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Synthesis of Star Polymers using Organocatalyzed Atom Transfer Radical Polymerization Through a Core-first Approach

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Abstract

Synthetic routes to higher ordered polymeric architectures are important tools for advanced materials design and realization. In this study, organocatalyzed atom transfer radical polymerization is employed for the synthesis of star polymers through a core-first approach using a visible-light absorbing photocatalyst, 3,7-di(4-biphenyl)-1-naphthalene-10-phenoxazine. Structurally similar multifunctional initiators possessing 2, 3, 4, 6, or 8 initiating sites were used in this study for the synthesis of linear telechelic polymers and star polymers typically possessing dispersities lower than 1.5 while achieving high initiator efficiencies. Furthermore, no evidence of undesirable star-star coupling reactions was observed, even at high monomer conversions and high degrees of polymerization. The utility of this system is further exemplified through the synthesis of well-defined diblock star polymers.

TOC image

Star polymers containing 3-8 arms and a linear telechelic polymer are synthesized from a core-first approach using visible-light induced organocatalyzed atom transfer radical polymerization.

Introduction

Synthetic polymers have become indispensable, with applications integrated into all facets of modern society. Advanced polymeric materials can be designed and imbued with specific functionalities for precise applications through exploitation of synthetic methods to form

chemical compositions and tune polymer architectures to influence the resulting properties.¹ Tailored materials are accessible through the use of complex polymeric architectures, one example of which is star polymers. Star polymers are macromolecules possessing three or more linear polymeric chains, or “arms”, radiating from a central branching point, or “core”, and offer an avenue toward advanced materials design stemming from their higher-order architecture and unique properties.² In comparison to their linear analogues, star polymers exhibit unique rheological and physical properties stemming from a compact, globular structure.^{3,4} Furthermore, star polymers are highly customizable, with tunable properties and numerous available applications through modification of arm and core sizes, functionalities, and compositions.⁵

There are 3 major methods for the synthesis of star polymers, each with their own advantages and disadvantages. These approaches include core-first, arm-first, and grafting-onto. Each set of synthetic approaches can be modulated for the synthesis of star polymers possessing desired properties and applications. The core-first approach relies on the use of a multifunctional initiator, which begins polymerization outward from the core. In this approach, the arm incorporation can be precisely controlled by the number of initiating sites on the initiator, which is best performed in systems with high initiator efficiencies. However, in these systems the core sizes are typically quite small and limited by the choice of multifunctional initiator. Furthermore, in radical polymerization methods star-star coupling reactions can occur, causing gelation, high dispersities, and uncontrolled properties.⁶ These undesirable termination events occur from the reaction of two intramolecular arm chain-ends, forming high molecular weight (MW) stars that can be observed via gel permeation chromatography (GPC). The arm-first approach relies on crosslinking of linear polymer chain-end groups with a multifunctional monomer species. In this approach, high MW stars can be synthesized using well-defined linear arms. However, arm incorporation into the star can be difficult to regulate and is typically controlled by reaction stoichiometry, arm size, and reaction component compositions.^{7,8,9} Star-star coupling reactions can also occur, resulting in star polymers with a high dispersity and unreacted polymer arms. Moreover, incorporation of arms with high numbers of monomer repeat units can be limited due to steric effects.¹⁰ The grafting-onto approach exploits post-polymerization modification steps to combine the chain-end group of a synthesized polymer with a core and is typically achieved through well-studied “click” reactions between polymer arm and core molecules with complementary functionality.¹¹ This method is advantageous in that it allows for complete characterization of both the arm and core molecules. Similar to the core-first approach, the core size is typically small and, as in the arm-first method, the incorporation of high MW arms can be challenging.¹²

Controlled radical polymerizations (CRPs) have emerged as powerful synthetic approaches for the synthesis of advanced materials with complex architectures due to robust monomer scope and reaction media compatibility to yield control over important polymerization metrics including dispersity (M_w/M_n), growth of MW, and retention of chain-end group functionality.^{13,14} The most widely studied CRP, atom transfer radical polymerization (ATRP), historically operates by reversible activation of a dormant alkyl halide species by a transition metal catalyst to generate a propagating carbon centered radical, which is deactivated through end-capping by the halogen to return the growing polymer to the

dormant state.^{15,16} Control over polymerization is imparted through a higher rate of deactivation in comparison to rates of propagation and initiation, maintaining a low concentration of radicals and minimizing undesirable bimolecular termination events.¹⁷

