

Photoinduced Synthesis of α,ω -Telechelic Sequence-Controlled Multiblock Copolymers

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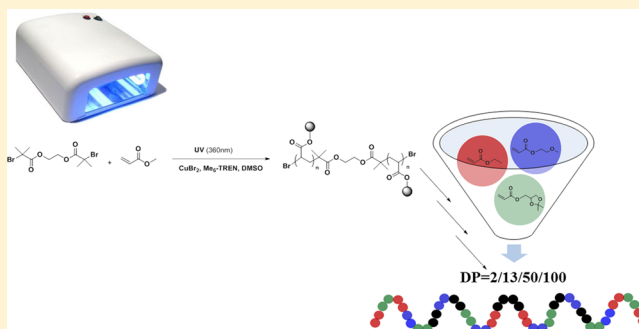
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S Supporting Information

ABSTRACT: Photoinduced living radical polymerization has been employed to synthesize α,ω -telechelic multiblock copolymers of a range of acrylic monomers including methyl acrylate (MA), ethyl acrylate (EA), ethylene glycol methyl ether acrylate (EGA), and solketal acrylate (SA). Under carefully optimized conditions, a well-defined tricosablock (23 blocks) copolymer was obtained ($\bar{D} = 1.18$) with high conversion (>98%) achieved throughout all the iterative monomer additions. Crucially, a reduced temperature (15 °C) was found to result in an observed decrease in the dispersities (1.14 vs 1.45) as opposed to when higher temperatures (50 °C) were employed. A number of bifunctional initiators were employed, including ethylene bis(2-bromoisobutyrate) (EbBiB), a PEG initiator (average $M_w = 1000 \text{ g mol}^{-1}$), and bis[2-(2'-bromoisobutyryloxy)ethyl] disulfide ((BiBOE)₂S₂), resulting in narrow dispersed multiblock copolymers in various molecular weights ($DP_n \sim 2/13/50/100$ per block). Impressively, a high molecular weight undecablock (11 blocks) copolymer of $M_n = 150\,000 \text{ g mol}^{-1}$ and $\bar{D} = 1.22$ was also synthesized. In order to demonstrate the symmetry of the resulting telechelic materials, a well-defined tridecablock (13 blocks, $\bar{D} = 1.18$, $M_n = 25\,000 \text{ g mol}^{-1}$) was synthesized utilizing a bifunctional disulfide initiator which was cleaved postpolymerization, yielding a narrow disperse polymer at half the molecular weight of the parent polymer ($\bar{D} = 1.10$, $M_n = 12\,400 \text{ g mol}^{-1}$).



INTRODUCTION

The development of reversible deactivation radical polymerization methods (RDRP) has profoundly changed the field of polymer science providing access to the facile synthesis of well-defined polymers with a range of diversity in both structure and function. Indeed, nitroxide-mediated radical polymerization (NMP),¹ atom transfer living radical polymerization (ATRP),^{2,3} single electron transfer living polymerization (SET-LRP),^{4,5} and reversible addition–fragmentation chain transfer polymerization (RAFT)⁶ have made significant contributions toward this field due to the ability to regulate molecular weight, end-group fidelity, monomer sequence, dispersity, and architecture.

Recently, there have been continued efforts to expand the scope of traditional RDRP through strategies that would regulate the activation and deactivation step via external stimuli.^{7–12} Of the various stimuli employed, light is very attractive⁷ due to its inherent properties (e.g., environmentally benign natural resource, widely available, noninvasive, etc.). With respect to photochemical control, many groups^{13–20} have independently contributed to the field, demonstrating sophisticated systems that allow not only for the control over the molecular weight distributions but also for spatiotemporal control upon demand.

A further major challenge for polymer chemistry is to mimic the complexity of biological macromolecules via synthetic methods. Natural polymers such as peptides and proteins are sophisticated complex structures that exhibit perfect monomer sequence in order to fulfill a predefined function. However, synthetic analogues of these domains have not yet been realized although notable progress has been made over the past few years to achieve better control over the polymer primary sequence.^{21,22} Various approaches have been explored to precisely control the monomer sequence including single monomer addition,²³ tandem monomer addition and modification,^{24,25} and kinetic control^{26–28} as well as solution^{29–34} and segregated³⁵ templating.

The implementation of single monomer addition via radical chain growth polymerization techniques is challenging, if not impossible, given the reactive nature of the radical. However, the ability to control the sequence of multiple discrete regions within a macromolecular structure allows the introduction of functional domains along the polymer backbone. Thus, many radical polymerization techniques^{36–39} have been developed for

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the synthesis of multiblock copolymers in an attempt to satisfy four major requirements: (i) quantitative or near-quantitative conversion for each block, (ii) no purification step involved between each monomer addition, (iii) narrow dispersities for all the blocks, and (iv) high end-group functionality.

