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Cu(0) Wire-mediated Single-electron Transfer-living Radical Polymerization of Oligo(ethylene oxide) Methyl Ether Acrylate by Selecting the Optimal Reaction Conditions

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Electronic Supplementary Information

Abstract The efficient Cu(0) wire-catalyzed single-electron transfer-living radical polymerization (SET-LRP) in organic solvents and mixtures of the organic solvents with water has been thoroughly investigated. Oligo(ethylene oxide) methyl ether acrylate was used as an exemplar oligomer monomer to determine the optimum polymerization conditions for rapid, controlled, and quantitative production of well-defined polymers. The effects of Cu(0)-wire length (12.5 or 4.5 cm), ligand type (tris(dimethylaminoethyl)amine, Me₆-TREN, or tris(2-aminoethyl)amine, TREN), and solvent type (dipolar aprotic solvents, cyclic ethers, alcohol, or acetone) on the polymerization have been evaluated. Kinetic experiments were performed for all polymerizations to assess the “living” behavior of each system employed. Importantly, TREN could be used as a replacement for Me₆-TREN in Cu(0) wire-catalyzed SET-LRP of oligomer monomer, which probably provides the most economical and efficient methodology since TREN is 80 times less expensive than Me₆-TREN. The high chain-end fidelity of resulting polymer was experimentally verified by thiol-Michael addition reaction at the α -Br chain end and subsequent chain extension with methyl acrylate.

Keywords Single-electron transfer-living radical polymerization; Oligo(ethylene oxide) methyl ether acrylate; Kinetics of polymerization; Modification

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INTRODUCTION

Cu(0)-mediated single-electron transfer living radical polymerization (SET-LRP) in organic media was introduced in 2002 by Percec *et al.*^[1] Zhang *et al.* subsequently made a great contribution to aqueous systems.^[2] SET-LRP gradually becomes a robust and versatile polymerization tool especially when the “ultrafast polymerization” of monomers (acrylates, methacrylates, and vinyl chloride) at ambient temperature was presented,^[3] which represents one of the simplest and most effective techniques to perform polymerization. Now, SET-LRP has been shown to produce polymers with narrow molecular weight distribution, nearly perfect retention of chain-end functionality even at quantitative conversion, and

ability to sustain *in situ* chain extension. The investigations on the critical aspects are most concerned with solvent, ligand, and catalyst in the Cu(0)-mediated SET-LRP. (i) The nature of the solvent plays an important role in Cu(0)-mediated SET-LRP. Although dimethyl sulfoxide (DMSO) and water are the most extensively studied solvents in SET-LRP, and alcohols have also exhibited excellent compatibility with SET-LRP, a variety of polar, dipolar aprotic, moderate polarity, and classical hydrocarbon non-polar solvents as well as homogeneous binary mixtures of them have also been used these days.^[4–7] Moreover, adding a small amount of water into organic solvents greatly accelerated the SET-LRP and improved the control of molecular weight distribution.^[8–11] (ii) The selection of an appropriate solvent-ligand combination is a key-point to the success of SET-LRP. Tris(dimethylaminoethyl)amine (Me₆-TREN) is the most widely employed reagent among commercially available ligands. Besides, pioneering experiments showed that tris(2-aminoethyl)amine (TREN) can also mediate an efficient disproportionation of Cu(I)X into Cu(0) and Cu(II)X₂

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in a variety of solvents, thus acting as a more attractive and economical alternative (TREN is 80 times less expensive than Me₆-TREN).^[12–16] (iii) Cu(0) wire is perhaps by far the most popular catalytic species used in SET-LRP as it could regulate polymerization rate more effectively, control the molecular weight distribution better, and remove and recycle more easily than Cu(0) powder could.^[7]

Among the monomers of SET-LRP, (meth)acrylates are the most widely studied objectives. Excitingly, the scope of acrylates suitable for SET-LRP has been greatly expanded during the last few years. Now, SET-LRP has represented the most efficient polymerization protocol for the accelerated synthesis of well-defined polymers from a great variety of monomers. In particular, the hydrophilic polymers prepared from oligo(ethylene glycol)-based acrylate monomers exhibit excellent thermoresponsive properties in various solvents.^[17–19] Nguyen *et al.* reported a comparative analysis on the SET-LRP of oligo(ethylene oxide) methyl ether acrylate (OEOMEA) in DMSO and H₂O in the absence and presence of air using the oligo(ethylene oxide)-derived macroinitiator.^[20,21] Deng *et al.* utilized covalent bonding to attach Br-bearing initiating groups onto the surface of exfoliated graphene oxide sheets followed by *in situ* growing thermo-sensitive poly(ethylene glycol) ethyl ether methacrylate *via* SET-LRP.^[22] Simula *et al.* synthesized the well-defined telechelic poly(meth)acrylate homopolymers and block copolymers in organic and aqueous media *via* Cu(0)-mediated SET-LRP of two kinds of oligomer monomers, poly(ethylene glycol) methyl ether acrylate and poly(ethylene glycol) methyl ether methacrylate, using poly(ethylene glycol) bis(2-bromoisobutyrate) initiator.^[23] Herein, a thorough investigation of SET-LRP of OEOMEA in diverse solvents is presented. Cu(0) wires of two different lengths were used as the Cu(0) source while both Me₆-TREN and TREN were employed as the ligand, highlighting the potential and limitations of each type (Scheme 1). The effect of disproportionation reaction on the polymerization rate and control over the molecular weight distribution has also been studied in different media, dictating the optimal polymerization protocol depending on the ligand and solvent employed.

EXPERIMENTAL

Materials

Oligo(ethylene oxide) methyl ether acrylate (average M_n =

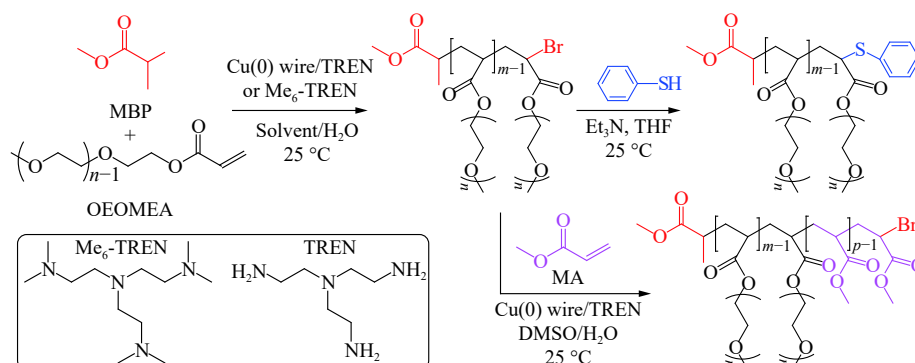
480, containing 100 ppm butylated hydroxytoluene (BHT) and 100 ppm hydroquinone monomethyl ether (MEHQ) as inhibitor, Aldrich), methyl acrylate (MA, 99%, Acros) which was filtered over a short column of basic Al₂O₃ prior to use in order to remove the radical inhibitor, TREN (99%), methyl 2-bromopropionate (MBP) (99%, Acros), DMSO (Fisher, Certified ACS, 99.9%), acetone (99.7% certified ACS, Fisher), and ethanol (200 proof, Decon) were used as received. Tetrahydrofuran (THF) was distilled over Na/benzophenone immediately before use. Triethylamine (NEt₃) (99.91% Chem-impex) was distilled under N₂ over CaH₂. Copper(0) wire (20 gauge wire, 0.812 mm diameter, Fischer) was activated with hydrazine hydrate (100%, Acros) (hydrazine 64% in water) prior to use. Me₆-TREN was synthesized as described in the literature.^[24]

