

Ultrahigh Molecular Weight Hydrophobic Acrylic and Styrenic Polymers through Organic-Phase Photoiniferter-Mediated Polymerization

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Cite This: *ACS Macro Lett.* 2020, 9, 613–618

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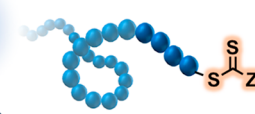
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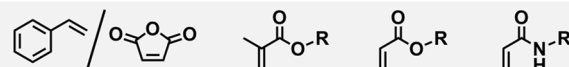
Supporting Information

ABSTRACT: As many physical properties of polymers scale with molecular weight, the ability to achieve polymers of nearly inaccessibly high molecular weight provides an opportunity to probe the upper size limit of macromolecular phenomena. Yet many of the most stimulating macromolecular designs remain out of reach of current ultrahigh molecular weight (UHMW) polymer synthetic approaches. Herein, we show that UHMW polymers of diverse composition can be achieved by irradiation of thiocarbonylthio photoiniferters with long-wave ultraviolet or visible light in concentrated organic solution. This facile photopolymerization strategy is general to acrylic-, acrylamido-, methacrylic-, and styrenic-based monomers, enabling the synthesis of well-defined macromolecules with molecular weights in excess of 10^6 g/mol. The high chain-end fidelity afforded by photoiniferter polymerization conditions facilitated the design of UHMW amphiphilic block copolymers, which were found to self-assemble into micellar morphologies up to 200 nm in diameter.

Photoiniferter-Mediated Ultra-High Molecular Weights



- ✓ M_n up to 5×10^6 g/mol
- ✓ $\bar{D} = 1.10 - 1.40$
- ✓ Facile blocking
- ✓ Micellar assemblies larger than 100 nm



Innovative developments in the field of reversible-deactivation radical polymerization (RDRP) have provided new synthetic routes to previously inaccessible materials and polymer architectures.^{1–4} Notably, recent advances in photo-mediated polymerization have proven exceptionally versatile due to their increased biocompatibility and ability to provide spatiotemporal control, enabling, for example, the design of materials capable of living additive manufacturing⁵ and synthetic cell surface engineering.⁶ Additionally, we recently demonstrated that long-wave ultraviolet (UV) irradiation of thiocarbonylthio compounds, in this case acting as photoiniferters,^{7,8} in the presence of vinyl monomers facilitates the synthesis of well-defined ultrahigh molecular weight (UHMW) polyacrylamides, defined here as linear chains with number-average molecular weights greater than 10^6 g/mol.⁹ Previous syntheses of UHMW polymers by RDRP techniques established that maximizing the rate of chain propagation relative to termination (i.e., increasing R_p/R_t) is critical to successfully achieving UHMWs.¹⁰ Several approaches achieve this effect,¹¹ for example, through the use of high pressure^{12,13} or heterogeneous conditions.^{14–17} Moreover, Destarac and co-workers introduced the idea of exploiting the high viscosities that result in “gel polymerization” to achieve UHMWs.¹⁸ Matyjaszewski et al. additionally showed that RAFT agents are activated by Cu(I) analogously to alkyl halides in atom-transfer polymerization while also acting as iniferters, leading to

(ultra)-high molecular weight polymers.¹⁹ Alternatively, aqueous photoiniferter-mediated polymerizations exploit the rate-enhancing effect of water on acrylamide polymerizations²⁰ to maximize R_p . In this system, both the chain diffusion-limiting effect of high viscosity at high monomer conversions²¹ and the lack of exogenous, low-molecular-weight radical initiators serve to minimize bimolecular termination (and therefore R_t), thus, enabling the synthesis of UHMW polymers under homogeneous conditions at ambient temperature and pressure.