These criteria were initially introduced by Whittaker and co-workers utilizing Cu(0)-mediated living radical polymerization to synthesize a well-defined ($\mathcal{D} \sim 1.20$) acrylic hexablock copolymer ($DP_n \sim 2$ per block) in a very high yield.^{37,40,41} When larger DP_n blocks were targeted ($DP_n \sim 100$ per block), triblocks and quasi-pentablock copolymers could be prepared; however, a limitation was reached as full monomer conversion could not be achieved throughout the monomer additions.⁴² The same technique was subsequently utilized by Haddleton and co-workers for the synthesis of multiblock glycopolymers with a good degree of monomer sequence control.^{43,44} The same group also demonstrated applicability of acrylamides reporting various acrylamide multiblock copolymers in <5 h^{5,45} employing aqueous Cu(0)-mediated living radical polymerization.⁵ Moreover, Haddleton et al. employed a photoinduced polymerization approach increasing the number of blocks to 12, while also achieving higher molecular weight multiblock copolymers.³⁹ A similar approach was also employed by Junkers, resulting in a well-defined decablock copolymer with narrow molecular weight distributions.⁴⁶ In this chemistry the irradiation is into the ligand in the near-UV which results in a photoreduction. The chemistry occurs most efficiently in polar solvents which are also favorable in promoting disproportionation of copper(I).⁵

An alternative approach utilizing RAFT has also been developed recently by Perrier and co-workers synthesizing an icosablock copolymer comprising of acrylamides in both organic and aqueous media.^{38,47–50} However, the high temperature (~ 70 °C) and the ability to obtain only acrylamide block copolymers (i.e., not acrylic, etc.) are two arguable limitations of this approach. High temperature in particular is disadvantageous for the polymerization of monomers that possess an LCST upon polymerization (e.g., NIPAM) while unavoidable termination and side reactions (e.g., backbiting, chain transfer) are also more likely to occur under these conditions.⁵¹

Herein, we report for the first time the synthesis of α,ω -telechelic multiblock copolymers utilizing various bifunctional initiators, including EbBiB, (BiBOE)₂S₂, and a PEG initiator. A photoinduced one-pot multistep sequential polymerization process was employed to yield a well-defined tricosablock copolymer (23 blocks, 12 chain extensions, $\mathcal{D} \sim 1.18$). Importantly, the reaction temperature was discovered to have a significant effect on the control over the molecular distributions as a dispersity of 1.45 was obtained for the nonadecablock copolymer at 50 °C (vs 1.14 when the polymerization was performed at 15 °C). Subsequently, the effect of chain length was investigated, allowing for higher molecular weight blocks to be obtained. Remarkably, an undecablock (11 blocks) copolymer of $M_n = 150\,000$ g mol⁻¹ and $\mathcal{D} = 1.22$ could be attained, which represents the highest molecular weight multiblock copolymer reported to date. Finally, when a disulfide initiator was employed, the final tridecablock (13 blocks, $M_n = 25\,000$ g mol⁻¹, $\mathcal{D} = 1.18$) copolymer was subsequently cleaved, yielding an impressively well-defined polymer at exactly half of the molecular weight ($M_n = 13\,400$ g mol⁻¹, $\mathcal{D} = 1.10$), thus illustrating the symmetrical nature of the materials prepared.

MATERIALS AND METHODS

All materials were purchased from Sigma-Aldrich or Fischer Scientific unless otherwise stated. Copper(II) bromide (CuBr₂) and tributylphosphine were used as received. All monomers were passed through a basic Al₂O₃ chromatographic column prior to use to remove the inhibitor. Tris(2-(dimethylamino)ethyl)amine (Me₆-Tren) was synthesized according to previously reported literature.⁵² Solketal acrylate was synthesized according to a reported procedure⁵³ and distilled under reduced pressure (45 °C, 10⁻¹ mbar) to yield a colorless liquid. EbBiB, PEG (average $M_w = 1000$ g mol⁻¹), and (BiBOE)₂S₂ were also synthesized according to literature protocols.^{54,55}

Instrumentation. ¹H NMR spectra were recorded on Bruker DPX-250 and DPX-300 spectrometers using deuterated chloroform (CDCl₃) obtained from Aldrich. Chemical shifts are given in ppm downfield from the internal standard tetramethylsilane. Size exclusion chromatography (SEC) measurements were conducted using an Agilent 1260 GPC-MDS fitted with differential refractive index (DRI), light scattering (LS), and viscometry (VS) detectors equipped with 2 × PLgel 5 mm mixed-D columns (300 × 7.5 mm), 1 × PLgel 5 mm guard column (50 × 7.5 mm), and autosampler. Narrow linear poly(methyl methacrylate) standards in range of 200–1.0 × 10⁶ g mol⁻¹ were used to calibrate the system. All samples were passed through 0.45 μm PTFE filter before analysis. The mobile phase was chloroform with 2% triethylamine at a flow rate of 1.0 mL/min. SEC data were analyzed using Cirrus v3.3. Matrix-assisted laser desorption/ionization mass spectrometry (MALDI-ToF-MS) was conducted using a Bruker Daltonics Ultraflex II MALDI-ToF-MS mass spectrometer, equipped with a nitrogen laser delivering 2 ns laser pulses at 337 nm with positive ion ToF detection performed using an accelerating voltage of 25 kV. Solutions in tetrahydrofuran (50 μL) of *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propylidene]malonitrile (DCTB) as matrix (saturated solution), sodium iodide as cationization agent (1.0 mg/mL), and sample (1.0 mg/mL) were mixed, and 0.7 μL of the mixture was applied to the target plate. Spectra were recorded in reflector mode calibrating PEG-Me 1100 kDa. The source of UV light was a UV nail gel curing lamp (available online from a range of suppliers) ($\lambda_{\max} \sim 360$ nm) equipped with four 9 W bulbs. The “cooling” plate utilized for this study was from CAMLAB (KP283).

