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Expanding the Scope of the Photoinduced Living Radical Polymerization of Acrylates in the Presence of CuBr_2 and $\text{Me}_6\text{-Tren}$

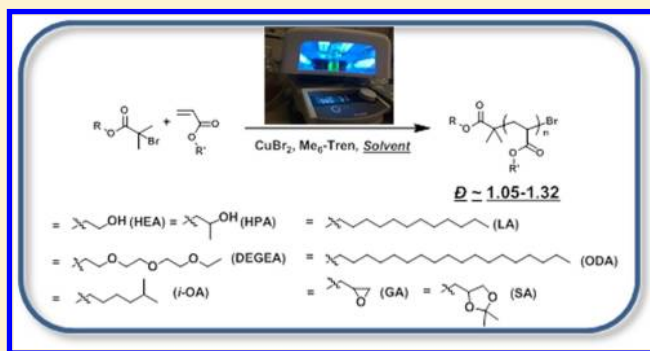
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Supporting Information

ABSTRACT: Photoinduced living radical polymerization of acrylates is achieved upon UV irradiation ($\lambda_{\text{max}} \approx 360$ nm) in the presence of an aliphatic tertiary amine ligand ($\text{Me}_6\text{-Tren}$) in the presence of low concentrations of CuBr_2 , yielding poly(acrylates) with near perfect retention of end group fidelity. The effect of the nature of the solvent on the rate of polymerization was investigated in order to expand the scope and identify the limitations of the system. Subsequently, a range of acrylic monomers containing hydrophobic and hydrophilic substituents have been screened, including lauryl acrylate, octadecyl acrylate and diethylene glycol ethyl ether acrylate, all of which present low dispersities ($\bar{D} \approx 1.1$) at very high conversions. Functional monomers, including glycidyl acrylate and solketal acrylate, were also found to be tolerant to the photomediated reaction. Finally, solketal acrylate was copolymerized with methyl acrylate which, following deprotection of the pendant ketal group, furnished an amphiphilic diblock copolymer. Self-assembly of this block copolymer into polymer micelles in aqueous media was exemplified by dynamic light scattering (DLS) and transmission electron microscopy (TEM).



INTRODUCTION

Controlled living radical polymerizations (CLRP) has revolutionized the field of polymer synthesis due to the ability to regulate molecular weight, monomer sequence and dispersity for a variety of vinyl polymer compositions and architectures. The current polymerization tools include reversible addition–fragmentation polymerization (RAFT),^{1,2} nitroxide mediated radical polymerization (NMP),^{3,4} as well as transition-metal-mediated methods including atom transfer living radical polymerization (ATRP)^{5–7} and single electron transfer living radical polymerization (SET-LRP).^{8–10} The latter two exploit the rapid and reversible catalytic activation of alkyl halide initiators by Cu^0/Cu^I species to generate carbon-based radicals. Control over polymerization is inferred by an accumulation of a higher oxidation state complex (Cu^{II}) which can arise as a result of either the persistent radical effect (PRE)^{11,12} or via disproportionation of Cu^I in the presence of an appropriate solvent and ligand.^{13–18} The deactivating Cu^{II} species adjusts the reaction equilibrium toward the dormant species ($\text{P}_n\text{-X}$) imparting control over the radical concentration (P_n^{\bullet}) and limiting the amount of termination events. Following these methods complex polymer architectures can be obtained in a quantitative yield, including stars, blocks, brushes, cycles, grafts, etc.^{19–23}

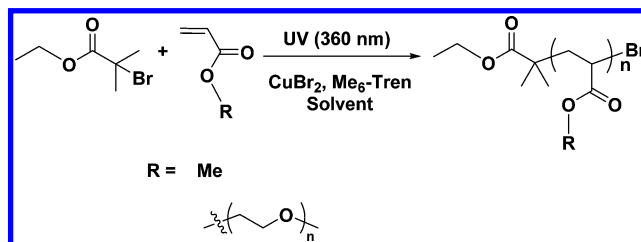
In recent years, there has been a continued effort to expand the scope of the current living polymerization protocols by

regulating the activation and deactivation steps via an external stimuli²⁴ such as electrochemical,²⁵ pressure,^{26,27} or photochemical.^{28–30} For photopolymerization, the use of photoinitiators provides access to rapid polymerization reactions, although little control and broad molecular weight distributions are often obtained.^{31,32} For application in the area of controlled radical polymerization, this necessitates the need for the development of photoregulated approaches that control both the initiation step and all of the subsequent activation/propagation reactions. To this end, Hawker et al. recently reported the CLRP of methacrylates using visible light with a photoactive iridium complex (*fac*-[Ir(ppy)₃] (ppy = 2-pyridyl-phenyl) which under appropriate irradiation gave very well-defined poly(methyl methacrylate) (poly(MMA)) with a dispersity of ~ 1.3 at 60% conversion.^{33,34}

Using a more traditional transition metal system Yagci has reported the polymerization of methyl methacrylate using various systems in both the presence and the absence of photoinitiators and photosensitizers at $\lambda = 400\text{--}500$ nm, maintaining good control over the molecular weight distributions (~ 1.3) after a reaction time of 8 h (85% conversion).^{35–39} Likewise, Matyjaszewski has investigated the visible and