Our initial studies demonstrated that unprecedented molecular weights ($M_n > 8 \times 10^6$ g/mol in some cases) could be achieved in aqueous solution, yet these conditions limited the scope of UHMW polymerizations to water-soluble monomers with high propagation rate constants (k_p). In pursuit of expanding the UHMW territory to include the full diversity of acrylic and even styrenic monomers, we sought to develop a protocol for this photoiniferter technique that

Received: March 10, 2020

Accepted: April 1, 2020

Published: April 7, 2020

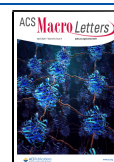


Table 1. Ultrahigh Molecular Weight Polymers Prepared through Photoiniferter Polymerization Conditions

entry	polymer	time (h)	monomer/iniferter	conversion ^a (%)	$M_{n,SEC}$ ^b (g/mol)	$M_{n,theo}$ ^c (g/mol)	M_w/M_n
1 ^d	PMA	8	19400:1	82	753000	1370000	1.75
2	PMA	4	20800:1	85	1770000	1520000	1.19
3	PMA	4	80000:1	83	5520000	5570000	1.10
4	PDMA	4	20200:1	77	1650000	1540000	1.23
5	PNAM	4	19300:1	95	1860000	2580000	1.26
6	PNIPAM	8	20700:1	85	1870000	1990000	1.19
7	PMA- <i>b</i> -PMA	8 + 8	(12500:1) + (11400:1)	>95 + >95	1830000	2060000	1.24
8	PMA- <i>b</i> -PDMA	8 + 8	(17000:1) + (14700:1)	>95 + >95	2200000	2690000	1.18
9	PMA- <i>b</i> -PNAM	8 + 8	(11800:1) + (11800:1)	>95 + >95	2630000	2920000	1.22
10	PDMA- <i>b</i> -PtBA	18 + 18	(14000:1) + (6000:1)	>95 + >95	1010000	2160000	1.37
11	PMMA	24	14000:1	85	750000	1190000	1.70
12 ^e	PMMA	24	20300:1	82	1370000	1670000	1.35
13 ^f	P(<i>S-alt</i> -MA _n)	24	8400	91	1540000	1840000	1.33
14 ^f	P(<i>S-alt</i> -BnMIm)	24	8500	85	2400000	2490000	1.10

^aMonomer conversion was determined with gas chromatography (GC) or ¹H NMR spectroscopy. ^bAbsolute number-average molecular weights ($M_{n,SEC}$) were determined by SEC equipped with a multiangle light-scattering detector assuming 100% mass recovery or a known dn/dc . ^cThe theoretical molecular weights ($M_{n,theo}$) were determined from the monomer conversion calculated by GC or ¹H NMR spectroscopy. ^dThis polymerization was conducted with [MA] = 2 M in DMSO. The remaining polymerizations were run at [monomer] = 4 M. ^eOne molar equivalent of tertiary amine (PMDETA) was included to enhance control. ^fThis polymerization was conducted under blue light irradiation in dioxane.

enables UHMW polymer synthesis in organic media. Specifically, polymerizing hydrophobic and low- k_p monomers would provide access to UHMW materials with tunable composition and functionality. Herein, we introduce a straightforward strategy to prepare polymers of ultralong chain lengths in nonaqueous solvents. The versatility of this new photoiniferter-mediated approach is demonstrated through the synthesis of well-defined polymers derived from acrylic-, acrylamido-, methacrylic-, and styrenic-based monomers, as well as the design of UHMW amphiphilic block copolymers capable of assembling into exceptionally large micellar morphologies.