General Procedure for the Preparation of Multiblock Copolymers by Photoinduced Living Radical Polymerization without Purification. Filtered monomer (DP_n eq), EbBiB (1 equiv), CuBr₂ (0.04 equiv), Me₆-Tren (0.24 equiv), and DMSO (2 mL) were added to a septum sealed vial and degassed by purging with nitrogen for 15 min. Polymerization commenced upon placement of the degassed reaction vessel under a UV lamp. Samples were taken periodically (0.05 mL), and conversions were measured using ¹H NMR and SEC analysis.

For the iterative chain extensions, an aliquot of a degassed monomer (DP_n eq) in DMSO (50% v/v) was added via a nitrogen-purged syringe, and again the solution was allowed to polymerize in the lamp. When required, a fresh solution of CuBr₂ (0.04 equiv) and Me₆-Tren (0.24 equiv) in DMSO was fed together with the monomer via a nitrogen-purged syringe. The above polymerization-extension procedure was repeated as required.

Disulfide Reduction. The reduction of the disulfide bond is adapted from a reported procedure.⁵⁴ A 50 mL round-bottom flask was charged with the final multiblock copolymer (0.1 g obtained via precipitation in methanol), tributylphosphine (100 equiv), and THF (10 mL). The reaction was allowed to stir for 2 h at ambient temperature. The volatiles were removed by rotary evaporation to yield the reduced product, which was subsequently characterized by ¹H NMR and SEC (Figure S15).

RESULTS AND DISCUSSION

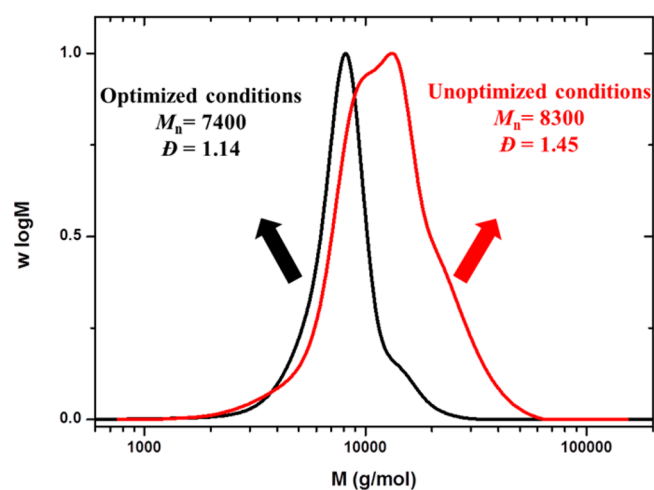
Recently, our group reported the photoinduced living radical polymerization of acrylates in the presence of ppm concentration of CuBr₂ and Me₆-Tren.^{13,56} The high end-group fidelity of the obtained polymers was subsequently exploited for the synthesis of acrylic multiblock copolymers without any

Table 1. Comparison of Multiblock Copolymers Obtained under Optimized Conditions (“Cooling” Plate) and Unoptimized Conditions via Photoinduced Living Radical Polymerization

| cycle | unoptimized conditions | | | | optimized conditions | | | |
|-------|------------------------|-----------------------------------|------------------------------------|-----------|----------------------|-----------------------------------|------------------------------------|-----------|
| | conv (%) | $M_{n,th}$ [g mol ⁻¹] | $M_{n,SEC}$ [g mol ⁻¹] | \bar{D} | conv (%) | $M_{n,th}$ [g mol ⁻¹] | $M_{n,SEC}$ [g mol ⁻¹] | \bar{D} |
| 1 | 100 | 700 | 265 | 1.40 | 100 | 700 | 400 | 1.20 |
| 2 | 99 | 1100 | 750 | 1.29 | 99 | 1100 | 950 | 1.20 |
| 3 | 99 | 1600 | 1400 | 1.27 | 99 | 1600 | 1500 | 1.19 |
| 4 | 99 | 2400 | 2000 | 1.26 | 99 | 2400 | 2200 | 1.16 |
| 5 | 98 | 2700 | 2900 | 1.26 | 98 | 2700 | 3000 | 1.14 |
| 6 | 99 | 3100 | 3800 | 1.25 | 99 | 3100 | 3600 | 1.14 |
| 7 | 98 | 3400 | 5000 | 1.26 | 98 | 3400 | 4700 | 1.13 |
| 8 | 99 | 4100 | 6000 | 1.28 | 99 | 4100 | 5500 | 1.14 |
| 9 | 99 | 4600 | 8000 | 1.35 | 99 | 4600 | 6500 | 1.15 |
| 10 | 99 | 5000 | 8300 | 1.45 | 98 | 5000 | 7400 | 1.14 |
| 11 | – | – | – | – | 99 | 5700 | 8200 | 1.19 |
| 12 | – | – | – | – | 99 | 6100 | 9600 | 1.18 |
| 13 | – | – | – | – | 100 | 6400 | 13000 | 1.28 |

need for purification between the iterative monomer additions. However, a limitation of this work was reached as “only” 12 blocks (11 chain extensions) could be achieved when utilizing a monofunctional initiator before accumulated termination had a detrimental effect on the dispersity. Moreover, a pentablock copolymer ($DP_n \sim 100$ per block, final $M_n = 80\,000$ g mol⁻¹, $\bar{D} = 1.21$) was found to be the upper limitation of this system, and higher molecular weight multiblock copolymers were not obtained.³⁹ We envisaged that the synthesis of α,ω -telechelic materials would be able to circumvent these issues as the same number of chain extensions would result in a higher number of blocks ($2n - 1$ blocks for n chain extensions) and thus less termination and side reactions. Furthermore, telechelic materials are of high interest due to the ability to functionalize both ends postpolymerization and further enhance their properties.⁵⁷ Moreover, the utility of bifunctional macroinitiators (e.g., PEG) allows for the incorporation of additional properties alongside the polymer backbone.⁵⁸ Finally, in an ideal system, the symmetrical nature of the telechelic materials should be very high if both sides initiate with equal efficiency, which could be demonstrated via polymerization from an α,ω -functional, redox cleavable (S–S) initiator.