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Table 1. Solvent Compatibility Study for the Photo-Mediated Polymerization of MA and PEGA.^a

entry	solvent	[M]	time [h]	convn ^b [%]	$M_{n,th}$ [g mol ⁻¹]	$M_{n,SEC}$ [g mol ⁻¹]	\bar{D}
1	EtOH	MA DP _n = 50	1.5	38	4500	2150	1.16
			24	99		4200	1.08
2	IPA		1.5	4		200	1.25
			24	100		3100	1.16
3	TFE		1.5	54		2000	1.14
			24	99		5200	1.09
4	TFP		1.5	3		160	1.26
			24	74		7000	1.10
5	toluene:MeOH [4]:[1]		1.5	8		500	1.22
			24	100		6300	1.08
6	toluene:IPA [4]:[1]		1.5	4		300	1.27
			24	96		6000	1.11
7	dioxane		1.5	52		3600	1.91
			24	99		5100	1.99
8	anisole		1.5	84		1900	2.27
			24	99		4300	1.46
9	DMSO	PEGA DP _n = 10	1.5	93	5000	6500	1.11
			24	99		6900	1.10
10	H ₂ O		1.5	95		6600	1.55
			24	99		7900	1.48
11	DMSO:H ₂ O [1]:[1]		1.5	94		6700	1.21
			24	99		7200	1.19
12	DMSO:H ₂ O [3]:[1]		1.5	92		6200	1.12
			24	99		6900	1.12

^a[I]:[Cu^{II}]:[Me₆-Tren] = [1]:[0.02]:[0.12] in (50%, v/v) solvent. ^bDetermined by ¹H NMR. ^cDetermined by CHCl₃ or DMF SEC analysis (see ESI).

sunlight photoinduced ATRP of methyl acrylate and methyl methacrylate in DMF utilizing TPMA, TPMA*, and PMDETA as the ligands, with optimized conditions achieving ~80% monomer conversion in 12 h.⁴⁰

Recently, we reported an efficacious photoactivated living polymerization of acrylates mediated by Cu^{II}Br₂ in the presence of excess aliphatic tertiary amine ligands presenting an outstanding degree of control (~1.10) and end group fidelity.⁴¹ Reaction rates were fast compared to related systems (>95% conversion was achieved in 80 min) and temporal control was possible during polymerization via intermittent light and dark reactions. Furthermore, when α -hydroxy and *vic*-diol functionalities were incorporated into the alkyl halide initiators with retention control epitomized by the low dispersities achieved. The use of different solvents, including DMSO, MeOH, MeCN, and DMF, was briefly probed to demonstrate the polymerization of a short chain alkyl acrylates in addition to poly(ethylene glycol) methyl ether acrylate (PEGA₄₈₀). The protocol has since been readily translated into a continuous-flow process whereby poly(MA) homopolymers and poly(MA)-*b*-(*n*BA) block copolymers were prepared in the micro- and milliflow reactors.⁴²

Herein, we report an expansion of the scope of this photomediated living radical polymerization. The use of

different solvents was further investigated, and several solvents are shown to be suitable for photomediated LRP. Notably, water was found to be an exception exhibiting poor molecular weight distribution control. The number of available solvents enables polymerization of a range of monomers including functional acrylates, (glycidyl acrylate and solketal acrylate), increasingly hydrophobic acrylates (isooctyl acrylate, lauryl acrylate, and stearyl acrylate) and thermoresponsive acrylates (diethylene glycol ethyl ether acrylate). Photomediated polymerization was exploited to synthesize well-defined block copolymers (poly(MA)-*b*-(SA)) in a one-pot process, which were rendered amphiphilic upon deprotection of the solketal diol. The amphiphilic block copolymers self-assemble in aqueous solution forming nanoparticles characterized by dynamic light scattering (DLS) and transmission electron microscopy (TEM).

MATERIALS AND METHODS

All materials were purchased from Sigma-Aldrich or Fisher Scientific unless otherwise stated. Copper(II) bromide (Cu^{II}Br₂) and ethyl 2-bromoisobutyrate (EBiB) were used as received. All monomers were passed through a basic Al₂O₃ column prior to use. Tris(2-(dimethylamino)ethyl)amine (Me₆-Tren) was synthesized according to a previously reported literature.⁴³ Solketal acrylate was synthesized

according to a reported procedure⁴⁴ and distilled under reduced pressure (45 °C, 10⁻¹ mbar) to yield a colorless liquid. GA was also synthesized following a literature protocol⁴⁵ and a flash column chromatography was utilized to obtain a colorless liquid.

Instrumentation. ¹H NMR spectra were recorded on Bruker DPX-300 and DPX-400 spectrometers using deuterated solvents 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. All samples were passed through 0.45 μm PTFE filter before analysis. The mobile phase was chloroform with 2% triethylamine eluent at a flow rate of 1.0 mL min⁻¹. SEC data was analyzed using Cirrus v3.3 with calibration curves produced using Varian Polymer laboratories Easi-Vials linear PMMA standards (200 to 4.7 × 10⁵ g mol⁻¹). UV/vis spectra were recorded on Agilent Technologies Cary 60 UV-vis in the range of 200–1100 nm using a cuvette with 10 mm optical length. The source of UV light was a UV nail gel curing lamp (available on ebay from a range of suppliers) (λ_{max} ~ 360 nm) equipped with four 9 W bulbs. DLS analysis was performed on a Malvern Instruments Zetasizer Nano-ZS machine. A polystyrene disposable cuvette was filled with 4.5 mL of deionized water which contained 0.05 mL of sample and placed into the instrument. The machine was configured to run analysis in a high resolution mode at 25 °C and determine total number of measurements automatically providing Z-average and PDI values. The measurement took approximately 2 min for each sample. TEM analysis was performed employing a JEOL 1200 EX-II microscope with a Gatan 1 k × 1 k CCD camera. Samples were collected on 200-mesh Cu grids and stained with 2% uranyl acetate prior to analysis. The mean diameter of the polymer micelles, coefficient of variation and normal distribution values were calculated by analyzing TEM images in ImageJ software.