We first investigated the polymerization of methyl acrylate (MA) with a trithiocarbonate iniferter under UV light. In aqueous conditions, high- k_p monomers can be polymerized to ultrahigh chain lengths under relatively dilute conditions ([monomer] = 1–2 M).^{9,18} However, when applying similar polymerization conditions to a hydrophobic monomer such as MA (2 M) in dimethylsulfoxide (DMSO), a polar aprotic solvent, poor molecular weight control was observed at high monomer conversions (Table 1, entry 1, Figure S1). Conversely, by doubling the monomer concentration, good agreement between theoretical and measured molecular weights were recorded with substantially lower dispersity and, predictably, enhanced polymerization rate (R_p ; Table 1, entry 2, Figures 1 and S2). Even when employing a monomer to iniferter ratio of 80000, the highest reported in our previous study, molecular weight control and dispersity observed were comparable to that found in traditional controlled radical polymerizations (Table 1, entry 3, Figure S3, $M_{n,theo}$: 5.57×10^6 g/mol, $M_{n,SEC}$: 5.52×10^6 g/mol, $\bar{D}$: 1.10, DP_n : 60400). Additionally, acrylamido monomers *N,N*-dimethylacrylamide (DMA), *N*-acryloyl morpholine (NAM), and *N*-isopropylacrylamide (NIPAM) were readily polymerized to ultrahigh and controlled chain lengths under these photoiniferter conditions in DMSO (Table 1, entries 4–6, Figures 2, S4, S5, and S6). With these conditions established, we targeted the synthesis of yet-unrealized UHMW homopolymers and block copolymers. In a one-pot procedure, a series of block copolymers were successfully prepared by chain extension of UHMW PMA with

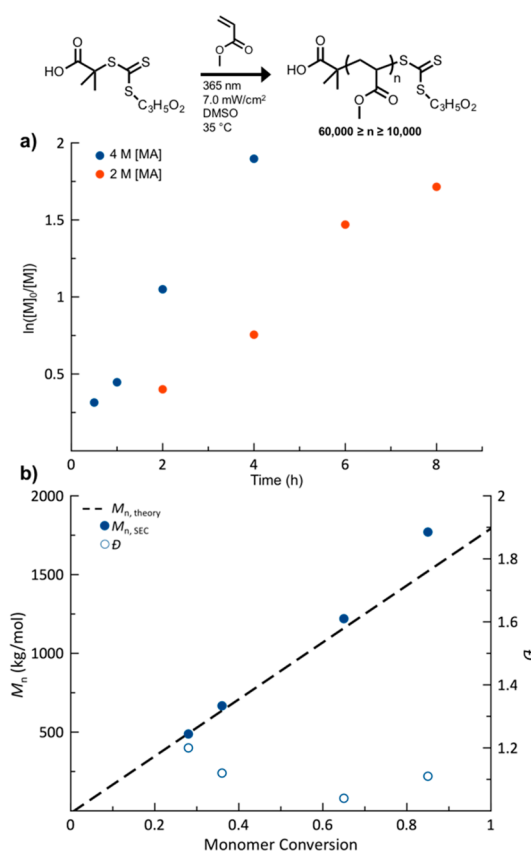


Figure 1. Ultrahigh molecular weight hydrophobic polymer synthesis performed in polar aprotic DMSO near room temperature (35 °C). Predetermined degrees of polymerization were targeted through the monomer to iniferter ratio, with ratio of 20000:1 measured in this example. (a) Increased methyl acrylate monomer concentration led to rapid polymerization rates and enabled access to ultrahigh molecular weight poly(methyl acrylate) (PMA) through increased solution viscosity. (b) Narrow molecular weight distributions and good agreement between theoretical and measured molecular weights were observed to high monomer conversion for the polymerization conducted at [MA] = 4 M.