Initially, the ability of the bifunctional initiator (EbBiB) to afford multiblock copolymers was investigated utilizing previously employed conditions.¹³ A feed ratio of [I]:[CuBr₂]:[Me₆-Tren] = [1]:[0.04]:[0.24] was employed in DMSO (50% v/v with respect to monomer) while an additional amount of [CuBr₂]:[Me₆-Tren] was injected in the reaction mixture upon every third monomer addition.³⁹ Upon sampling conversions were determined by ¹H NMR analysis (Figure S2), using the signals at 5.5–6.5 ppm and at 3.5 ppm which are attributed to the acrylic and OCH₃ groups, respectively. After 10 h, full monomer conversion was attained ($\bar{D} = 1.41$, Figure S3), and a deoxygenated solution of EA and DMSO (2:1) was subsequently injected in the reaction mixture. The relatively high dispersity of the first block was maintained throughout the monomer additions ($\bar{D} = 1.25$ – 1.35 , Table 1 and Table S1). In particular, the final nonadecablock (10 chain extensions) copolymer presented a bimodal molecular weight distribution ($\bar{D} = 1.45$, Figure 1 and Figure S3), thus suggesting considerable termination events and/or side reactions under these conditions. A greater extent of termination for a telechelic initiator (in comparison with a monofunctional analogue) is

**Figure 1.** Comparison of final molecular weight distributions (nonadecablock copolymer) obtained under optimized conditions (“cooling” plate) and unoptimized conditions via photoinduced living radical polymerization.

not surprising given the increase in the number of initiating sides (2-fold).

We envisaged that a lower reaction temperature might suppress the unwanted termination events and/or side reactions. It should be noted that in our initial publication no difference in the rate (or the control) between a typical UV experiment (~ 50 °C), and the one carried out at lower temperature (~ 25 °C) was observed for the synthesis of a homopolymer.¹³ However, since multiblock copolymers are more complex structures (and the system is forced to reach full conversion multiple times, thus termination is more likely to accumulate), we hypothesized that any termination and side reaction would be highlighted in such a system. In order to verify this hypothesis, the effect of temperature was investigated using a cold plate (Figure S1) to maintain the temperature at ~ 15 °C. Encouragingly, the homopolymerization of MA was found to proceed with similar rates and furnished poly(MA) with narrower final molecular weight distributions ($\bar{D} = 1.20$ vs $\bar{D} = 1.40$ for the typical UV experiment, Figure 1). Following several monomer additions, a nonadecablock copolymer (10 chain extensions) was obtained, and the low dispersity was retained ($\bar{D} = 1.14$ vs $\bar{D} = 1.45$ for the typical UV experiment,