Characterization

¹H-NMR spectra (500 MHz) were recorded on a Bruker DRX500 NMR instrument at 25 °C in CDCl₃ with tetramethylsilane (TMS) as an internal standard. Gel permeation chromatography (GPC) analysis of the polymer samples was performed on a PerkinElmer Nelson Analytical 900 Series integration data station, equipped with a Shimadzu LC-20AD high performance liquid chromatography pump, three AM gel columns (a guard column, a 50 nm, 10 μm column, and a 10.4 nm, 10 μm column) and a Shimadzu RID-10A refractive index (RI) detector. THF (Fischer, HPLC grade) was used as an eluent at a flow rate of 1 mL/min. The number-average (M_n) and weight-average (M_w) molecular weights of the resulting polymer samples were determined using polystyrene standards purchased from American Polymer Standards.

Activation of Commercial Cu(0) Wire

A 20 gauge Cu(0) wire was first cut into 12.5 or 4.5 cm and held with pliers and then scratched along the length of the wire with a clean paper soaked with acetone in the perpendicular direction. This process was repeated 8–10 times, during which the wire was rotated each time to scratch the entire surface. A Teflon-coated stirring bar wrapped by the above Cu(0) wire was placed in a 25 mL Schlenk tube containing NH₂NH₂ hydrate (10.3 mmol/L) and DMSO (2 mL). The stirring bar with the Cu(0) wire was held above the solution mixture by applying a small magnet and the tube was sealed using a rubber septum. After two freeze-pump-thaw cycles, the tube was filled with N₂ and the Cu(0) wire



Scheme 1 Me₆-TREN and TREN-mediated SET-LRP of OEOMEA in binary mixtures of organic solvents with H₂O in the presence of hydrazine-activated Cu(0) wire, and further “thio-bromo click” modification of the corresponding PEOMEA with thiophenol

was dropped down into the $\text{NH}_2\text{NH}_2/\text{DMSO}$ mixture and was stirred for 30 min at $(25 \pm 0.5)^\circ\text{C}$. The activated wire was pulled up using the magnet and was rinsed with 20 mL of degassed methanol under positive N_2 pressure. The stirring bar with the $\text{Cu}(0)$ wire was quickly transferred to a separate 25 mL Schlenk tube under a strong flow of N_2 and dried under vacuum before use.

Typical Procedure for SET-LRP of OEOMEA

In a 25 mL Schlenk tube, the reagents were added in the following order under gentle stirring: initiator MBP (4.5 μL , 0.042 mmol), monomer (OEOMEA, 1 g, 2.1 mmol), ligand ($\text{Me}_6\text{-TREN}$, 1.1 μL , 4.2 μmol or TREN , 0.8 μL , 4.2 μmol), and solvent (or in a mixture of organic solvent with H_2O , 0.5 mL). After six freeze-pump-thaw cycles, the Schlenk tube was filled with N_2 and the activated $\text{Cu}(0)$ wire wrapping around a Teflon-coated stir bar was transferred to the Schlenk tube containing the reaction mixture under a positive flow of N_2 . Two more freeze-pump-thaw cycles were carried out while holding the stir bar on the top of the Schlenk tube using an external magnet. After that, the Schlenk tube was filled with N_2 and the reaction mixture was placed in a water bath thermostated at 25°C . Then, the stir bar wrapped with $\text{Cu}(0)$ wire was dropped into the reaction mixture. This was considered as time zero. Samples were taken at different time intervals throughout the reaction using an airtight glass syringe and stainless steel needles. During sampling, the side arm of the Schlenk tube was purged with N_2 for 2 min to avoid the introduction of oxygen into the reaction mixture. Samples were dissolved in CDCl_3 and quenched by air bubbling. After that, the monomer conversion was measured by $^1\text{H-NMR}$ spectroscopy. In order to determine the molecular weight and molecular weight distribution, the samples were dissolved in distilled THF and passed through a short small basic Al_2O_3 chromatographic column to remove any residual copper and analyzed by GPC. The resulting polymer, PEOMEA-Br, was precipitated in cold methanol and dried under vacuum until constant weight to perform the chain end analysis by $^1\text{H-NMR}$ spectroscopy before and after the thioetherification reaction.

Functionalization of PEOMEA-Br via Thio-bromo “Click” Reaction

In a 25 mL Schlenk tube, thiophenol (11.3 μL , 0.11 mmol) and distilled NEt_3 (15.2 μL , 0.11 mmol) were added into a

solution of PEOMEA-Br (0.022 mmol) in 1–2 mL distilled THF under N_2 . The reaction mixture was stirred at 25°C for 3 h, and the polymer was precipitated two times in 20 mL cold methanol. After removal of methanol, the final polymer was dried under vacuum until constant weight.

General Procedure for the Chain Extension of PEOMEA-Br with MA

Into a 25 mL Schlenk tube, MA (0.5 mL, 5.55 mmol), DMSO (0.4 mL), H_2O (0.1 mL), TREN , and the macromonomer PEOMEA-Br (750 mg, 0.06 mmol) were added in the order mentioned. The reaction mixture was deoxygenated following the previously described procedure by six freeze-pump-thaw cycles and one extra cycle with the $\text{Cu}(0)$ wire (12.5 cm) wrapping around a Teflon-coated stirring bar held above. The reaction mixture was placed into a water bath thermostated at 25°C with stirring. The polymerization was allowed to proceed until presupposed conversions and then, the reaction was stopped by bubbling air into the mixture. The resulting polymer was precipitated into cold methanol and placed under high vacuum until constant weight.