The reversible activation mechanism orchestrated by ATRP results in retention of a functional halogen chain-end group. This functionality facilitates the synthesis of advanced materials, such as through chain-extension to form block copolymer structures or further reactivity for post-polymerization modifications.¹⁸ ATRP has been employed for the synthesis of star polymers using all 3 of classes of synthetic approaches.^{19,20,10,21,22} In particular, for the core-first approach a variety of different catalytic systems have shown to be effective in star synthesis using a range of monomers and multifunctional initiators.^{23,24,25,26} However, in some cases star-star coupling reactions have been observed, becoming more prevalent with increased number of arms and higher monomer conversion. This effect has been controlled through use of dilute systems and limiting polymerization to low monomer conversions in copper catalyzed ATRP systems.²⁷ Recently, photoinduced ATRP catalyzed by a copper catalyst synthesized star polymers containing, 4, 6, and 21 arms from a core-first approach, reaching above 80% conversion before star-star coupling reactions were observed.²⁸

A newly developed variant of ATRP, organocatalyzed ATRP (O-ATRP) uses a photoredox catalyst to mediate the catalytic cycle through an oxidative quenching pathway and is proposed to proceed through 4 central steps (Figure 1 A).²⁹ First, irradiation of the ground state PC generates the excited state PC*. Next, PC* reduces an alkyl halide initiator during activation to simultaneously form an active carbon-centered radical species and $^2\text{PC}^+ + \text{X}^-$. The third step is polymerization propagation of the carbon centered radical to grow the polymer chain. Finally, the last step of the cycle is deactivation, which occurs through end-capping of the active polymer chain with the halide group, returning the polymer to the dormant state and the catalyst to the ground state PC. Analogous to ATRP, control over polymerization is imparted through a fast rate of deactivation in comparison to propagation and activation.

Since 2014, research in our group has centered on the development of O-ATRP through the establishment of PC design principles gained from increased mechanistic understanding.^{30,31,32,33,34} This progress has been achieved through a combined computational and experimental approach, largely studying the polymerization of methyl methacrylate (MMA) for the synthesis of linear poly(methyl methacrylate) (PMMA) to study PC success. Recently, we have reported on the use of 3,7-di(4-biphenyl)-1-naphthalene-10-phenoxazine (**1**) as a photocatalyst capable of operating a well-controlled O-ATRP under a variety of irradiation conditions³⁵ as well as in both batch and scalable continuous flow reactors.³⁶ Beyond O-ATRP, **1** also can be used as a PC in several small molecule transformations.³⁷ **1** possesses several desirable attributes of a PC for O-ATRP, including efficient visible light absorption, with a λ_{max} at 388 nm, ϵ_{max} of $26,635 \text{ M}^{-1}\text{cm}^{-1}$, paired with a strong triplet excited state reduction potential of -1.70 V vs SCE, and oxidation potential of +0.42 V vs SCE. Furthermore, **1** has a high triplet quantum yield ($\Phi = 0.9$) with a sufficiently long excited state lifetime ($\tau = 480 \text{ }\mu\text{s}$). Lastly, **1** is stable to reversible redox processes necessary for a PC. With these considerations in mind, we sought to expand the synthetic capabilities

of this PC in O-ATRP to include well-defined star polymer synthesis through a core-first approach. 4 structurally similar multifunctional initiators, with number of initiating sites (n) ranging from 3-8, were employed in the synthesis of PMMA star polymers. To fully understand the capabilities of O-ATRP and a core-first approach, a similar initiator with 2 initiating sites was also employed to produce a telechelic linear polymer (Figure 1 B).