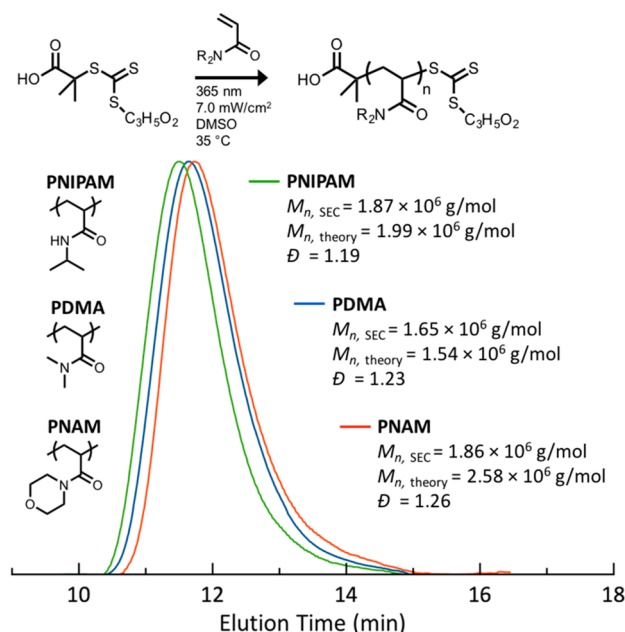
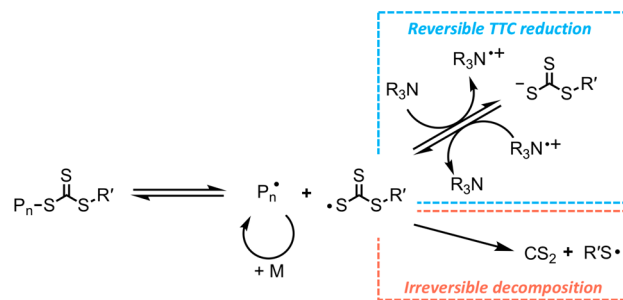


Figure 2. Series of ultrahigh molecular weight polyacrylamides were prepared through nonaqueous photoiniferter polymerization conditions.

MA, DMA, or NAM. We observed good agreement between theoretical and measured molecular weights and narrow molecular weight distributions for each of these UHMW block copolymers (Table 1, entries 7–9, Figures S7, S8, and S9). The high viscosities generated in these concentrated systems likely play a critical role in maintaining polymerization control. Chain diffusion is more significantly restricted in viscous media compared to small-molecule diffusion; therefore, it is possible the rate of the diffusion-controlled bimolecular termination reaction is reduced relative to the rate of propagation. Furthermore, reduced diffusion of the deactivating trithiocarbonate-centered radical away from active chain ends potentially facilitates more rapid chain deactivation and improved control.

We also suspected that this nonaqueous photopolymerization procedure, in which R_p is enhanced through increased monomer concentration and solution viscosity, could enable UHMW polymer synthesis from monomers with lower k_p , such as methyl methacrylate (MMA). However, our initial attempts at polymerizing MMA to ultralong chain lengths resulted in lower-than-expected molecular weights and high dispersities (Table 1, entry 11). This result is similar to that previously observed by Qiao and co-workers, who also found that control over the photoiniferter-mediated polymerization of methacrylates can be improved through addition of a tertiary amine reductant.²² In this case, the trithiocarbonate (TTC) sulfanyl radical generated upon photoiniferter photolysis was proposed to undergo spontaneous decomposition to CS_2 and an alkylthiyl radical,²³ which detrimentally affects polymerization control. In the presence of single-electron reductants like tertiary amines, however, the TTC sulfanyl radical is reduced to a TTC anion, which is not prone to degradation (Scheme 1). Accordingly, when this strategy was implemented in our system via the addition of N,N,N',N'',N'' -pentamethyldiethylenetriamine (PMDETA), good agreement between theoretical and measured molecular weights was observed (Table 1, entry 12, Figure S10).

Scheme 1. Main Photoiniferter-Mediated Polymerization Equilibrium along with Products of Trithiocarbonate (TTC) Reduction by Trialkylamines (above) and the Previously Proposed Mechanism of TTC Radical Decomposition (below)



Yet this outcome, in which the addition of a tertiary amine is necessary for methacrylates but not acrylates or acrylamides, leads us to suspect that the mechanism of TTC radical degradation is more than a unimolecular process. If this decomposition pathway is indeed unimolecular, the loss of control should occur, to some extent, regardless of the identity of the polymerizing monomer. However, this is contrary to the good results we have previously observed in our UHMW polymerizations that utilize very low concentrations of photoiniters. Alternatively, we find it plausible that the TTC sulfanyl radical could engage in α -H atom abstraction of a propagating chain end, especially considering it is well-known that propagating methacrylyl radicals are prone to termination by disproportionation.²⁴