RESULTS AND DISCUSSION

SET-LRP of OEOMEA Catalyzed by $\text{Cu}(0)$ Wire/ $\text{Me}_6\text{-TREN}$ in DMSO and DMSO/ H_2O

As described previously, DMSO performed excellently as a SET-LRP solvent in $\text{Cu}(0)$ wire/ $\text{Me}_6\text{-TREN}$ -mediated polymerization.^[20,21,25,26] The living characteristic of polymerization was validated through the linear evolution of $\ln([M]_0/[M])$ along with polymerization time, the narrow molecular weight distribution, and the almost quantitative chain end functionality. Therefore, polymerization of commercial OEOMEA without any treatment (contains inhibitors) was initially assessed in DMSO and carried out under the following conditions: $[\text{OEOMEA}]_0/[\text{Initiator}]_0/[\text{Ligand}]_0 = 50/1/0.1$. The results are summarized in Table 1. The kinetic experiments of SET-LRP of OEOMEA with inhibitor catalyzed by 12.5 cm activated $\text{Cu}(0)$ wire/ $\text{Me}_6\text{-TREN}$ and initiated by MBP are shown in Fig. 1. The polymerization exhibits a linear kinetics in the concentrations of monomer and propagating radicals with $k_p^{\text{app}} = 0.0311 \text{ min}^{-1}$. The kinetic experiments revealed a linear evolution of number-average molecular weight (M_n) with conversion and narrow molecular weight distribution (M_w/M_n), associated with the

Table 1 Characteristics of $\text{Cu}(0)$ wire/ $\text{Me}_6\text{-TREN}$ -mediated SET-LRP of OEOMEA in DMSO, DMSO/ H_2O mixtures, and pure H_2O ^a

Entry	Reaction medium (V/V)	k_p^{app} (min^{-1})	Time (min)	Conversion ^b (%)	$M_{n(\text{th})}$ ^c (kDa)	$M_{n(\text{GPC})}$ (kDa)	M_w/M_n	I_{eff} ^d (%)
1	DMSO ^e	0.0311	65	84	19.6	19.1	1.20	100
2	DMSO/ H_2O (9/1)	0.0369	60	88	21.3	20.9	1.26	100
3	DMSO/ H_2O (8/2)	0.0428	48	87	21.0	21.7	1.22	98
4	DMSO/ H_2O (6/4)	0.0204	90	82	19.8	22.9	1.21	83
5	DMSO/ H_2O (4/6)	0.0081 0.0203	180	92	22.2	21.5	1.28	100
6	H_2O	0.0071	240	79	19.1	21.3	1.22	81
7	DMSO ^f	0.0357	57	85	20.6	20.1	1.23	97
8	DMSO/ H_2O (9/1)	0.0408	45	82	19.8	20.1	1.22	96
9	DMSO/ H_2O (8/2)	0.0912	34	95	23.0	22.9	1.25	99

^a Reaction conditions: OEOMEA 1.0 g, DMSO ($+\text{H}_2\text{O}$) 0.5 mL; $[\text{OEOMEA}]_0/[\text{MBP}]_0/[\text{Me}_6\text{-TREN}]_0 = 50/1/0.1$, hydrazine-activated $\text{Cu}(0)$ wire 12.5 cm of 20 gauge wire; ^b Obtained by $^1\text{H-NMR}$ spectroscopy using the equation: $1 - (S_{3\text{H,Acrylate}}/3)/(S_{2\text{H,CH}_2}/2)$, methylene is linked directly to the acrylate group; ^c $M_{n(\text{th})} = [\text{Conversion}(\%) \times ([\text{OEOMEA}]/[\text{MBP}]) \times M_{n,\text{OEOMEA}} + M_{n,\text{MBP}}]/1000$, where $M_{n,\text{OEOMEA}} = 480$ and $M_{n,\text{MBP}} = 167$ are the molar masses of monomer OEOMEA and initiator MBP, respectively. $[\text{OEOMEA}]/[\text{MBP}] = 50$; ^d Initiator efficiency; ^e Entries 1–6 used OEOMEA with inhibitor; ^f Entries 7–9 used OEOMEA without inhibitor