General Procedure for Photoinduced Polymerization. Filtered monomer (DP_n equiv), EBiB (1 equiv), CuBr₂ (0.02 equiv), Me₆-Tren (0.12 equiv), and DMSO (2 mL) were added to a septum-sealed vial and degassed by purging with nitrogen for 15 min. Polymerization commenced upon exposure of the degassed reaction mixture to the UV lamp. The reaction vial was placed in the center of a commercial polychromatic UV nail curing lamp (λ_{max} = 360, 4 × 9 W), which was placed on top of a magnetic stirrer for agitation (Figure S1, Supporting Information). Samples were taken periodically and conversions measured using ¹H NMR and SEC analysis.

General Procedure for in Situ Chain Extension Reactions. Filtered MA (1 mL, 11.1 mmol, 50 equiv), EBiB (32 μL, 0.22 mmol, 1 equiv), CuBr₂ (1.0 mg, 4.4 μmol, 0.02 equiv), Me₆-Tren (7 μL, 22.0 μmol, 0.12 equiv), and DMSO (1 mL) were added to a septum sealed vial and degassed by purging with nitrogen for 15 min. Polymerization commenced upon exposure of the degassed reaction mixture to the UV lamp. The reaction vial was placed in the center of a commercial polychromatic UV nail curing lamp (λ_{max} = 360, 4 × 9 W), which was placed on top of a magnetic stirrer for agitation (Figure S1). After 90 min a 1:0.5 mixture of degassed SA (100 equiv) and DMSO was added to the reaction mixture via degassed syringe. Samples were taken periodically and conversions were measured using ¹H NMR and SEC analysis.

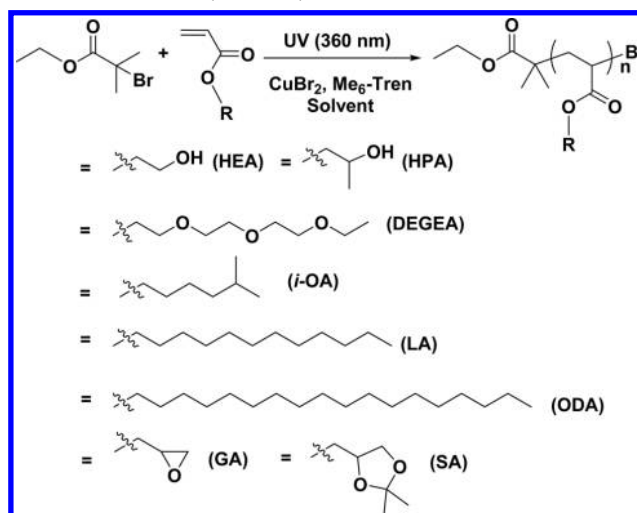
RESULTS AND DISCUSSION

Initially, various solvents were screened to ascertain their compatibility with the photomediated process. Methyl acrylate (MA) was selected as the model monomer and subjected to previously reported polymerization conditions with [MA]/[I]/[CuBr₂]/[Me₆-Tren] = [50]/[1]/[0.02]/[0.12]. Alcohols were found to be compatible with this technique although a slower rate of polymerization was observed relative to DMSO. For example, when ethanol (EtOH) was employed as solvent a

lower conversion (38%) was obtained in 90 min as compared to >95% in DMSO. Likewise, in isopropanol (IPA) conversion was limited within a 90 min reaction time (4%). However, both EtOH and IPA resulted in full conversion (>99%) in 16 h with low dispersity values obtained from SEC analysis (\bar{D} = 1.08, Table 1, entry 1 and 1.16, entry 2, Figure S2 and S3, respectively). Fluorinated alcohols, including 2,2,2-trifluoroethanol (TFE) and 2,2,3,3-tetrafluoropropanol (TFP) have recently been reported as good solvents for SET-LRP as catalyzed by Cu(0) wire.^{46–49} These solvents possess interesting properties, such as considerably higher melting points and lower boiling temperatures, strong H-bond donor properties and acidic character compared to nonfluorinated counterparts. Under photomediated polymerization conditions, TFE gave rise to 54% conversion after 90 min while TFP exhibited a suppression in the rate (3% in 90 min), in line with the analogous nonfluorinated alcohols (EtOH, IPA). Nevertheless, full conversion (>99%) was again obtained within 16 h, and low dispersities were retained (\bar{D} < 1.10, Table 1, entries 3–4, Figures S4 and S5).

Full dissolution of monomer is important for maintaining control during the Cu(0)-mediated polymerization of alkyl acrylates proceeding in both homogeneous and self-generating heterogeneous media.^{50,51} Thus, the polymerization of MA was investigated in less polar solvent systems. Polymerization in toluene was previously reported to proceed with loss of control and furnished polymers with higher dispersities.⁴¹ This was attributed, in part, to the limited solubility of the [Cu^{II}Br₂] complexes in toluene. Consequently, mixtures of toluene with methanol or IPA (toluene/alcohol: 4/1) were investigated as an alternative solvent system to satisfy required monomer and [CuBr₂] solubility. Although relatively slower rates of polymerization were observed, quantitative yields were obtained without compromising the polymerization control and dispersity (\bar{D} ~ 1.10, Table 1, entries 5–6, Figures S6 and S7). Dioxane and anisole were also utilized as neat solvent systems, however, the limited solubility of the [CuBr₂] complexes again resulted in uncontrolled polymers with dispersities of 2 and 1.46 respectively (Table 1, entries 7–8, Figures S8 and S9).