Experimental Section

Materials

Chemicals—Methyl methacrylate (MMA) was purchased from VWR and benzyl methacrylate (BzMA) was purchased from Sigma Aldrich. The monomers were dried over calcium hydride, distilled, and stored under inert atmosphere at $-10\text{ }^{\circ}\text{C}$. ACS-grade *N,N*-Dimethylacetamide (DMAc) with a sure-seal was purchased from Sigma Aldrich, stored under inert atmosphere, and used as received. Ethylene bis(2-bromoisobutyrate) and pentaerythritol tetrakis(2-bromoisobutyrate) multifunctional initiators were purchased from Sigma Aldrich and used as received. All other reagents for catalyst and multifunctional initiator synthesis were purchased from Sigma Aldrich or VWR and used as received. 1,1,1-Tris(2-bromoisobutyryloxymethyl)ethane, dipentaerythritol hexakis(2-bromoisobutyrate), and tripentaerythritol octakis(2-bromoisobutyrate) were synthesized according to modified literature procedures.^{38,39} PC 3,7-Di(4-biphenyl) 1-Naphthalene-10-Phenoxazine (**1**) was synthesized according to literature procedure.³⁴

Characterization—Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance-III 300 MHz spectrometer or a Varian Inova 400 MHz spectrometer. Chemical shifts were referenced using internal solvent resonance, 7.26 ppm for CDCl_3 and 7.16 ppm for C_6D_6 . Deuterated chloroform was purchased from Cambridge Isotope Laboratories.

Analysis of polymer molecular weight and dispersity was performed using gel permeation chromatography (GPC) coupled with multi-angle light scattering (MALS), using an Agilent HPLC fitted with one guard column and three PLgel 5 μm MIXED-C gel permeation columns in series. The detectors used were a Wyatt Technology TrEX differential refractometer and a Wyatt Technology miniDAWN TREOS light scattering detector, which allows the direct measurement of absolute M_w and does not require any correction factor for accurate MW measurement. The solvent used was THF with a flow rate of 1.0 mL/minute.

General star polymer synthesis using core-first approach—Using the difunctional initiator as an example for a typical polymerization using the core-first approach, the stoichiometry was determined as follows for a targeted degree of polymerization of 50 for each arm: $[\text{MMA}]:[\text{RBr}_n]:[\text{PC}]$ is $[1000]:[10]:[1]$, where RBr_n is the molar amount of multifunctional initiator used. To set up polymerization, a 20 mL scintillation vial with a polypropylene lined cap was charged with a small stir bar and 33.8 mg (9.39×10^{-2} mmol) of multifunctional ATRP initiator, then brought into a glovebox with nitrogen atmosphere. Then 5.74 mg (9.39 μmol) PC from a stock solution was added, followed by 1.00 mL (9.39 mmol) of methyl methacrylate (MMA). At that time, the vial was capped and placed in a photoreactor and irradiated by white LEDs (Figure S1). Once the reactions exhibited

increased viscosity an additional 1 mL of DMAc was added, typically in the 3rd hour. Aliquots were taken for kinetic analysis by quenching approximately 75 μ L of reaction mixture into 0.7 mL of deuterated chloroform containing 250 ppm of butylated hydroxytoluene as radical inhibitor. For each aliquot collected, 0.5 mL of the quenched aliquot was used for ^1H NMR analysis. Conversion was determined through relative integration of the methyl ester monomer peak at 3.46 ppm to the methyl ester polymer peak at 3.32 ppm. The remaining 0.2 mL of quenched aliquot was dried under ambient conditions for a minimum of 24 hours, then fully dissolved in THF, filtered through a syringe filter, and analyzed by GPC for molecular weight and dispersity analysis. See supplemental information for full details on the synthesis of each type of star polymer.

Chain extension experiments—Star polymer macroinitiator synthesis was carried out by setting up a standard polymerization experiment with initial stoichiometry targeting a degree of polymerization of 50 for each arm. Each macroinitiator synthesis used 1 molar equivalent of **1** for 10 molar equivalents of initiator. Polymerization was stopped at 1.5 hours, targeting conversions between 35% and 45%. An aliquot was taken for ^1H NMR analysis to determine monomer conversion. The resulting macroinitiator was purified by precipitation into cold methanol, followed by isolation via gravity filtration through a fine filter frit. The resulting white powder was dried overnight under vacuum at 50 $^{\circ}\text{C}$. Chain extension of these macroinitiators was carried out through reintroduction to polymerization conditions using benzyl methacrylate (BzMA) as monomer, targeting an additional 100 monomer units for each star arm. All chain extensions used 1 molar equivalent of **1** for 10 molar equivalents of initiator. See supplemental information for full experimental details.