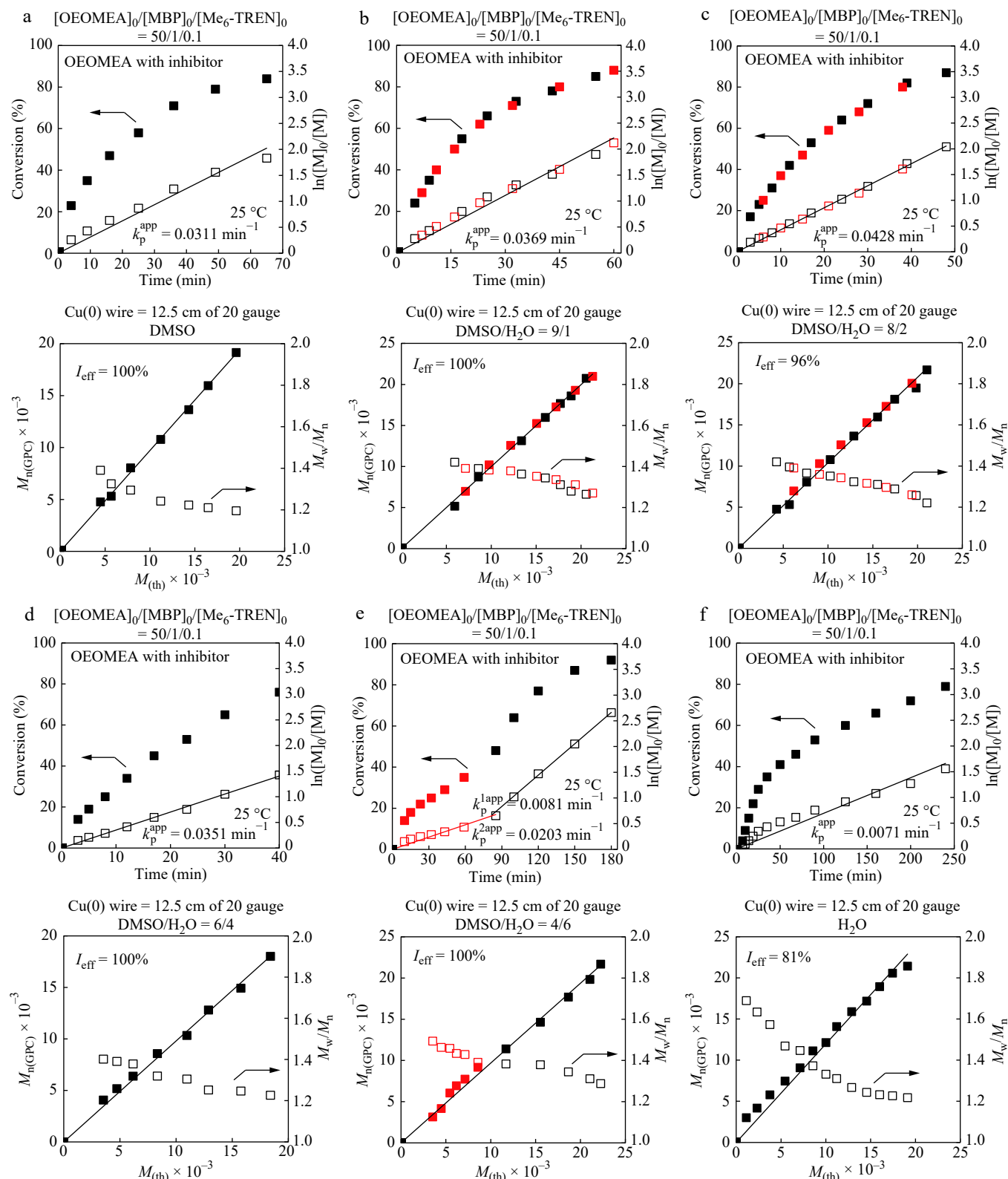


Fig. 1 Kinetic plots, molecular weight, and dispersity evolution for the SET-LRP of OEOMEA with inhibitor catalyzed by 12.5 cm hydrazine-activated Cu(0) wire/Me₆-TREN in (a) DMSO, (b) DMSO/H₂O (9/1, *V/V*), (c) DMSO/H₂O (8/2, *V/V*), (d) DMSO/H₂O (6/4, *V/V*), (e) DMSO/H₂O (4/6, *V/V*), and (f) H₂O

“living” nature of the polymerization and showing good agreement between the theoretical and experimental values. Importantly, GPC traces revealed a mono-modal polymer peak distribution shifting to the higher molecular weights

throughout the polymerization, while the molecular weight distributions were slightly reduced during the reaction with a final value of 1.20 (Table 1).

Nguyen *et al.*^[8,9] and Leng *et al.*^[10] reported that the addi-

tion of H₂O to organic solvents could change the rate and accelerate the activation process of SET-LRP. Herein, it is shown that the addition of 20% H₂O in DMSO led to a linear increase of k_p^{app} from 0.0311 min⁻¹ in DMSO to 0.0428 min⁻¹ (Table 1). Interestingly, by adding 40%–60% H₂O in DMSO, the decrease of k_p^{app} was accompanied by a still high I_{eff} (Figs. 1d and 1e). Differently, two first-order linear kinetic domains were observed and $k_p^1 \text{app} < k_p^2 \text{app}$ in DMSO containing 60% H₂O (Table 1). The decrease in the polymerization rate at higher water content may be attributed to the self-assemblies of OEOMEA in water.^[18] While the mixture of PEG in DMSO (or mixed with a small amount of H₂O) is a molecular solution, the polymerization with the increased amount of H₂O is complicated by the physical barrier between the reactive center of monomer and the initiator with heterogeneous Cu(0) wire catalyst. Further increasing

the amount of H₂O, k_p^{app} and I_{eff} decreased evidently (Fig. 1f and Table 1); meanwhile, a small amount of gelation appeared after the polymerization in pure H₂O, which can be observed directly from the digital image of the reaction mixture (Fig. S1e, in the electronic supplementary information, ESI), suggesting that cross-linking might occur during this polymerization. On the basis of the above results, the benefit was even more evident in the homologous DMSO/water (8/2, V/V) system.

Subsequently, OEOMEA was passed through two short columns of basic Al₂O₃ prior to use in order to remove the radical inhibitor. The first three experiments were performed in pure DMSO as well as DMSO containing 10% and 20% H₂O for comparison purposes. All the polymerizations also exhibit the linear kinetics (Figs. 2a–2c). SET-LRP of OEOMEA without inhibitor in DMSO proceeded with $k_p^{\text{app}} =$