Finally, water was employed as solvent for the photo-mediated polymerization of poly(ethylene glycol) methyl ether acrylate (PEGA₄₈₀). Surprisingly, the aqueous polymerization of PEGA presented poor control over the molecular weight distribution when full conversion was attained (\bar{D} = 1.48, Table 1, entry 10, Figure S10). However, the identical polymerization in DMSO proceeded with comparable control to that observed during the polymerization on MA in DMSO (\bar{D} = 1.10, Table 1, entry 9, Figure S11), indicating that the solvent (H₂O) was responsible for this loss of control. In an attempt to understand this observation a UV-vis spectroscopy experiment was performed. A deoxygenated solution of [Cu^{II}Br₂]:[Me₆-Tren] = [1]:[6] to mimic polymerization conditions in H₂O, revealed the characteristic absorbance at λ_{max} = 950 nm with an additional absorbance at λ = 750 nm both attributed to the d–d transitions of the d⁹ Cu^{II}–tertiary amine complex. The mixture was subsequently exposed to UV irradiation for 90 min proceeding with no detectable decrease in the absorbance. Identical results were observed following irradiation for 24 h, suggesting that Cu^{II} could not be efficiently reduced in aqueous solution (Figure S12). This is in line with the relative stabilities of Cu^{II} and Cu^I amine complexes in H₂O, in which the disproportionation equilibrium is significantly shifted toward

Table 2. Photomediated Polymerization of a Variety of Acrylate Monomers^a

entry	[M]	solvent	[M]/[I]	time [h]	convn ^b [%]	$M_{n,th}$ [g mol ⁻¹]	$M_{n,SEC}$ ^c [g mol ⁻¹]	\bar{D}
1	HEA	DMSO	20	1.5	98	2300	4500	1.10
2	HPA		20	1.5	92	2600	6200	1.32
3	ODA	Tol/IPA [4]:[1]	15	1.5	4	4800	150	1.10
				10	99		4500	
4a	LA	IPA Tol/MeOH [4]:[1]	50	3.5	83	12 900	9900	1.18
				16	100		10 300	1.21
				7	88		8000	1.05
4b				24	99		11 400	1.07
5a	nBA	DMF DMSO	50	10	99	6400	6700	1.06
				1.5	97			
5b							6800	1.16
6	DEG	DMSO	20	1.5	80	4300	4100	1.10
				17	99		4800	1.13
7	GA		20	1.5	99	2600	2900	1.19
8	SA		100	1.5	80	18 600	11 500	1.10
				10	99		16 000	1.07
9	iOA	Tol/MeOH [4]:[1]	25	1.5	3	4600	100	1.17
				10	100		2800	

^a[I]: [Cu^{II}]: [Me₆-Tren] = [1]: [0.02]: [0.12] in (50%, v/v) solvent. ^bDetermined by ¹H NMR. ^cDetermined by CHCl₃ SEC analysis (see Supporting Information).

the higher oxidation Cu^{II} species ($K_{dis} > K_{com}$). Nevertheless, for cases where the presence of water is desirable, the polymerization of PEGA₄₈₀ was screened in mixtures of H₂O: DMSO. In 50% aqueous solution (DMSO:H₂O = 1:1) the reaction proceeded with comparable rates to pure DMSO media furnishing final polymer with a dispersity of 1.19 (Table 1, entry 11, Figure S13). Decreasing the water content to 25% (DMSO:H₂O = 3:1) had no effect on the rate of polymerization but resulted in an improvement in dispersity (\bar{D} = 1.12, Table 1, entry 12, Figure S14).

In an attempt to expand the scope of this photoinduced system, hydroxyethyl acrylate (HEA) was polymerized using DMSO as solvent under the following reaction conditions: [M]/[I]/[CuBr₂]/[Me₆-Tren] = [20]/[1]/[0.02]/[0.12]. The polymerization proceeds rapidly with near quantitative monomer conversion (>97%) achieved within 90 min, as determined by the ¹H NMR analysis. SEC analysis revealed a symmetrical, monomodal molecular weight distribution with low dispersity (\bar{D} = 1.10, Table 2, entry 1, Figure S15a) with no

observable evidence of high or low molecular weight termination events. Hydroxypropyl acrylate (HPA) was polymerized under identical conditions and high conversion was attained within 90 min (92%). A slight deviation in polymerization control was represented by a broader molecular weight distribution by SEC (\bar{D} = 1.30, Table 2, entry 2, Figure S16a). Diethylene glycol ethyl ether acrylate (DEGEA) forms thermoresponsive homopolymers with an LCST of ~13 °C. As such it has previously been incorporated into block copolymer compositions to tune the cloud point or phase transition temperature for higher order assembled structures. Pleasingly, DEGEA was found to be compatible with the photomediated reaction conditions, yielding a well controlled polymer with a final dispersity = 1.11 (Table 2, entry 6, Figure S17a).

The photoinduced living radical polymerization of monomers with increasingly hydrophobic acrylates was also investigated. Lauryl acrylate (LA) is insoluble in DMSO and although it has previously been polymerized in this solvent system,⁵⁰ discrepancies in molecular weight data and high