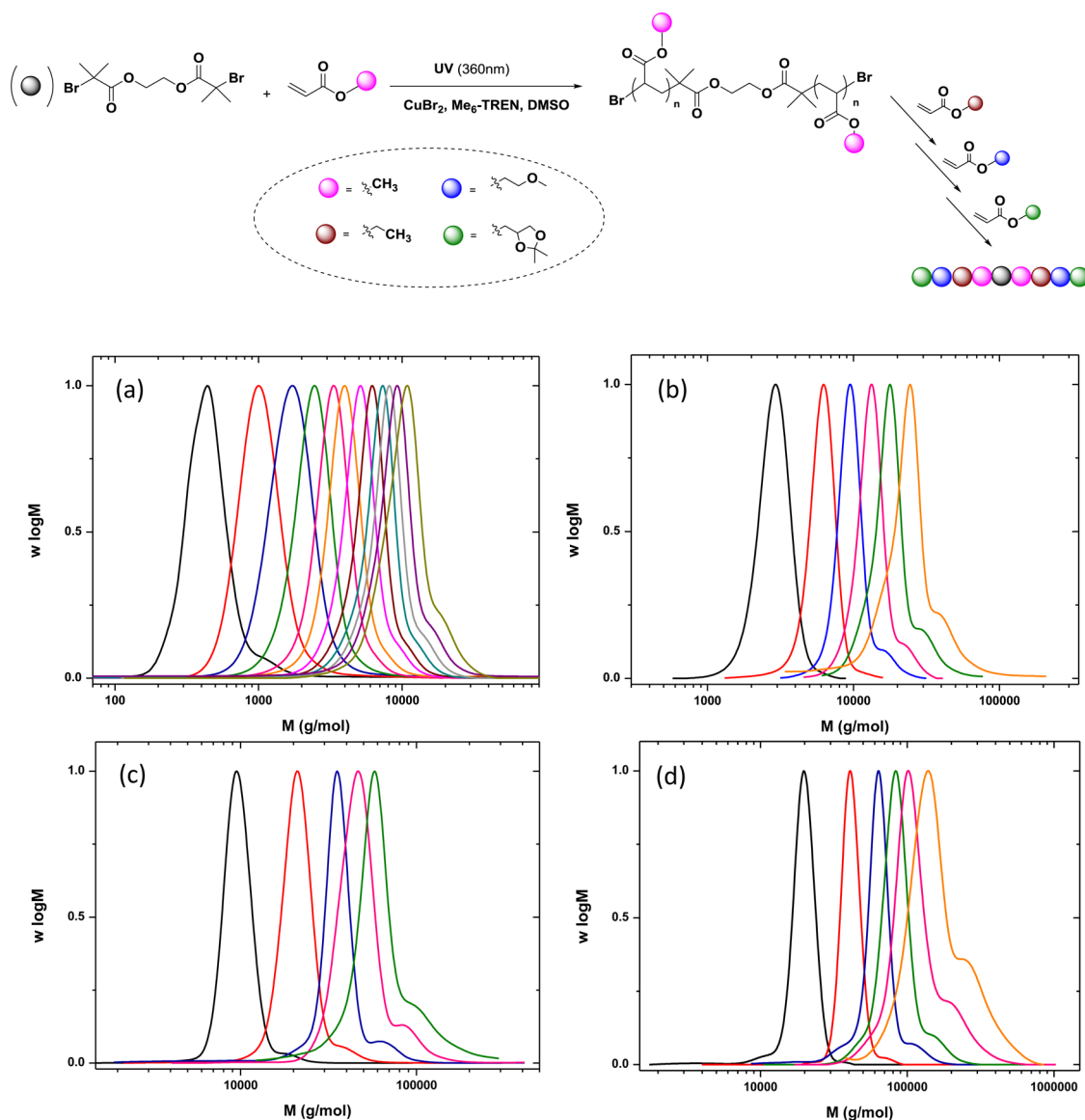


Figure 2. Molecular weight distributions for successive cycles during the synthesis of (a) a tricoblock copolymer ($DP_n = 2$), (b) an undecablock copolymer ($DP_n = 13$), (c) a nonablock copolymer ($DP_n = 50$), and (d) an undecablock copolymer copolymer ($DP_n = 100$).

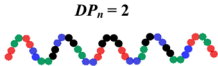
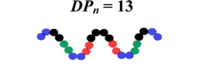
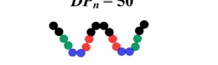

Figure 1 and Table 1). Remarkably, under the optimized “cooling” conditions the nonablock copolymer could be further chain extended to yield a tricoblock copolymer, poly(EA_2 -*b*- SA_2 -*b*- EA_2 -*b*- EGA_2 -*b*- SA_2 -*b*- MA_2 -*b*- EGA_2 -*b*- MA_2 -*b*- SA_2 -*b*- EGA_2 -*b*- EA_2 -*b*- MA_2 -*b*- MA_2 -*b*- EA_2 -*b*- EGA_2 -*b*- SA_2 -*b*- MA_2 -*b*- EGA_2 -*b*- MA_2 -*b*- SA_2 -*b*- EA_2) (or poly(MA_2 -*b*- EA_2 -*b*- EGA_2 -*b*- SA_2 -*b*- MA_2 -*b*- EGA_2 -*b*- MA_2 -*b*- EGA_2 -*b*- MA_2 -*b*- SA_2 -*b*- EGA_2 -*b*- EA_2 -*b*- EA_2)₂ ($\bar{D} = 1.18$, $M_n = 9600$). Beyond this, further chain extensions resulted in broader molecular weight distributions (Figure S5). Nevertheless, a pentacosablock copolymer (25 blocks, 13 chain extensions, Table S2) was attained in a quantitative manner (100% conversion, $\bar{D} = 1.28$, $M_n = 13\,000$, Figures S4 and S5), which represents the largest number of blocks reported in the literature to date.

We were also interested to investigate whether the optimized conditions carried out on the “cooling” plate would support the multiblock copolymerization of higher molecular weight block lengths. Thus, a multiblock copolymer composed of 13 repeat units per block (or 26 repeat units per chain extension) was attempted. Excellent end-group fidelity was confirmed by

MALDI-ToF-MS for the initial homopolymer with the main polymer peak distribution corresponding to poly(MA) initiated by the EbbiB and terminated by two bromine atoms (Figure 3 and Figure S6). Pleasingly, upon 6 chain extensions, this photoinduced polymerization protocol afforded a well-defined undecablock copolymer (11 blocks, 6 chain extensions, $\bar{D} = 1.17$, $M_n = 26\,000$, Figure 2b, Table 2, Table S3, Figure S7). A small high molecular weight shoulder can be observed in SEC which could be attributed to bimolecular coupling as indicated by the M_p value of the shoulder being at double the molecular weight as opposed to the main polymer peak distribution. However, it is important to note that for bifunctional initiators (and resulting telechelic polymers) termination by bimolecular coupling still maintains a near-perfect bifunctional polymer with bromine chain ends.