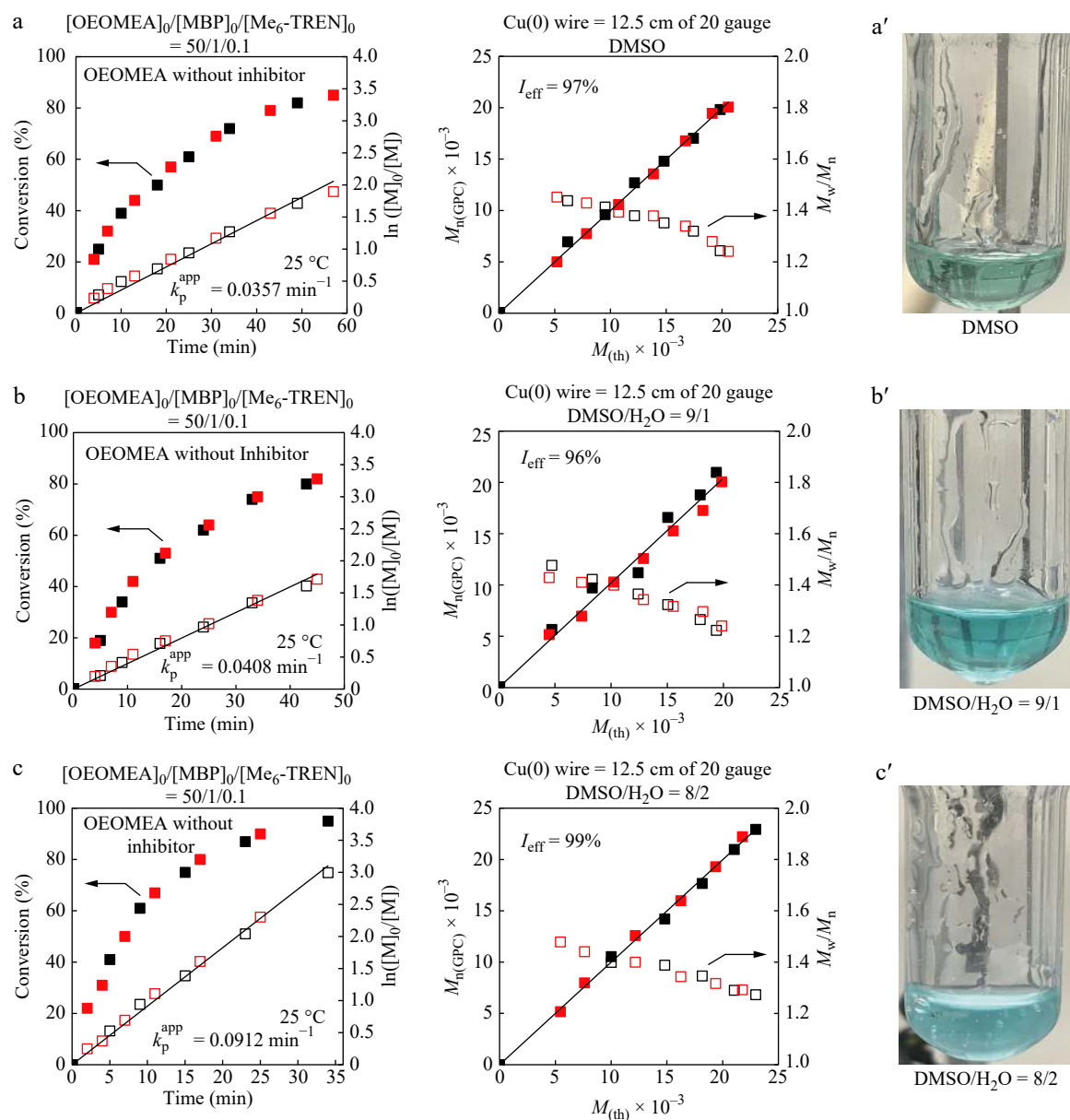


Fig. 2 Kinetic plots, molecular weight, dispersity evolution, and visualization of the reaction mixture for SET-LRP of OEOMEA without inhibitor catalyzed by 12.5 cm hydrazine-activated Cu(0) wire/TREN in (a, a') DMSO, (b, b') DMSO/H₂O (9/1, V/V), and (c, c') DMSO/H₂O (8/2, V/V)

0.0357 min⁻¹ which is slightly higher than that of OEOMEA with inhibitor (Fig. 1a). It should be noted that although I_{eff} was higher than 97% and M_w/M_n at the end of the polymerization was lower than 1.25 in all cases, significant differences in terms of k_p^{app} and the conversion were observed between the polymerizations carried out in these three systems. The addition of 10% and especially 20% H₂O in the SET-LRP processes improved k_p^{app} (0.0912 min⁻¹) sharply with 95% high conversion (Table 1). The visualization of the green-blue one-phase reaction media obtained with DMSO and DMSO containing 10% water is illustrated in Figs. 2(a') and 2(b'), respectively. The SET-LRP of OEOMEA in DMSO containing 20% water also exhibits a single phase till the end of the polymerization but slightly opaque (Fig. 2c') due to the relatively high conversion (95%).

SET-LRP of OEOMEA without Inhibitor Catalyzed by Cu(0) Wire/TREN in DMSO and DMSO/H₂O at Different Degrees of Polymerization

Recent studies suggested that TREN has been used as a replacement for Me₆-TREN in Cu(0) wire catalyzed SET-LRP of methyl and *n*-butyl acrylates performed in biphasic-binary mixtures of dipolar aprotic solvents with water.^[12–15] However, the lower apparent rate constants and a broader molecular weight distribution were observed when TREN was employed as the ligand, and the system finally exhibited a decreased living character or even lost it. Fortunately, the external addition of Cu(II)Br₂ deactivator to the water phase could significantly improve the control of biphasic SET-LRP systems mediated by TREN.^[14] Fig. 3(a) depicts SET-LRP of OEOMEA in DMSO, employing TREN as the ligand and

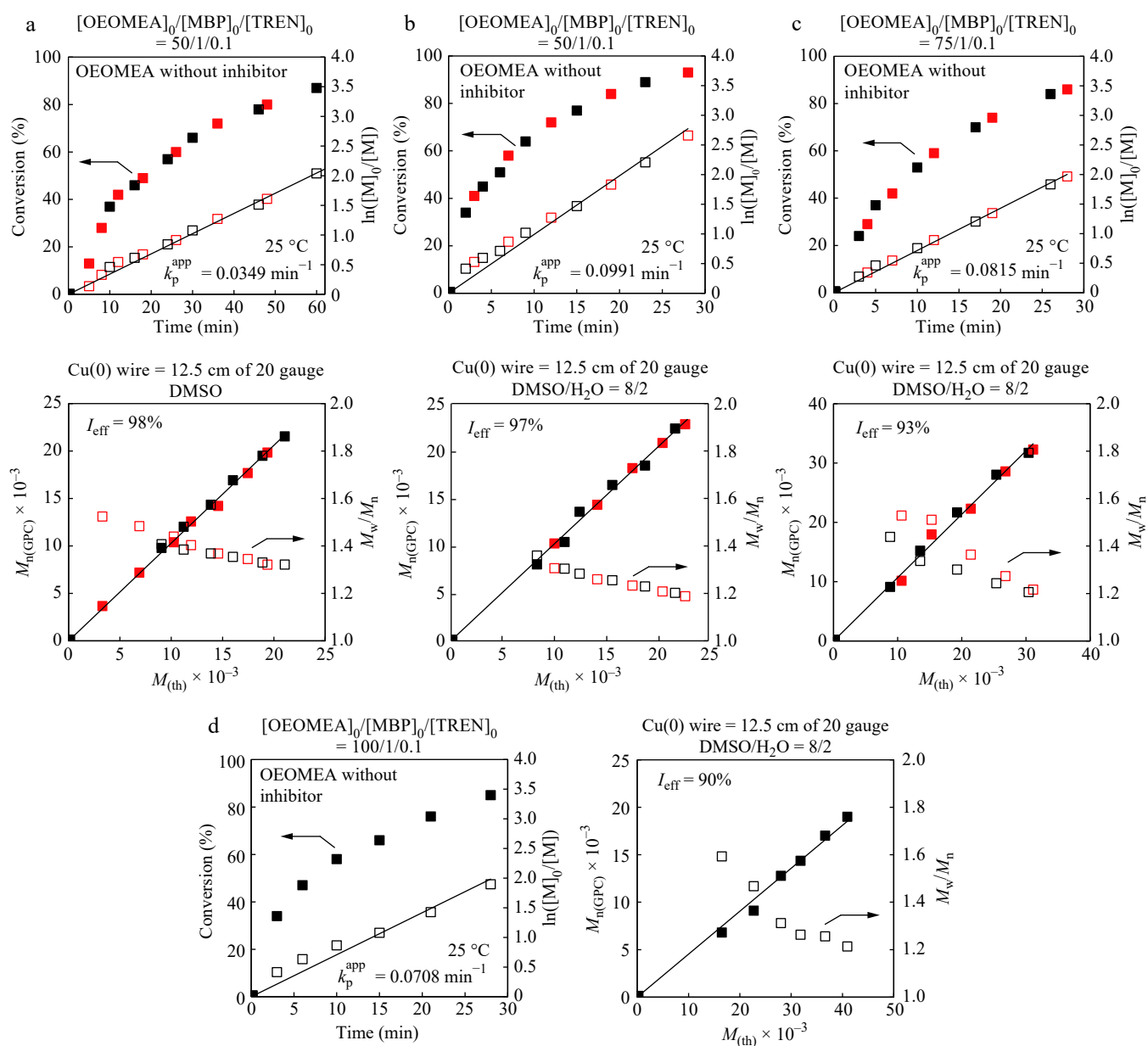


Fig. 3 Kinetic plots, molecular weight, and dispersity evolution for 12.5 cm hydrazine-activated Cu(0) wire/TREN catalyzed SET-LRP of OEOMEA without inhibitor in (a) DMSO or DMSO/H₂O (8/2, V/V) with the ratios between monomer, initiator, and ligand equal to (b) 50/1/0.1, (c) 75/1/0.1, and (d) 100/1/0.1.