UHMW polymers derived from styrenic monomers represent one of the most difficult classes of materials to prepare through low-temperature photopolymerizations. Because of its low k_p , styrene is typically polymerized at high temperatures or high pressures to achieve high MWs under reasonable periods of time.^{12,25} Indeed, attempts to synthesize polystyrene under the conditions described above did not lead to UHMW polymers, and relatively broad molecular weight distributions were observed. However, we found that copolymerization of styrene with maleic anhydride (MAN) or maleimides produced UHMW styrene-containing copolymers. In addition to a strong tendency toward alternation, copolymerization of styrene with MAN/maleimides exhibits higher values of R_p than that of styrene alone,^{26–28} even at low temperatures.²⁹ It was therefore expected that our low-temperature photoiniferter conditions would be suitable for the synthesis of UHMW poly(styrene-*alt*-maleic anhydride) (PS-*alt*-PMAN). However, we observed poor control over the photoiniferter-mediated copolymerization of styrene and maleic anhydride, which we attributed to background initiation of the styrene/MAN charge-transfer complex under UV irradiation.³⁰ Because TTC and dithiobenzoate iniferters also undergo photolysis under visible light irradiation,^{31,32} we reasoned that it may be possible to selectively initiate the photoiniferter-mediated process without also activating the styrene/MAN complex. Indeed, the use of a dithiobenzoate iniferter and blue light irradiation (450 nm) afforded well-defined UHMW PS-*alt*-PMAN with good agreement between theoretical and measured molecular weights while maintaining a narrow molecular weight distribution (Table 1, entry 13, Figures 3 and S11). This functional UHMW polystyrene copolymer could potentially be encoded with periodic

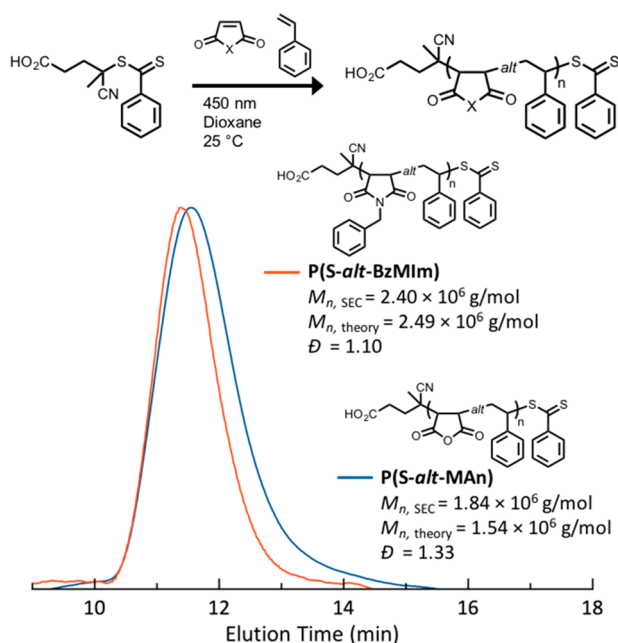


Figure 3. UHMW poly(styrene-*alt*-benzyl-maleimide) and poly(styrene-*alt*-maleic anhydride) were prepared in dioxane at room temperature (25 °C). Predetermined degrees of polymerization were targeted through the monomer to iniferter ratio, with monomer to iniferter ratios greater than 20000:1. Blue light irradiation (450 nm) allowed for photoiniferter polymerizations to high monomer conversion without UV activation of the comonomer charge-transfer complex.

anhydride-based monomers.³³ As an example, a functionalized benzyl-maleimide (BzMIIm)-based monomer was polymerized with styrene to UHMW with excellent molecular weight control (Table 1, entry 14, Figures 3 and S12).