Results and Discussion

The investigation into the synthesis of star polymers from a core-first approach using O-ATRP launched with the examination of the effect of different reaction concentrations on efficient and well-controlled star polymer synthesis. This investigation was motivated by the desire to avoid undesirable star-star coupling events, mitigate potential issues stemming from viscosity caused by high MW polymers, and to determine optimized conditions for the synthesis of well-defined star polymers using O-ATRP.

Initial polymerization conditions employed a 1:2 volumetric ratio of MMA:DMAc using multifunctional initiators possessing 2, 3, 4, 6, and 8 alkyl bromide initiating functionalities, targeting a degree of polymerization of 50 monomer units for each arm. Under these conditions, the results for all stars indicated a well-controlled system at monomer conversions above 50%. However, closer analysis of the polymerization revealed less control at lower monomer conversions. For all stars, this relatively less-controlled regime is characterized by high $\bar{M}_w/\bar{M}_n$, and low initiator efficiencies (I^*) (see supplemental information for full details). Furthermore, the $\bar{M}_w/\bar{M}_n$ of these polymers could be artificially low because for complex globular and compact polymeric architectures a difference in actual and measured dispersity caused by changes in elution behavior from GPC has been theoretically predicted and experimentally observed.^{40,41} A high I^* is indicative of agreement between theoretically calculated number average molecular weight ($M_{n(\text{theo.})}$) and measured number average molecular weight ($M_{n(\text{actual.})}$). The lesser degree of control found in these initial experiments

can perhaps be attributed to inefficient activation caused by low PC concentrations, resulting in insufficient amounts of $^2\text{PC}^{*+}$ and subsequently poor deactivation.

In the case of the linear polymer synthesized from the difunctional initiator, polymerization after 8 hours reached 78% conversion with an M_n of 9.2 kDa, $\bar{M}_w$ of 1.30 and $P^* = 89\%$. Synthesis of a 3-arm star under these conditions gave 66% conversion, $M_n = 14.2$ kDa, $\bar{M}_w$ of 1.13 and $P^* = 74\%$. The synthesis of the 4-arm star polymer yielded a product with $\bar{M}_w = 1.45$, $M_n = 11.1$ kDa, and $P^* = 115\%$ at 60% conversion while the 6-arm star gave $\bar{M}_w = 1.33$, $M_n = 19.5$ kDa, and $P^* = 91\%$ at 56% conversion. The 8-arm star was synthesized to a polymer with $\bar{M}_w = 1.47$, $M_n = 25.4$ kDa, $P^* = 108\%$ at 65% conversion. Importantly in this case, there was no deleterious increase in reaction solution viscosity, shown by an observed uniform stirring rate during the course of polymerization times.

Observing that for all stars control over polymerization was decreased at low monomer conversions using dilute conditions, further studies using a 1:1 volumetric ratio of MMA:DMAc at the onset of polymerization was performed. To prevent undesirable effects from increased viscosity at high polymer MWs, an additional 1.0 mL of DMAc was added at the 3rd hour of polymerization. These experiments resulted in increased control over the polymerization at all stages of monomer conversion. After 8 hours of polymerization under these conditions, the use of the difunctional initiator was polymerized to a linear polymer with M_n of 13.6 kDa, $\bar{M}_w$ of 1.29, and $P^* = 83\%$ at 84% conversion (Table 1, entry 1). A $\bar{M}_w$ of 1.18, M_n of 11.6 kDa and $P^* = 89\%$ at 65% conversion was realized for the 3-arm star (Table 1, entry 2). An analysis of the 4-arm, 6-arm, and 8-arm star showed 70% conversion $\bar{M}_w = 1.30$, $M_n = 15.1$, $P^* = 97\%$ and 50% conversion, $\bar{M}_w = 1.22$, $M_n = 17.1$ kDa, $P^* = 95\%$ and 60% conversion, $\bar{M}_w = 1.33$, $M_n = 25.4$ kDa, and $P^* = 101\%$ respectively (Table 1, entries 3, 4, 5). The results for 1:1 MMA:DMAc and 1:2 MMA:DMAc concentrations, as well as corresponding GPC traces for 1:1 MMA:DMAc conditions can be exemplified for the 3-arm and 8-arm stars in Figure 2.