activated Cu(0) wire as the catalyst. Although Me₆-TREN allowed for an effective SET-LRP of OEOMEA, the polymerization using TREN as the ligand also exhibits linear first-order kinetics. Compared to the polymerization catalyzed with Cu(0) wire/Me₆-TREN in DMSO, the polymerization using TREN was slightly slower, indicated by a lower apparent rate constant of propagation ($k_p^{\text{app}} = 0.0349 \text{ min}^{-1}$). In addition, a broader molecular weight distribution was observed even at the highest conversion (Table 2). Excitingly, the polymerization could be performed in a controlled manner in a DMSO/water (8/2, *V/V*) mixture in the absence of Cu(II)Br₂ (Fig. 3b). Remarkably, k_p^{app} increased to 0.0991 min^{-1} , higher than that obtained from catalyzed with Cu(0) wire/Me₆-TREN, and this is the fastest polymerization reported in this study (Table 1). Also remarkable is that polymer of $M_n = 22.9 \text{ kDa}$ and $M_w/M_n = 1.19$ could be isolated after less than 30 min.

Importantly, Cu(0)-mediated polymerization of OEOMEA in a DMSO/water (8/2, *V/V*) mixture was also carried out with increased degrees of polymerization (DP = 75 and 100) to obtain the resulting polymers with higher molecular weights. Polymerizations proceeded relatively quickly at ambient temperature, attaining high conversion (> 85%) in approximately 30 min (Figs. 3c and 3d). GPC analysis revealed a linear increase of M_n with the increasing conversion, which is in excellent agreement with the theoretical M_n and relatively low M_w/M_n (1.21–1.22, Table 2). Kinetic analysis revealed a largely first-order dependence on monomer and propagating radical for the majority of the polymerization. However, k_p^{app} would reduce when DP increased because the viscosity of the polymerization system raised evidently at high DP, which influenced the stirring rate of SET-LRP and thus led to a dramatic deceleration of the SET-LRP.^[27]

SET-LRP of OEOMEA without Inhibitor Catalyzed by Cu(0) Wire/TREN in Different Organic Solvents and Mixtures of the Organic Solvents with H₂O

Inspired by the results above, further experiments were

carried out in another three types of typical organic solvents (acetone, ethanol, and THF) and their mixtures with 20% H₂O. Polymerizations were also performed using the activated Cu(0) wire under the following conditions: [OEOMEA]₀/[MBP]₀/[TREN]₀ = 50/1/0.1. Selected kinetic data of the experiments are presented in Fig. 4. First-order kinetics was observed in three systems with an increase of k_p^{app} from THF to acetone and ethanol. Polymers with M_w/M_n values of about 1.25 were obtained in all cases indicating a good control over the molecular weight distribution (Table 2). Under the same reaction conditions, the external addition of 20% H₂O to organic phase significantly improved k_p^{app} , and also realized high conversion, good agreement between the theoretical and experimental M_n , and low M_w/M_n in all the biphasic homologous systems as described above (Table 2, Fig. 4). It is important to point out that SET-LRP of OEOMEA in all systems proceeded in a single phase throughout the entire reaction, resulting in a clear, homogeneous, and transparent reaction mixture even at high conversion.

To expand the scope of the activated Cu(0) wire/TREN catalytic system under biphasic homologous conditions, the last series of experiments were performed with Cu(0)-wire lengths decreased from 12.5 cm to 4.5 cm under the condition of [OEOMEA]₀/[MBP]₀/[TREN]₀ = 50/1/0.1. All kinetic experiments reached above 80% conversion in 90 min reaction time and exhibited linear first-order kinetics in different organic solvents with 20% H₂O (Fig. 5). A decrease in the surface area of Cu(0) wire catalyst still resulted in a polymerization with a linear kinetics. Also in these systems, M_n increased linearly with the conversion and remained correlative between experimental and theoretical values; meanwhile, narrow M_w/M_n was observed at high conversion regardless of the solvent choice (Table 2). All these results were also in agreement with a previous publication, confirming a surface-mediated activation of SET-LRP of OEOMEA catalyzed by activated Cu(0) wire. Considering the fact that all the tested solvents are miscible with water, it is important to emphasize that monophasic reaction mixture was visualized

Table 2 Catalyst and solvent influences on Cu(0) wire/TREN-mediated SET-LRP^a of OEOMEA without inhibitor

Entry	Reaction medium (<i>V/V</i>)	k_p^{app} (min^{-1})	Time (min)	Conversion ^b (%)	$M_{n(\text{th})}$ ^c (kDa)	$M_{n(\text{GPC})}$ (kDa)	M_w/M_n	I_{eff} ^d (%)
1	DMSO ^e	0.0349	60	87	21.0	21.6	1.31	98
2	DMSO/H ₂ O (8/2)	0.0991	28	93	22.4	22.9	1.19	97
3	DMSO/H ₂ O (8/2) ^f	0.0815	28	86	31.1	32.3	1.22	93
4	DMSO/H ₂ O (8/2) ^g	0.0708	28	85	40.9	38.1	1.21	90
5	EtOH	0.0286	75	88	21.3	21.8	1.23	93
6	EtOH/H ₂ O (8/2)	0.0801	30	91	22.0	21.5	1.18	98
7	Acetone	0.0223	88	88	20.3	19.7	1.22	95
8	Acetone/H ₂ O (8/2)	0.0683	35	90	21.8	21.6	1.23	97
9	THF	0.0172	90	82	19.8	20.0	1.26	96
10	THF/H ₂ O (8/2)	0.0312	55	81	19.6	19.7	1.20	91
11	DMSO/H ₂ O (8/2) ^h	0.0313	50	82	19.8	21.7	1.21	93
12	EtOH/H ₂ O (8/2)	0.0409	50	87	21.0	20.3	1.22	88
13	Acetone/H ₂ O (8/2)	0.0357	65	88	21.3	21.8	1.20	83
14	THF/H ₂ O (8/2)	0.0206	88	85	20.6	21.9	1.22	92