The livingness of a system is strongly correlated with the DP_n targeted. Thus, the next target was to assess if multiblock copolymers exhibiting longer blocks could also result in well-defined polymers under our conditions. High molecular weight blocks are of great interest due to their ability to self-assemble

Table 2. Summary of Multiblock Copolymers Prepared Utilizing EbBiB

| Multiblock Copolymer (Average DP per block) | No. of blocks | Conversion ^a (%) | $M_{n,th}$ (g.mol ⁻¹) | $M_{n,SEC}$ (g.mol ⁻¹) | \mathcal{D} |
|---|------------------|--------------------------------|--------------------------------------|---------------------------------------|---------------|
|  $DP_n = 2$ | 23 | 99 | 6100 | 9600 | 1.18 |
|  $DP_n = 13$ | 11 | 99 | 19000 | 22000 | 1.17 |
|  $DP_n = 50$ | 9 | 98 | 59000 | 56000 | 1.18 |
|  $DP_n = 100$ | 9 | 99 | 144000 | 150000 | 1.19 |

^a¹H NMR, CDCl₃. Overall monomer conversion for all additions. Conversions for each iteration are tabulated in the Supporting Information.

and phase-separate forming higher ordered structures.^{59–61} When each block was composed by 50 repeat units (100 repeat units per chain extension) the one pot, multistep sequential photoinduced polymerization furnished a nonablock copolymer (5 chain extensions) with narrow molecular weight distributions ($\mathcal{D} = 1.18$, Figure 2c) and quantitative or near-quantitative (>98%) conversions maintained throughout the sequential monomer additions (Figure 2c, Table 1, Table S4, Figure S8). It should be noted that quantitative conversions are important to ensure the structural integrity of the multiblocks and the high yield of the final material. Moreover, when the polymerizations are carried out to complete or high conversions, the monomer concentration decreases significantly and thus the propagation process is slow, whereas bimolecular termination, being second order with respect to radical concentration, becomes more prominent. Thus, pushing this system to reach full conversion upon each monomer addition further demonstrates the robustness and the versatility of the technique.

Identical conditions were subsequently applied for a multiblock copolymerization with even higher chain length ($DP_n = 200$ per addition or 100 per block). The first three

chain extensions proceeded as expected, with a final dispersity = 1.09 while good correlation between the theoretical and the experimental values further confirms the controlled/living character of the polymerization. However, during the polymerization of the heptablock copolymer, cessation of the stirring was observed (Figure 3) due to the increased viscosity. Unfortunately, the addition of the fourth aliquot of monomer did not restore the stirring, and two layers were formed in the reaction vial (upper layer: monomer, bottom layer: macroinitiator), disturbing the efficient mixing of the monomer with the macroinitiator. However, with the use of a vortex mixer (2 min) the mixture became homogeneous again, and subsequently the vial was re-exposed to UV irradiation. Although stirring ceased again after a few hours, the polymerization surprisingly reached quantitative conversion, and the dispersity of the nonablock copolymer remained low ($\mathcal{D} = 1.19$, Table S5). The procedure was repeated, yielding a well-defined undecablock copolymer (13 blocks, 6 chain extensions, $\mathcal{D} = 1.22$, $M_n = 150\,000$ g mol⁻¹, Figure 2d, Table 1, Figure S9).

It should be noted that in a living radical polymerization (ATRP, SET-LRP, RAFT, etc.) which involves radicals termination will always occur despite the best efforts to suppress this. Termination events and side reactions are best highlighted by plotting the evolution of molecular weight with each addition of monomer (Figure 4). In the absence of termination, M_n should increase linearly, with little deviation from $M_{n,th}$. This is indeed the case for $DP_n = 13/50/100$ (Figure 4b,c,d), where the good correlation between theoretical and experimental values confirms the controlled/living character of the polymerizations. However, a deviation in the final molecular weight is observed for lower targeted DP_n (Figure 4a), where good agreement is maintained only up to the sixth chain extension. After this point, an upward shift in M_n was observed which can be attributed to coupling reactions that occur as a result of the increased reaction times. Nevertheless, such highly complex structures can be obtained in very high yields with very narrow molecular weight distributions for all the DP_n targeted.

The use of PEG macroinitiators (both monofunctional and bifunctional) is common in the synthesis of block copolymer and has attracted considerable interest for various applications.⁵⁸ Thus, we were interested to test the versatility of this

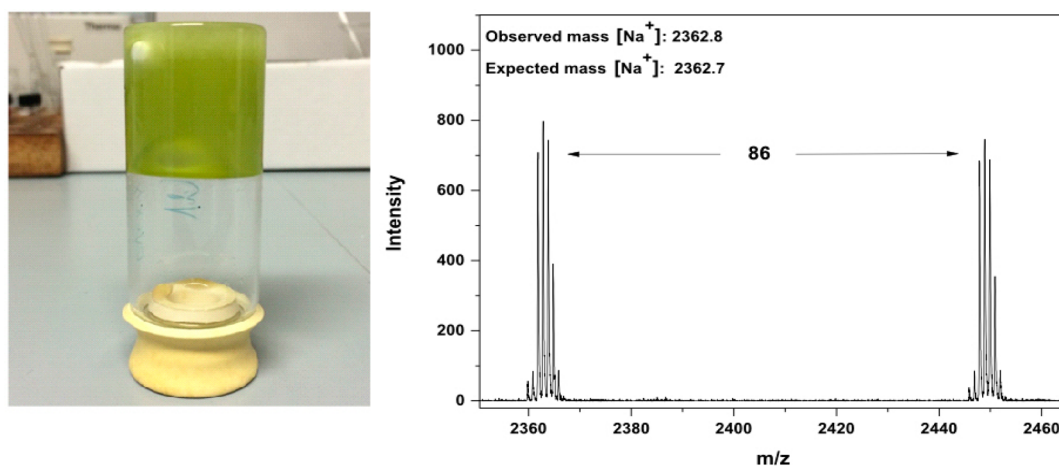


Figure 3. Photo of the undecablock copolymer ($DP = 200$ per chain extension or $DP = 100$ per block) obtained upon cessation of the stirring in DMSO at 15 °C (left) and MALDI-ToF-MS of the first chain extension ($DP = 26$ or $DP = 13$ per block) of the undecablock copolymer in DMSO at 15 °C, utilizing EbBiB (right).