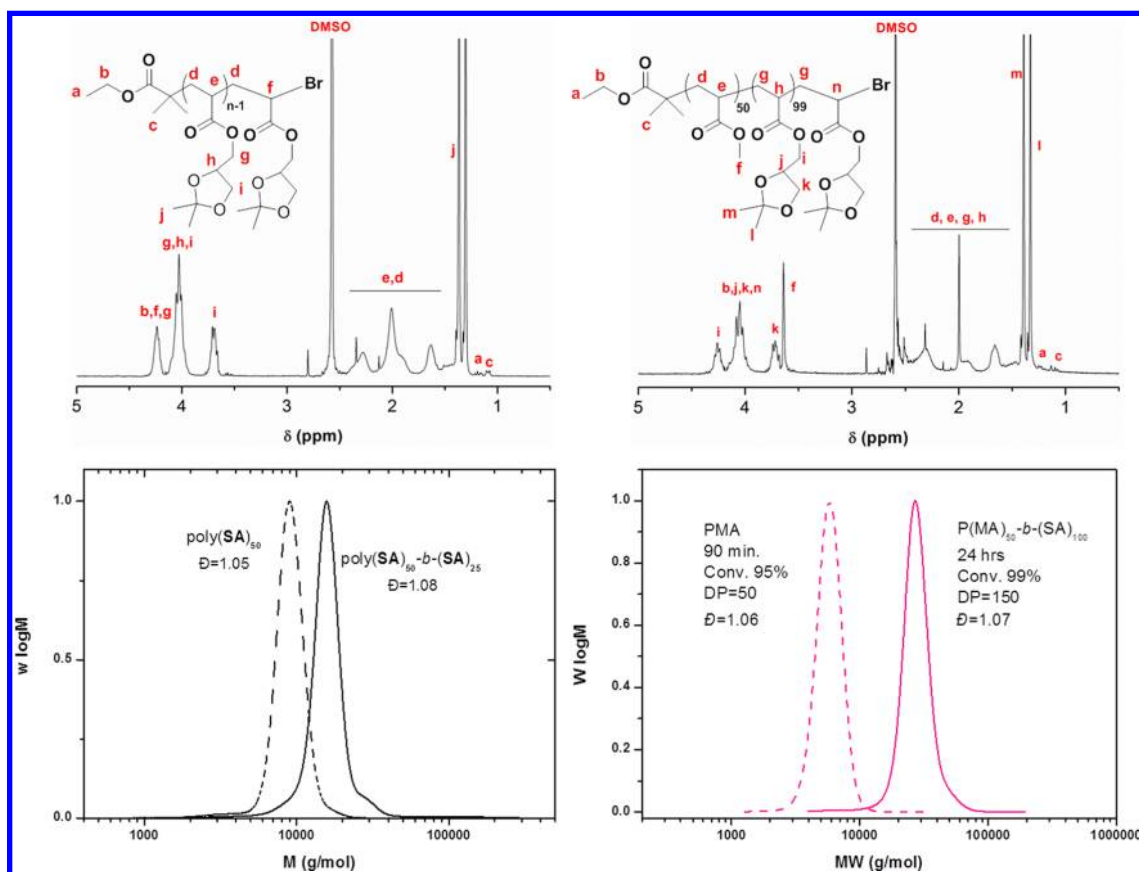


Figure 1. In situ chain extension of poly(SA) and block copolymerization from a poly(MA) macroinitiator. Initial conditions for block copolymerization: [MA]:[EbiB]:[CuBr₂]:[Me₆-Tren] = [50]:[1]:[0.02]:[0.12], DMSO (50% v/v). Block copolymerization achieved by addition of SA (100 equiv) in DMSO (50% v/v).

dispersity values were obtained, indicative of a poorly controlled system. The importance of monomer solubility in Cu-mediated polymerization was reported previously,^{50,51} thus, IPA was initially employed as solvent for the polymerization of LA reaching 83% conversion within 3.5 h with a dispersity = 1.18. Quantitative conversion was attained within 10 h, furnishing a well controlled polymer (\bar{D} = 1.21, Table 2, entry 4a, Figure S18a). The polymerization of LA in IPA has been reported to proceed in a self-generating biphasic system without detrimental effect on the polymerization.⁵¹ This was replicated in the photomediated reaction whereby interruption of the agitation imposed upon the reaction medium resulted in phase separation, yielding a polymer-rich lower phase and a catalyst-rich upper phase. Repeating the polymerization in a toluene/MeOH (4:1) solvent system, to retain homogeneity throughout the reaction, resulted in quantitative conversion (>99%) within 12 h. Crucially, the homogeneity retained throughout the reaction appeared to confer a greater degree of control (\bar{D} = 1.07, Table 2, entry 4b, Figure S18c) than observed in the self-generating biphasic system. The photomediated polymerization of *n*BA in DMSO was recently reported to also proceed in self-generated biphasic media, furnishing poly(*n*BA) with a dispersity = 1.16 (Table 2, entry 5b, Figure S19c).⁴¹ We were interested to see whether repeating this polymerization in a homogeneous system had any effect on the final polymer obtained in accordance with the poly(LA) system. Using DMF as solvent, thus retaining monomer (*n*BA), CuBr₂ and propagating polymer in solution, again resulted in narrower dispersities (\bar{D} = 1.06, Table 2, entry

5a, Figure S19a) at full conversion (>99%). The concomitance of the phase data for LA and *n*BA implies that under photomediated conditions, homogeneity is preferable, conferring maximal control over the polymerization reactions. Consequently, to complete the investigation of hydrophobic acrylates, photomediated polymerizations of isooctyl (*i*OA) and octadecyl (stearyl, ODA) acrylate were performed in toluene/MeOH (4:1) and toluene/IPA (4:1) solvent systems, respectively. Very high conversions (>99%) were achieved within 10 h for both monomers and the anticipated control over the reaction was confirmed by SEC, yielding dispersity values of 1.17 and 1.10 respectively (Table 2, entries 9 and 2, Figures S20 and S21).