^a Reaction conditions: OEOMEA 1.0 g, solvent (+H₂O) 0.5 mL; [OEOMEA]₀/[MBP]₀/[TREN]₀ = 50/1/0.1, hydrazine-activated Cu(0) wire 12.5 or 4.5 cm of 20 gauge wire; ^b Obtained by ¹H-NMR spectroscopy using the equation $1 - (S_{3\text{H}_2\text{Acrylate}}/3)/(S_{2\text{H}_2\text{CH}_2}/2)$, methylene is linked directly to acrylate group; ^c $M_{n(\text{th})} = [\text{Conversion} (\%) \times ([\text{OEOMEA}]_0/[\text{MBP}]_0) \times M_{n,\text{OEOMEA}} + M_{n,\text{MBP}}]/1000$, where $M_{n,\text{OEOMEA}} = 480$ and $M_{n,\text{MBP}} = 167$ are the molar masses of monomer OEOMEA and initiator MBP, respectively; [OEOMEA]₀/[MBP]₀ = 50; ^d Initiator efficiency; ^e Entries 1–10 used 12.5 cm Cu(0) wire for SET-LRP; ^f [OEOMEA]₀/[MBP]₀/[TREN]₀ = 75/1/0.1; ^g [OEOMEA]₀/[MBP]₀/[TREN]₀ = 100/1/0.1; ^h Entries 11–14 used 4.5 cm Cu(0) wire for SET-LRP

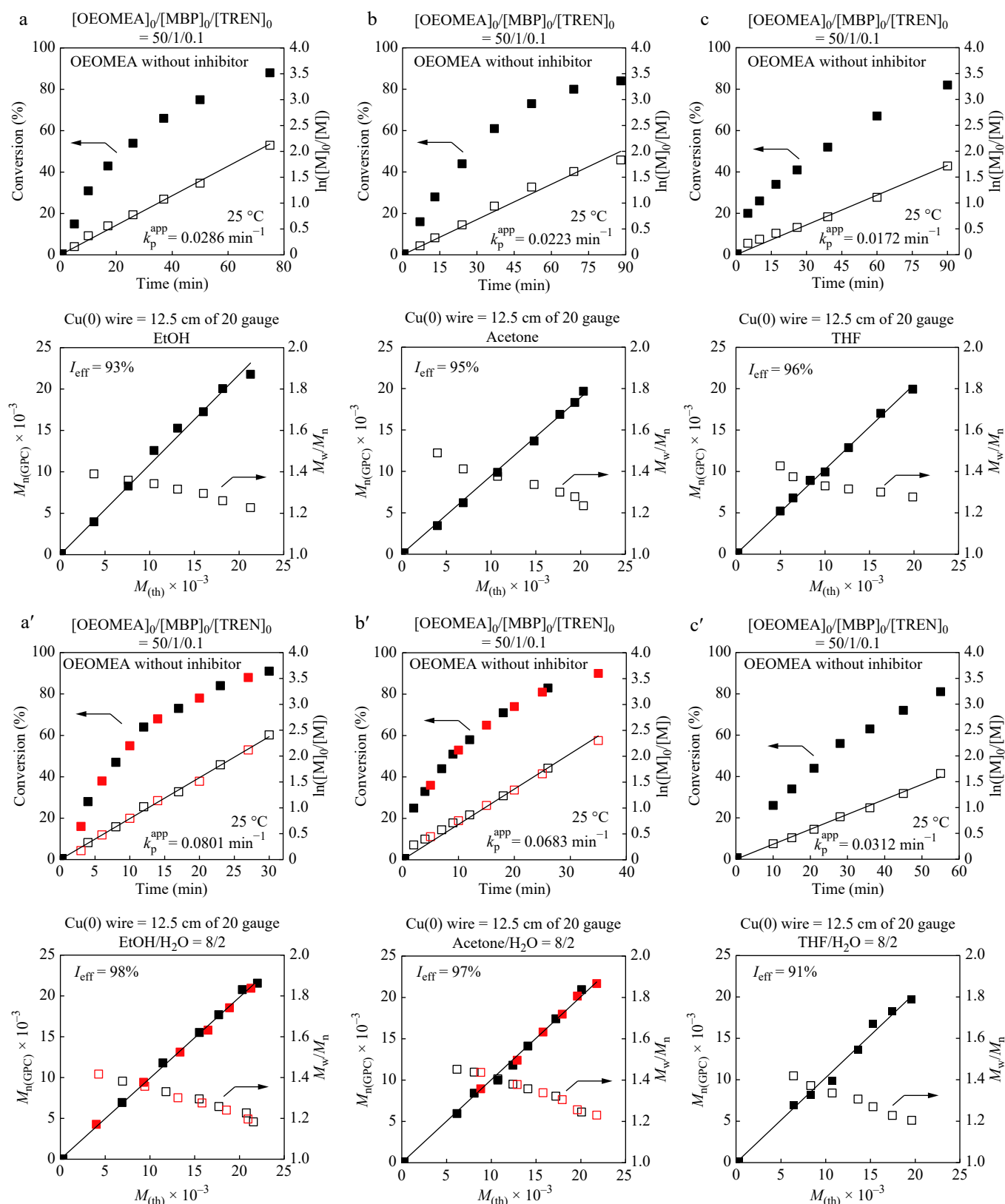


Fig. 4 Kinetic plots, molecular weight, and dispersity evolution for SET-LRP of OEOMEA without inhibitor catalyzed by 12.5 cm hydrazine-activated Cu(0) wire/TREN in (a, a') EtOH, EtOH/H₂O (8/2, *V/V*), (b, b') acetone, acetone/H₂O (8/2, *V/V*), and (c, c') THF, THF/H₂O (8/2, *V/V*)

in all systems from the beginning to the end of SET-LRP.

Fig. 6 also shows the digital images of the reaction mixtures

taken at the highest conversion, which display the clear and homogeneous systems.