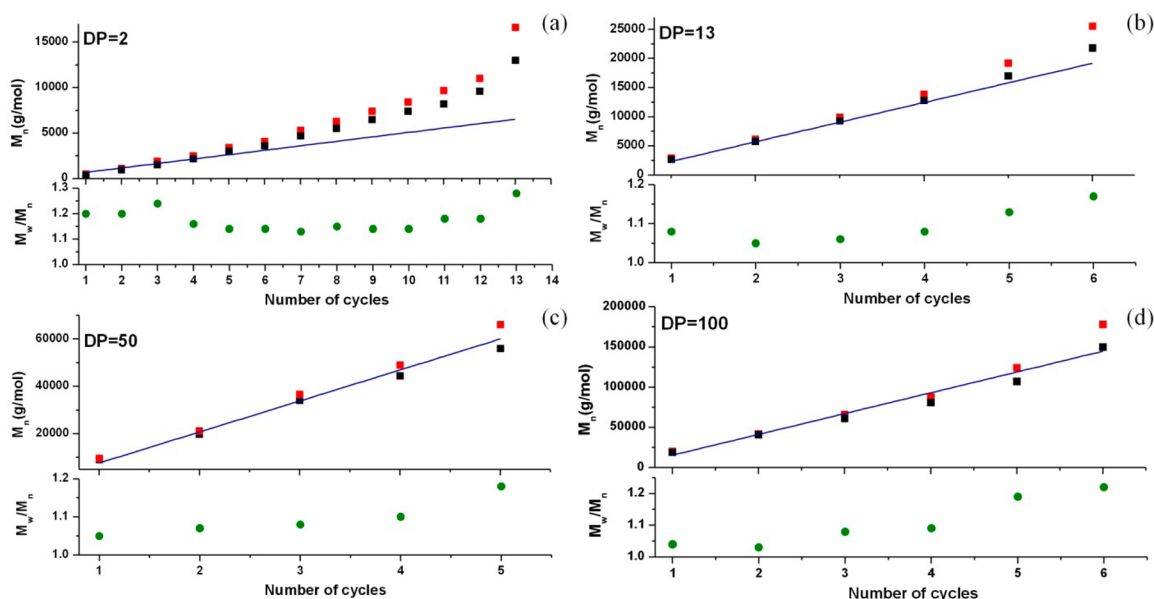


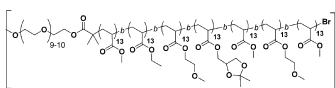
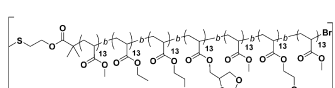
Figure 4. Evolution of number-average molecular weights and dispersity with the number of blocks or the preparation of (a) a tricosablock copolymer ($DP_n = 2$), (b) an undecablock copolymer ($DP_n = 13$), (c) a nonablock copolymer ($DP_n = 50$), and (d) an undecablock copolymer copolymer ($DP_n = 100$). The blue line represents the theoretical molecular weight; black and red squares represent the experimental M_n and M_w from SEC; green cycles represent the dispersity from SEC.

technique utilizing a bifunctional PEG initiator, which was synthesized according to a literature protocol (Figure S10).⁵⁵ From the perspective of multiblock preparation it should be noted that the incorporation of a PEG macroinitiator would result in $2n + 1$ blocks for n chain extensions. Pleasingly, a well-defined tridecablock copolymer was attained ($DP_n = 26$ per addition, $DP_n = 13$ per block, $\bar{D} = 1.15$, $M_n = 24\,600$, Figure S11). Further chain extensions resulted in broader molecular weight distributions. Nevertheless, a pentadecablock copolymer could be obtained in a quantitative manner (Figure S11) with $M_n = 29\,000\text{ g mol}^{-1}$ and $\bar{D} = 1.24$ (Table 3 and Table S6). Thus, macroinitiators were proved to be compatible with the optimized polymerization conditions.