Finally, in an effort to probe the effect of ultralong chain lengths on macromolecular phenomena, we synthesized UHMW amphiphilic diblock copolymers and studied their self-assembly behavior in water. First, we prepared assemblies from two block copolymers, PMA-*b*-PDMA (Table 1, entry 8) and PMA-*b*-PNAM (Table 1, entry 9), by dialysis of 5 ng/mL solutions in THF against water. In both cases, very large (≤ 1 μ m) and polydisperse aggregates were observed (Figures S8 and S9). Because unimer exchange at these very high molecular weights (>2 MDa in both cases) is either very slow or nonexistent, we expect that the assemblies would be unable to adopt their thermodynamically preferred morphology and instead remain kinetically trapped in irregular aggregates. We also considered the possibility that the low glass transition temperature of the poly(methyl acrylate) block may cause the assemblies to deform upon drying.³⁴ Consequently we synthesized a new block copolymer, polyDMA-*b*-poly(*tert*-butyl acrylate) (PDMA-*b*-PtBA, Table 1, entry 10) at a lower molecular weight ($M_n = 1.01 \times 10^6$ g/mol) and imaged the assemblies with cryogenic TEM. Images obtained by this approach reveal large (100 ± 50 nm) micellar assemblies (Figure 4). While still somewhat polydisperse, these micelles are exceptionally large compared to those accessible by block copolymers of conventional molecular weights and likely feature extraordinarily low critical micelle concentrations, possibly enabling utility in applications such as water remediation.

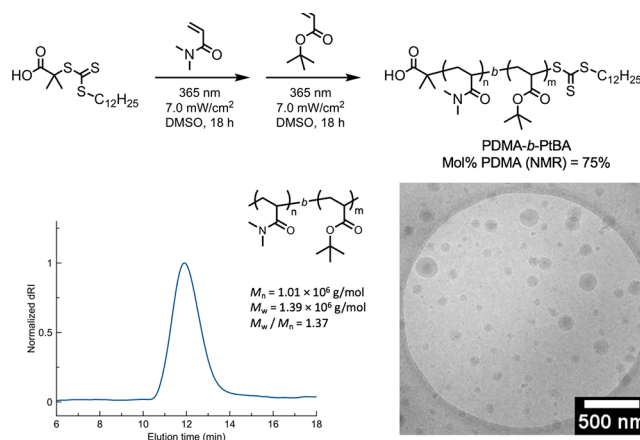


Figure 4. Synthesis of the amphiphilic diblock copolymer poly(*N,N*-dimethylacrylamide-*b*-*tert*-butyl acrylate) ($M_n = 1.01 \times 10^6$ g/mol, $M_w/M_n = 1.37$) and cryogenic TEM image of assemblies formed upon solvent switch of a 1.04 mg/mL solution in THF to water.

In conclusion, the approach described herein, which relies on high monomer concentrations and, in some cases, judicious comonomer pairing, enabled the synthesis of UHMW polymers from hydrophobic and low- k_p monomers under mild UV and visible light in the presence of thiocarbonylthio iniferters. Unlike previous attempts toward UHMW polymers, high chain lengths were realized without the presence of metal catalyst, exogenous initiators, or high pressures. Importantly, these photopolymerizations resulted in high chain-end fidelity and facilitated the design of UHMW amphiphilic block copolymers in a one-pot process, the products of which were capable of assembling into exceptionally large micellar nanoparticles. The potential of this underexplored class of new UHMW materials could prove useful for biomedical applications, hydrogel toughening, and mechanochromic sensing, among other areas.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsmacrolett.0c00203>.

Experimental and characterization details (PDF)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This material is based on work supported by the National Science Foundation (DMR-1904631) and the National Science Foundation Graduate Research Fellowship (DGE-1315138; M.B.S.). John B. Garrison is gratefully acknowledged for his assistance in collecting dry-state TEM images. Cryogenic TEM images were acquired using the instrumentation at IMRI (<https://imri.uci.edu>) facilities at UCI.

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