In general, for all the stars using 1:1 MMA:DMAc by volume reaction conditions, dispersity typically decreased over time (Figures 2 and 3), with the exception of the 8-arm star, where $\bar{M}_w$ remained nearly constant until 58% conversion and rose to 1.47 at 65% conversion (Figure 2 E). Significantly, no detectable star-star coupling events were observed in all cases as evidenced by monomodal and symmetrical GPC traces coupled with high P^* s. However, it was observed that $\bar{M}_w$ tended to increase with an increasing number of arms. Without any GPC evidence of star-star coupling, this increasing can be attributed to a higher number of other radical termination events, causing loss of chain-end functionality and increased molecular weight distributions. In a comparison of both reaction concentration conditions tested, all experiments after ~50% conversion showed similar results (See SI for full experimental results). In an analysis of the effect of relative photocatalyst concentrations to both moles of initiator and moles of bromide initiating sites, a universal ratio of [10]:[1] of moles of multifunctional initiator to moles of **1** was found effective in synthesizing star polymers with a high degree of control over polymerization for all initiators used in this study (Table S3).

Additional studies of star polymer synthesis using O-ATRP was performed using 1:1 of MMA:DMAc. This system was further extended to include the synthesis of higher MW star polymers targeting a degree of polymerization of 100 monomer units for each arm. In the case of the telechelic polymer and stars with 3, 4, and 6 arms the synthesis was well-controlled (Figure 4 A, B, C, D), resulting in $\bar{M}_w/\bar{M}_n = 1.33, 1.50, 1.44$, and 1.61 as well as $PDI = 1.03, 1.02, 1.03$, and 1.04 , respectively (Table 2). However, when using the octo-functional initiator (Figure 4 E) loss of control was observed after 53% conversion, upon which dispersity rose from 1.67 to 2.00, the growth of molecular weight ceased to be linear, and PDI rose to 1.65. With conversions ranging from 84% to 90%, no star-star coupling events were observed in the GPC traces or molecular weight results (See SI for full GPC traces). However, in the case of the 3-arm and 6-arm star polymers, dispersity began to rise after 80% conversion, perhaps as a consequence of increased radical termination events.

To confirm chain-end group fidelity of the synthesized star polymers, diblock star polymer synthesis was performed through a chain-extension experiment. Chain-extension was achieved through star polymer macroinitiator synthesis under the optimized polymerization conditions, targeting conversions between 35% and 45% to ensure chain-end group fidelity, followed by macroinitiator isolation and subsequent reintroduction to polymerization conditions of the star polymer as the multifunctional initiator species (Figure 5 A). For all stars, chain-extension using benzyl methacrylate was successful, as evidenced by baseline resolved shifts in GPC traces (Figure 5 B). Similar to the synthesis of star homopolymers, was observed to increase with a corresponding increase in number of arms. In total, the ability to efficiently synthesize diblock star polymers provides a platform for targeted macromolecular engineering using O-ATRP.

Conclusions

Star polymers possessing 3, 4, 6, and 8 arms as well as a linear telechelic polymer were successfully synthesized using O-ATRP and a core-first approach. These reactions produced well-defined products using uniform stoichiometric conditions, reliant on maintaining a relatively concentrated reaction solution at the onset of polymerization. Significantly, star-star coupling events were not observed at monomer conversions as high as 87%. The synthesis was further expanded to include high MW star polymers with a high degree of polymerization of each arm. The success of this polymerization methodology for the synthesis of star polymers was further highlighted through the chain-extension of star polymers, providing an efficient and well-controlled method for the synthesis of higher order architectures using O-ATRP.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.

(A) Proposed catalytic cycle for core-first star synthesis using O-ATRP (left) and structure and properties of PC **1** used in this study (right). (B) Structures of multifunctional initiators used in this study containing n number of initiating sites.

Figure 2.