The preparation of functional scaffolds is highly desirable and the incorporation of reactive functional groups can facilitate postpolymerization modification reactions enroute to introducing functionality not necessarily compatible with the selected polymerization protocol.^{52,53} Glycidyl acrylate (GA), containing pendant epoxy functionality, was synthesized following a standard literature procedure.⁴⁵ The epoxide functional group is susceptible to nucleophilic ring-opening by amine, thiol and carboxylic acid functional groups.^{54,55} Indeed this has been exploited to furnish a variety of functional linear and hyperbranched polymers in a variety of compositions including (block) copolymers, and more recently sequence controlled multiblock glycopolymers.^{45,56,57} Subjected to photomediated polymerization conditions in DMSO, GA was completely consumed within 90 min providing well-controlled poly(GA) (\bar{D} = 1.19, Table 2, entry 7, Figure S22a). Solketal acrylate (SA)

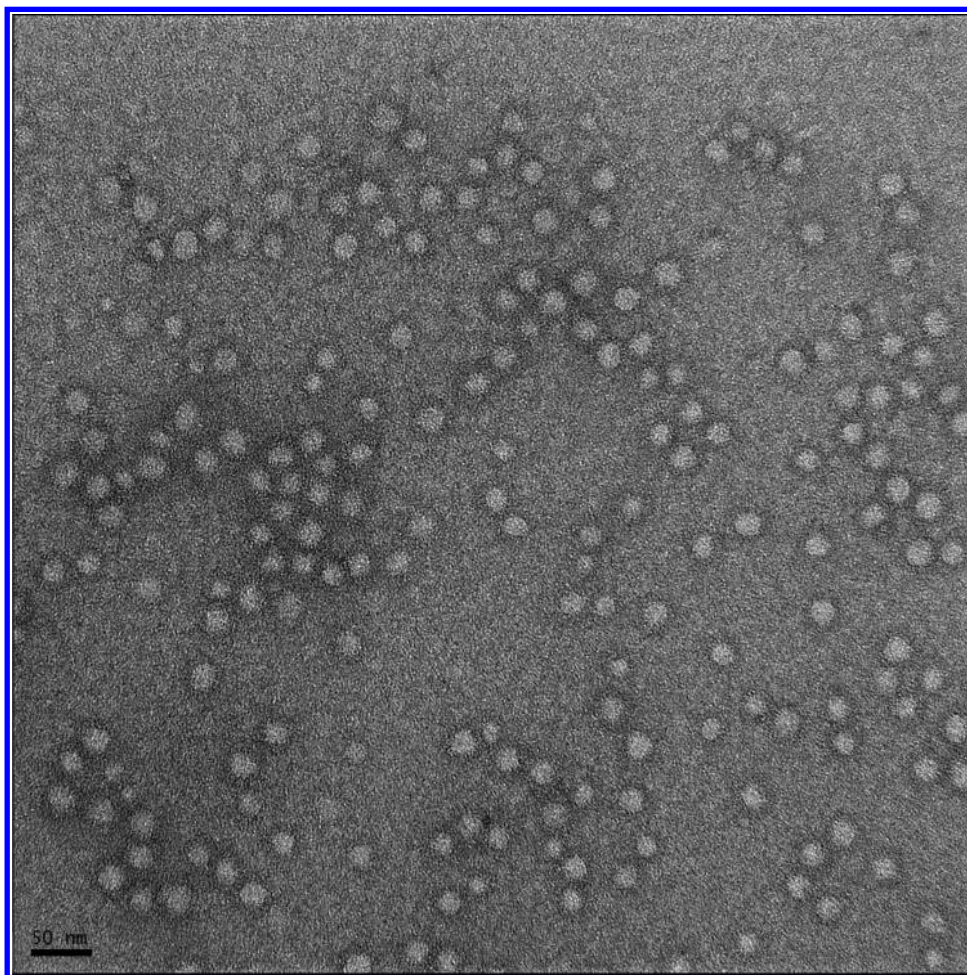


Figure 2. TEM images of micellized amphiphilic poly(MA)₅₀-*b*-(GA)₁₀₀ block copolymer. Scale bar = 50 nm.

possesses ketal protected *vic*-diol pendant functionality which can implement a hydrophobic–hydrophilic switch, via ketal deprotection under acidic conditions. Homopolymerization of SA was complete (>99%) within 10 h and comparable control was retained ($\bar{D} = 1.10$, Table 2, entry 8, Figure S23a) compared to that observed for poly(MA).

To evaluate the integrity of the ω -Br chain end of the functional poly(SA) homopolymer, a second aliquot of deoxygenated SA in DMSO was injected into the unpurified reaction mixture. Excellent control was observed as the molecular weight distribution shifted completely to higher molecular weight, with minimal detectable termination during the initial homopolymerization, and low dispersities were retained ($\bar{D} = 1.08$, Figure 1). The hydrophobic–hydrophilic switch was utilized during the one-pot synthesis of an amphiphilic diblock copolymer. Initially poly(MA) was synthesized by photomediated polymerization in DMSO, providing a macroinitiator with optimum ω -Br chain end fidelity (95% conv., 4700 g/mol, $\bar{D} = 1.06$). Without isolation or purification of the macroinitiator, a deoxygenated solution of SA in DMSO was injected into the reaction mixture and subjected to photomediated polymerization. Within 24 h a well-defined poly(MA)-*b*-(SA) diblock copolymer was obtained (99%, $\bar{D} = 1.07$, Figure 1). Hydrolysis of the pendant ketal protecting groups unmasked the hydrophilic *vic*-diol groups, inflicting amphiphilic character on the diblock copolymer. Self-assembly of the amphiphilic block copolymer was realized via

the direct dissolution method forming the classical core–shell micelles with an average size of 30 nm, as confirmed by dynamic light scattering (DLS, Table S1, Figure S25). Subsequent transition electron microscopy (TEM) analysis supported the results from DLS revealing nanoparticles with an average size of 20 nm (Figure 2).

