiPAM as the shell. On the other hand, when heptane was used instead of water, a stable opalescent solution was formed. The TEM image in Figure 6b shows spherical micelles formed with PNiPAM as the core and PI as the corona. These micelles tend to aggregate on copper grid before TEM measurement.

**Cleavage and “Click” Reactions of Block Copolymers.** One feature of the block copolymers in the present work is that the thiocarbonylthio moiety is located at the junction of the two segments. This renders the copolymer products degradability into parts of component homopolymers and affinity to gold surfaces as a whole. It was reported that thiocarbonylthio termini of the RAFT-based polymerization products can be hydrolyzed, aminolyzed, or reduced into thiocarbonyl species and thiols.64–68 However, the dithioesters produced in the present work, either small molecule or macro-CTAs, are difficult to be completely hydrolyzed, aminolyzed, or reduced in the presence of primary amines, potassium tert-butoxide (t-BuOK), KOH, and NaBH4, respectively (Supporting Information). A possible reason is that the Z-group, α,α-diphenylalkyl, may stabilize the thiocarbonylthio moiety. Therefore, a stronger base, e.g., s-BuLi, is used to cleave a model diblock copolymer, PI13-b-PS68 with $M_{n,\text{NMR}} = 21\,000\,\text{g/mol}$, prepared from PI13- CSSR (R = phenylethyl) of $M_{n,\text{GPC}} = 11\,000\,\text{g/mol}$ in a similar procedure. As shown in Figure 7, the copolymer is cleaved into species of $M_{n,\text{GPC}} \approx 10\,000\,\text{g/mol}$ after treatment with excess s-BuLi in THF at room temperature. The peak after cleavage may be overlapping of the two components. Besides, a small shoulder appears at the same position to the precursor, which may be ascribed to addition product of s-BuLi toward thiocarbonylthio moiety. The possible reaction mechanism is shown in Scheme 3.69

**Table 2. Characterization Results of Block Copolymers**

<table>
<thead>
<tr>
<th>copolymer PI13-b-PS68</th>
<th>$M_{n,\text{GPC}}$ (Da)</th>
<th>$M_{n,\text{NMR}}$ (Da)</th>
<th>$M_{n}/M_{s}$ (GPC)</th>
<th>$M_{n,\text{GPC}} \times 10^{-3}$ (Da)</th>
<th>$M_{n,\text{NMR}} \times 10^{-3}$ (Da)</th>
<th>$M_{w}/M_{n}$ (GPC)</th>
<th>conv</th>
</tr>
</thead>
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<tr>
<td>PI13-b-PS68</td>
<td>1300</td>
<td>1000</td>
<td>1.08</td>
<td>13.8</td>
<td>15.5</td>
<td>1.19</td>
<td>0.45</td>
</tr>
<tr>
<td>PI13-b-PS68</td>
<td>2100</td>
<td>1500</td>
<td>1.08</td>
<td>18.0</td>
<td>20.2</td>
<td>1.21</td>
<td>0.58</td>
</tr>
<tr>
<td>PI13-b-PS68</td>
<td>2100</td>
<td>1500</td>
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<td>24.8</td>
<td>14.7</td>
<td>1.45</td>
<td>0.50</td>
</tr>
<tr>
<td>PI13-b-PS68</td>
<td>2100</td>
<td>1500</td>
<td>1.08</td>
<td>26.0</td>
<td>1.36</td>
<td>0.34</td>
<td>0.58</td>
</tr>
<tr>
<td>PI13-b-PS68</td>
<td>11000</td>
<td>5500</td>
<td>1.05</td>
<td>34.2</td>
<td>36.4</td>
<td>1.25</td>
<td>0.58</td>
</tr>
<tr>
<td>PI13-b-PS68</td>
<td>4400</td>
<td>3500</td>
<td>1.05</td>
<td>17.6</td>
<td>31.3</td>
<td>1.16</td>
<td>0.52</td>
</tr>
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<td>PI13-b-PS68</td>
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<td>3500</td>
<td>1.05</td>
<td>19.0</td>
<td>1.46</td>
<td>0.23</td>
<td>0.44</td>
</tr>
</tbody>
</table>

“Benzyl as the leaving group, phenylethyl as the leaving group in all other systems.”

$^a$Determined by $^1$H NMR. For example, $M_{n,\text{NMR}}$ of PI13-b-PS could be calculated: $M_{n,\text{NMR}} = [\{104\, (C_8H_8) \times A_s / S \times M_{n,\text{NMR,PI}}\} / (68\, (C_2H_4) \times A_t / 2)] + M_{n,\text{NMR,PI macro-CTA}}^b$ where $A_s$ is the area of aromatic protons from polystyrene segment. $^b$Determined by gravimetry. $^c$Determined by GPC. $^d$Determined by $^1$H NMR.
polymer brushes (inset a in Figure 8). In mixed solvents of DMF and n-hexane (1/3, v/v, DMF/n-hexane), which are selective solvents for PS and PI, respectively, the hybrid material forms Pickering emulsion with large sized oil-in-oil (o/o) droplets due to self-assembly of the particles at the interfaces (inset b of Figure 8). Thus, the current study explores a facile approach to functionalize Au surface with mixed polymer brushes, which has been attracting continuous attention in the scientific community.76–80

Scheme 4. “Click” Reaction of Diblock Copolymers onto Au Nanoparticles and Assembly of the Resulting Hybrid Particles at n-Hexane/DMF Interface

![Figure 8. TGA curve of PI75-g-AuNPs-g-PS85. Insets: (a) solution of PI75-g-AuNPs-g-PS85 in toluene and its TEM image; (b) Pickering emulsion of DMF in n-hexane stabilized by PI75-g-AuNPs-g-PS85.](image)

**CONCLUSIONS**

The model reaction indicates that the addition reaction of carbanion, end-capped with DPE, toward CS$_2$ is quantitative and exclusively in C-addition style. This facilitates direct transformation of the living anionic propagating center into dithioester moiety that can subsequently mediate RAFT polymerization. Both monofunctional and bifunctional macro-CTAs (PS-SSR, PI-SSR, and RSS-PI-SSSR) are prepared by this method. The end-group functionality can be as high as 95% with the aid of crown ether or the chelating agent in the reaction of dithiocarboxylic anion with alkylboronides. Amphiphilic block copolymers of mechanistically incompatible monomers, such as isoprene/NIPAM and isoprene/HEA, are successfully synthesized. These block copolymers, carrying a thiocarbonylthio moiety at the connecting point of the chains, are not only cleavable by strong base but also clickable as a “V-shaped” precursor to Au surface through sulfur–Au complexation chemistry.

**ASSOCIATED CONTENT**

Supporting Information
Figures S1–S6. 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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