Top: A schematic representation of the synthesis of star polymers. Bottom: Plots of number average molecular weight (blue diamonds), dispersity (red squares), and theoretical M_n (black line) versus monomer conversion for the O-ATRP of MMA using (A) 1:2 MMA:DMAc by volume and (B) 1:1 MMA:DMAc by volume with (C) corresponding GPC traces for 1:1 MMA:DMAc by volume for a 3-arm star polymer. The results for an 8-arm star polymer are shown for (D) 1:2 MMA:DMAc by volume and (E) 1:1 MMA:DMAc by volume with (F) corresponding GPC traces for 1:1 MMA:DMAc by volume.

Figure 3.

Plots of number average molecular weight (blue diamonds), dispersity (red squares), and theoretical M_n (black line) versus monomer conversion for the O-ATRP of MMA using 1:1 MMA:DMAc by volume for (A) linear polymer, (B) 4-arm, and (C) 6-arm star polymers with corresponding GPC traces for the (D) the linear polymer, and (E) 4-arm, and (F) 6-arm star polymers.

Figure 4.

Plots of number average molecular weight (blue diamond), dispersity (red square), and theoretical M_n (black line) versus monomer conversion for the O-ATRP of MMA targeting a degree of polymerization of 100 for each polymer arm using 1:1 MMA:DMAc by volume for (A) linear polymer, and (B) 3-arm, (C) 4-arm, (D) 6-arm, and (E) 8-arm star polymers.

Figure 5.

(A) Reaction scheme for chain-extension of telechelic linear polymer and 3, 4, 6, and 8 arm PMMA star polymers extended with benzyl methacrylate to produce diblock star polymers and (B) corresponding GPC traces with the star polymer macroinitiator (purple) and diblock star polymer (orange).

Results of O-ATRP of MMA after 8 hours using multifunctional initiators with 2, 3, 4, 6, and 8 number initiating sites and an initial 1:1 MMA:DMAc ratio, by volume.^a

Table 1

Entry	# arms	[MMA]:[RBr _n]:[PC]	Conv. (%) ^b	<i>M_n</i> (actual) ^c (kDa)	<i>M_n</i> (theo.) (kDa) ^d	(<i>M_w</i> / <i>M_n</i>) ^e	<i>P</i> [*] (%) ^f
1	2	[1000]:[10]:[1]	84	13.6	8.8	1.29	83
2	3	[1500]:[10]:[1]	65	11.6	10.3	1.18	89
3	4	[2000]:[10]:[1]	70	15.1	14.7	1.30	97
4	6	[3000]:[10]:[1]	50	17.1	16.2	1.22	95
5	8	[4000]:[10]:[1]	60	25.4	25.7	1.33	101

^a Polymerization conditions are using 1:1 MMA:DMAc by volume with a total reaction volume of 2 mL, with addition of 1 mL of DMAc after 3 hours of polymerization. Each polymer arm is targeting a degree of polymerization of 50 at 100% monomer conversion. The polymerization is irradiated by white LEDs.

^b Determined by ¹H NMR spectroscopy.

^c Measured using GPC.

^d Calculated by $(Conv \times [Mon])/[Init.] \times Mw_{Mon})/1000$.

^e Calculated by $(Theo. M_n / Calc. M_n) \times 100$.

Results of O-ATRP of MMA after 8 hours using multifunctional initiators with 2, 3, 4, 6, and 8 number of initiating sites and targeting a degree of polymerization of 100.^a

Table 2

Entry	# arms	[MMA]:[RBr _n]:[PC]	Conv. (%) ^b	M_n (actual) (kDa) ^b	M_n (theo.) (kDa) ^b	$(M_w/M_n)^b$	P^* (%) ^b
1	2	[2000]:[10]:[1]	90	19.6	18.3	1.33	93
2	3	[3000]:[10]:[1]	87	26.3	26.7	1.50	102
3	4	[4000]:[10]:[1]	87	34.3	35.5	1.44	103
4	6	[6000]:[10]:[1]	85	50.3	52.3	1.61	104
5	8	[8000]:[10]:[1]	84	41.5	68.4	1.90	165

^a Polymerizations using 1:1 MMA:DMAc by volume with a total reaction volume of 2 mL, with addition of 1 mL of DMAc after 3 hours of polymerization. The polymerization is irradiated by white LEDs.

^b See footnote for Table 1 for details.