CONCLUSIONS

The scope of photomediated living radical polymerization in the presence of CuBr₂ and Me₆Tren has been expanded to include a range of hydrophilic, hydrophobic and functional acrylates. An investigation into solvent compatibility proved to be particularly instructive for increasingly hydrophobic acrylates that have been shown to polymerize in both homogeneous and self-generating biphasic systems. Optimal control was conferred when homogeneity of the monomer, CuBr₂ and propagating polymer was retained throughout the polymerization. Epoxide and ketal-protected *vic*-diol functional groups were shown to be compatible with the reaction conditions. The protected *vic*-diol functional group presents the possibility of a hydrophilic–hydrophobic switch which was exploited upon copolymerization with MA to prepare an poly(MA)-*b*-(SA) diblock copolymer. Subsequent acid catalyzed ketal hydrolysis provided, an amphiphilic diblock copolymer that self-assembled into core–shell polymeric micelles in aqueous solution.

■ ASSOCIATED CONTENT

● Supporting Information

Figures showing typical set up for photo-induced polymerization, molecular weight distribution plots, UV-vis and ^1H NMR spectra, and DLS trace and a table of the average size and dispersity of the nanoparticles. 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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■ REFERENCES

- (1) Moad, G.; Rizzardo, E.; Thang, S. H. *Aust. J. Chem.* **2009**, *62* (11), 1402–1472.
- (2) Chiefari, J.; Chong, Y. K.; Ercole, F.; Krstina, J.; Jeffery, J.; Le, T. P. T.; Mayadunne, R. T. A.; Meijs, G. F.; Moad, C. L.; Moad, G.; Rizzardo, E.; Thang, S. H. *Macromolecules* **1998**, *31* (16), 5559–5562.
- (3) Hawker, C. J.; Bosman, A. W.; Harth, E. *Chem. Rev.* **2001**, *101* (12), 3661–88.
- (4) Nicolas, J.; Guilleaume, Y.; Lefay, C.; Bertin, D.; Gimes, D.; Charleux, B. *Prog. Polym. Sci.* **2013**, *38* (1), 63–235.
- (5) Kato, M.; Kamigaito, M.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1995**, *28* (5), 1721–1723.
- (6) Wang, J.-S.; Matyjaszewski, K. J. *Am. Chem. Soc.* **1995**, *117* (20), 5614–5615.
- (7) Haddleton, D. M.; Jasieczek, C. B.; Hannon, M. J.; Shooter, A. J. *Macromolecules* **1997**, *30* (7), 2190–2193.
- (8) Percec, V.; Popov, A. V.; Ramirez-Castillo, E.; Monteiro, M.; Barboiu, B.; Weichold, O.; Asandei, A. D.; Mitchell, C. M. *J. Am. Chem. Soc.* **2002**, *124* (18), 4940–1.
- (9) Percec, V.; Guliashevili, T.; Ladislav, J. S.; Wistrand, A.; Stjern Dahl, A.; Sienkowska, M. J.; Monteiro, M. J.; Sahoo, S. J. *Am. Chem. Soc.* **2006**, *128* (43), 14156–65.
- (10) Rosen, B. M.; Percec, V. *Chem. Rev.* **2009**, *109* (11), 5069–119.
- (11) Fischer, H. *Chem. Rev.* **2001**, *101* (12), 3581–3610.
- (12) Fischer, H. *Macromolecules* **1997**, *30* (19), 5666–5672.
- (13) Lligadas, G.; Percec, V. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46* (20), 6880–6895.
- (14) Rosen, B. M.; Jiang, X.; Wilson, C. J.; Nguyen, N. H.; Monteiro, M. J.; Percec, V. *J. Polym. Sci., Part A: Polym. Chem.* **2009**, *47* (21), 5606–5628.
- (15) Nguyen, N. H.; Percec, V. *J. Polym. Sci., Part A: Polym. Chem.* **2011**, *49* (19), 4227–4240.
- (16) Levere, M. E.; Nguyen, N. H.; Leng, X. F.; Percec, V. *Polym. Chem.* **2013**, *4* (5), 1635–1647.
- (17) Nguyen, N. H.; Sun, H.-J.; Levere, M. E.; Fleischmann, S.; Percec, V. *Polym. Chem.* **2013**, *4* (5), 1328–1332.
- (18) Tsarevsky, N. V.; Braunecker, W. A.; Matyjaszewski, K. J. *Organomet. Chem.* **2007**, *692* (15), 3212–3222.
- (19) Anastasaki, A.; Waldron, C.; Wilson, P.; Boyer, C.; Zetterlund, P. B.; Whittaker, M. R.; Haddleton, D. *ACS Macro Lett.* **2013**, *2* (10), 896–900.
- (20) Soeriyadi, A. H.; Boyer, C.; Nystrom, F.; Zetterlund, P. B.; Whittaker, M. R. *J. Am. Chem. Soc.* **2011**, *133* (29), 11128–31.
- (21) Boyer, C.; Soeriyadi, A. H.; Zetterlund, P. B.; Whittaker, M. R. *Macromolecules* **2011**, *44* (20), 8028–8033.
- (22) Boyer, C.; Derveaux, A.; Zetterlund, P. B.; Whittaker, M. R. *Polym. Chem.* **2012**, *3* (1), 117–123.