Typically, the synthesis of near perfect bifunctional polymers can be demonstrated experimentally by postpolymerization modification, halogen exchange experiments, and chain extension.⁶² Chain extension verifies the functionality of the prepared poly(acrylates) by demonstrating that at least one chain end has active bromine end groups. However, it does not

confirm that polymerization is initiated from both α,ω -chain ends. In order to assess the retention of both chain ends, a disulfide initiator was employed for the preparation of a multiblock copolymer. MALDI-ToF-MS of the initial homopolymer confirmed the existence of the α,ω -bromine functional polymer chains and the presence of the initiator (and thus the S–S moieties, Figure S12) in the polymer backbone. This high end-group fidelity was subsequently exemplified by one-pot sequential additions, yielding a tridecablock copolymer with narrow molecular weight distribution ($\bar{D} = 1.18$) and final M_n of $25\,000\text{ g mol}^{-1}$ (Table 3, Table S7, Figure S13). Subsequently, an excess of tributylphosphine was added in order to reduce the disulfide bond. Within 2 h quantitative reduction was observed as indicated by the complete shift of the molecular peak distribution from $M_n = 25\,000\text{ g mol}^{-1}$ ($\bar{D} = 1.18$) to $M_n = 12\,400\text{ g mol}^{-1}$ while maintaining narrow molecular weight distributions ($\bar{D} = 1.10$, Figure 5 and Figure S13). Despite the high complexity of these multiblock structures, this is indicative of a telechelic polymerization proceeding throughout the multistep additions.

Table 3. Summary of Multiblock Copolymers Obtained Utilizing a PEG and a Disulfide Bifunctional Initiator

| Multiblock Copolymer | Conv. (%) | $M_{n,th}$ (g.mol ⁻¹) | $M_{n,SEC}$ (g.mol ⁻¹) | \bar{D} |
|---|-----------|-----------------------------------|------------------------------------|-----------|
|  | 98 | 22000 | 29000 | 1.24 |
|  | 99 | 21000 | 25000 | 1.18 |

¹H NMR, CDCl₃. Overall monomer conversion for all additions. Conversions for each iteration are tabulated in the Supporting Information.

CONCLUSION

The synthesis of α,ω -telechelic multiblock copolymers via photoinduced living radical polymerization of acrylic monomers is reported. Various bifunctional initiators were successfully employed to yield well-defined multiblock copolymers in high yields, exhibiting low dispersity values ($\bar{D} < 1.19$) with different chain lengths ($DP_n \sim 4/26/100/200$ per chain extension or $DP_n \sim 2/13/50/100$ per block). Crucially, low temperatures were found to decrease the dispersity values from 1.45 (50 °C) to 1.14 (15 °C), suggesting increased termination and side reactions at elevated temperatures. Under these optimized conditions, a well-defined tricosablock copolymer ($\bar{D} = 1.18$, $M_n = 9500\text{ g mol}^{-1}$, $DP_n \sim 2$ per block) and a high molecular weight undecablock copolymer ($\bar{D} = 1.22$, $M_n = 150\,000\text{ g mol}^{-1}$) were obtained which represent the highest number of blocks and the highest molecular weight

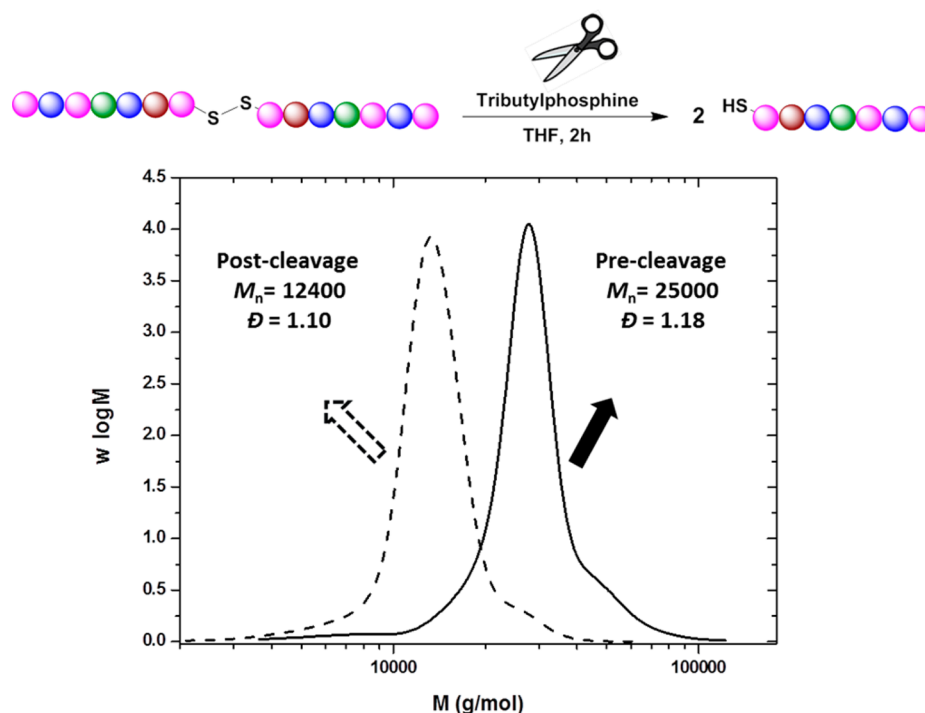


Figure 5. Complete reduction of the tridecablock copolymer utilizing tributylphosphine.

multiblock, respectively, to date. Finally, the symmetrical nature of the telechelic materials was demonstrated by cleaving the S–S bond of a tridecablock copolymer (initiated by a disulfide initiator), furnishing a well-defined multiblock copolymer at half of the molecular weight of the telechelic starting material.

■ ASSOCIATED CONTENT

Supporting Information

Figures showing typical setup for the photoinduced polymerization in a cold plate, molecular weight distributions plots, ^1H NMR spectra, MALDI-ToF-MS spectra, and plots of M_n , M_w , M_{th} , and \bar{D} vs number of blocks. 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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