- (23) Waldron, C.; Anastasaki, A.; McHale, R.; Wilson, P.; Li, Z.; Smith, T.; Haddleton, D. M. *Polym. Chem.* **2014**, *5* (3), 892.
- (24) Leibfarth, F. A.; Mattson, K. M.; Fors, B. P.; Collins, H. A.; Hawker, C. J. *Angew. Chem., Int. Ed.* **2013**, *52* (1), 199–210.
- (25) Magenau, A. J. D.; Strandwitz, N. C.; Gennaro, A.; Matyjaszewski, K. *Science* **2011**, *332* (6025), 81–84.
- (26) Rzaev, J.; Penelle, J. *Macromolecules* **2002**, *35* (5), 1489–1490.
- (27) Rzaev, J.; Penelle, J. *Angew. Chem., Int. Ed.* **2004**, *43* (13), 1691–1694.
- (28) Tanabe, M.; Vandermeulen, G. W. M.; Chan, W. Y.; Cyr, P. W.; Vanderark, L.; Rider, D. A.; Manners, I. *Nat. Mater.* **2006**, *5* (6), 467–470.
- (29) Yamago, S.; Nakamura, Y. *Polymer* **2013**, *54* (3), 981–994.
- (30) Xu, J.; Jung, K.; Atme, A.; Shanmugam, S.; Boyer, C. *J. Am. Chem. Soc.* **2014**, *136* (14), 5508–5519.
- (31) Decker, C. *Prog. Polym. Sci.* **1996**, *21* (4), 593–650.
- (32) Tasdelen, M. A.; Uygun, M.; Yagci, Y. *Macromol. Rapid Commun.* **2011**, *32* (1), 58–62.
- (33) Fors, B. P.; Hawker, C. J. *Angew. Chem., Int. Ed.* **2012**, *51* (35), 8850–8853.
- (34) Poelma, J. E.; Fors, B. P.; Meyers, G. F.; Kramer, J. W.; Hawker, C. J. *Angew. Chem., Int. Ed.* **2013**, *52* (27), 6844–6848.
- (35) Tasdelen, M. A.; Uygun, M.; Yagci, Y. *Macromol. Chem. Phys.* **2010**, *211* (21), 2271–2275.
- (36) Yagci, Y.; Jockusch, S.; Turro, N. J. *Macromolecules* **2010**, *43* (15), 6245–6260.
- (37) Tasdelen, M. A.; Uygun, M.; Yagci, Y. *Macromol. Chem. Phys.* **2011**, *212* (18), 2036–2042.
- (38) Tasdelen, M. A.; Ciftci, M.; Yagci, Y. *Macromol. Chem. Phys.* **2012**, *213* (13), 1391–1396.
- (39) Taskin, O. S.; Yilmaz, G.; Tasdelen, M. A.; Yagci, Y. *Polym. Int.* **2014**, *63* (5), 902–907.
- (40) Konkolewicz, D.; Schröder, K.; Buback, J.; Bernhard, S.; Matyjaszewski, K. *ACS Macro Lett.* **2012**, *1* (10), 1219–1223.
- (41) Anastasaki, A.; Nikolaou, V.; Zhang, Q.; Burns, J.; Samanta, S. R.; Waldron, C.; Haddleton, A. J.; McHale, R.; Fox, D.; Percec, V.; Wilson, P.; Haddleton, D. M. *J. Am. Chem. Soc.* **2014**, *136* (3), 1141–9.
- (42) Wenn, B.; Conradi, M.; Carreiras, A. D.; Haddleton, D. M.; Junkers, T. *Polym. Chem.* **2014**, *5* (8), 3053–3060.
- (43) Ciampolini, M.; Nardi, N. *Inorg. Chem.* **1966**, *5* (1), 41–44.
- (44) Oguchi, K.; Sanui, K.; Ogata, N.; Takahashi, Y.; Nakada, T. *Polym. Eng. Sci.* **1990**, *30* (8), 449–452.
- (45) Zhang, Q.; Anastasaki, A.; Li, G.-Z.; Haddleton, A. J.; Wilson, P.; Haddleton, D. M. *Polym. Chem.* **2014**.
- (46) Samanta, S. R.; Anastasaki, A.; Waldron, C.; Haddleton, D. M.; Percec, V. *Polym. Chem.* **2013**, *4* (22), 5563–5569.
- (47) Samanta, S. R.; Percec, V. *Polym. Chem.* **2014**, *5* (1), 169–174.
- (48) Samanta, S. R.; Anastasaki, A.; Waldron, C.; Haddleton, D. M.; Percec, V. *Polym. Chem.* **2013**, *4* (22), 5555–5562.
- (49) Samanta, S. R.; Sun, H.-J.; Anastasaki, A.; Haddleton, D. M.; Percec, V. *Polym. Chem.* **2014**, *5* (1), 89–95.
- (50) Boyer, C.; Atme, A.; Waldron, C.; Anastasaki, A.; Wilson, P.; Zetterlund, P. B.; Haddleton, D.; Whittaker, M. R. *Polym. Chem.* **2013**, *4* (1), 106–112.
- (51) Anastasaki, A.; Waldron, C.; Nikolaou, V.; Wilson, P.; McHale, R.; Smith, T.; Haddleton, D. M. *Polym. Chem.* **2013**, *4* (15), 4113–4119.
- (52) Gauthier, M. A.; Gibson, M. I.; Klok, H.-A. *Angew. Chem., Int. Ed.* **2009**, *48* (1), 48–58.
- (53) Günay, K. A.; Theato, P.; Klok, H.-A. *J. Polym. Sci., Part A: Polym. Chem.* **2013**, *51* (1), 1–28.

- (54) Benaglia, M.; Alberti, A.; Giorgini, L.; Magnoni, F.; Tozzi, S. *Polym. Chem.* **2013**, *4* (1), 124–132.
- (55) Barbey, R.; Klok, H.-A. *Langmuir* **2010**, *26* (23), 18219–18230.
- (56) McEwan, K. A.; Slavin, S.; Tunnah, E.; Haddleton, D. M. *Polym. Chem.* **2013**, *4* (8), 2608–2614.
- (57) Basuki, J. S.; Esser, L.; Duong, H. T. T.; Zhang, Q.; Wilson, P.; Whittaker, M. R.; Haddleton, D. M.; Boyer, C.; Davis, T. P. *Chem. Sci.* **2014**, *5* (2), 715–726.