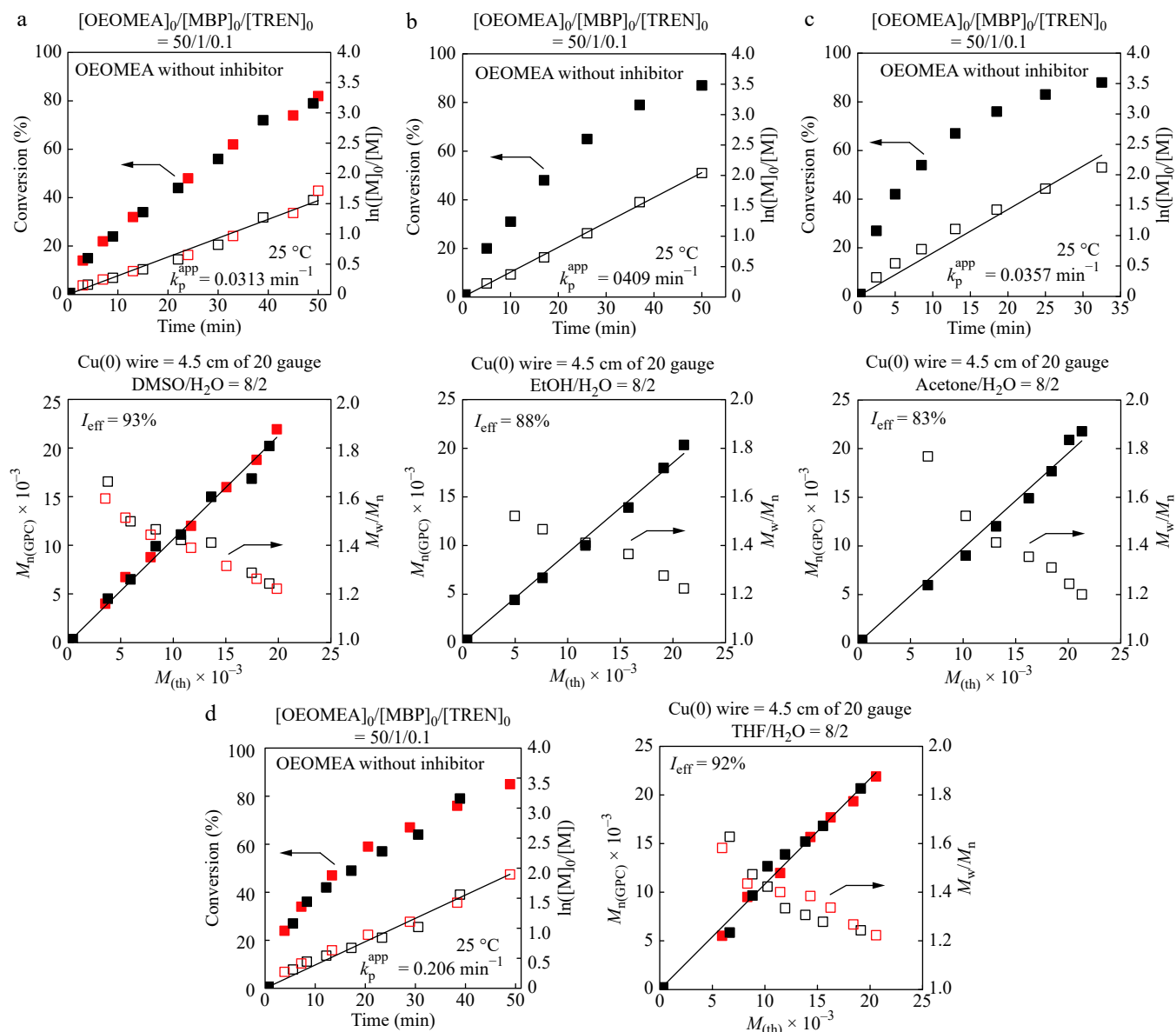


Fig. 5 Kinetic plots, molecular weight, and dispersity evolution for the SET-LRP of OEOMEA without inhibitor catalyzed by 4.5 cm hydrazine-activated Cu(0) wire/TREN in (a) DMSO/H₂O (8/2, *V/V*), (b) EtOH/H₂O (8/2, *V/V*), (c) acetone/H₂O (8/2, *V/V*), and (d) THF/H₂O (8/2, *V/V*)

Chain-end Analysis of PEOMEA-Br Obtained from the SET-LRP Process Catalyzed by Cu(0) Wire/TREN in DMSO/H₂O

From a technological point of view, TREN offers several advantages over Me₆-TREN, especially for its commercial availability at a relatively low cost. However, for TREN to be a successful replacement of Me₆-TREN, it is necessary to consider the chain-end functionality of the resulting samples because analysis of the chain-end functionality of polymers prepared by LRP is crucial both to demonstrating the living characteristics of the system and for most technological applications.^[28] The resulting polymer isolated from TREN-mediated SET-LRP performed in the mixtures of DMSO and H₂O was selected as a representative example because DMSO is an excellent solvent for SET-LRP polymers and has been frequently used alone or in mixtures with H₂O as a solvent for SET-LRP. Remarkable is also that this system

provided the highest rate of polymerization reported in this publication. The functionality of polymers isolated at about 36% and 93% conversion $[1-(S_{3H,Acrylate}/3)/(S_{2H,CH_2}/2)]$ from an experiment under the condition $[OEOMEA]_0/[MBP]_0/[TREN]_0 = 50/1/0.1$ was determined by ¹H-NMR spectroscopy before and after “thio-bromo click” modification of the bromine chain end with thiophenol. As shown in Fig. 7, the ratio between the integrals of signals corresponding to the protons from the MBP initiator (H_c) and the bromine or thiophenyl chain ends (H_g or H_k) was used to demonstrate a nearly perfect retention of chain-end functionality (97% and 98%). ¹H-NMR spectroscopy also supported this transformation with the up-field shift of the methine proton (H_g) signal at the ω-chain end from about 4.35 ppm to 2.78 ppm. All these analyses confirmed that the percentage of chains without —Br was negligible under the conditions investigated.

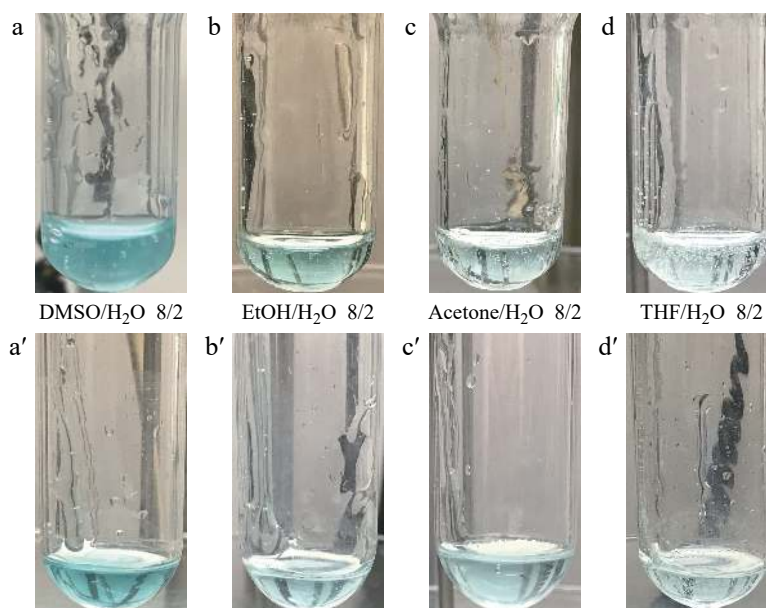


Fig. 6 Visualization of the reaction mixture after SET-LRP of OEOMEA without inhibitor catalyzed by 12.5 and 4.5 cm hydrazine-activated Cu(0) wire/TREN in (a, a') DMSO/H₂O (8/2, *V/V*), (b, b') EtOH/H₂O (8/2, *V/V*), (c, c') acetone/H₂O (8/2, *V/V*), and (d, d') THF/H₂O (8/2, *V/V*)

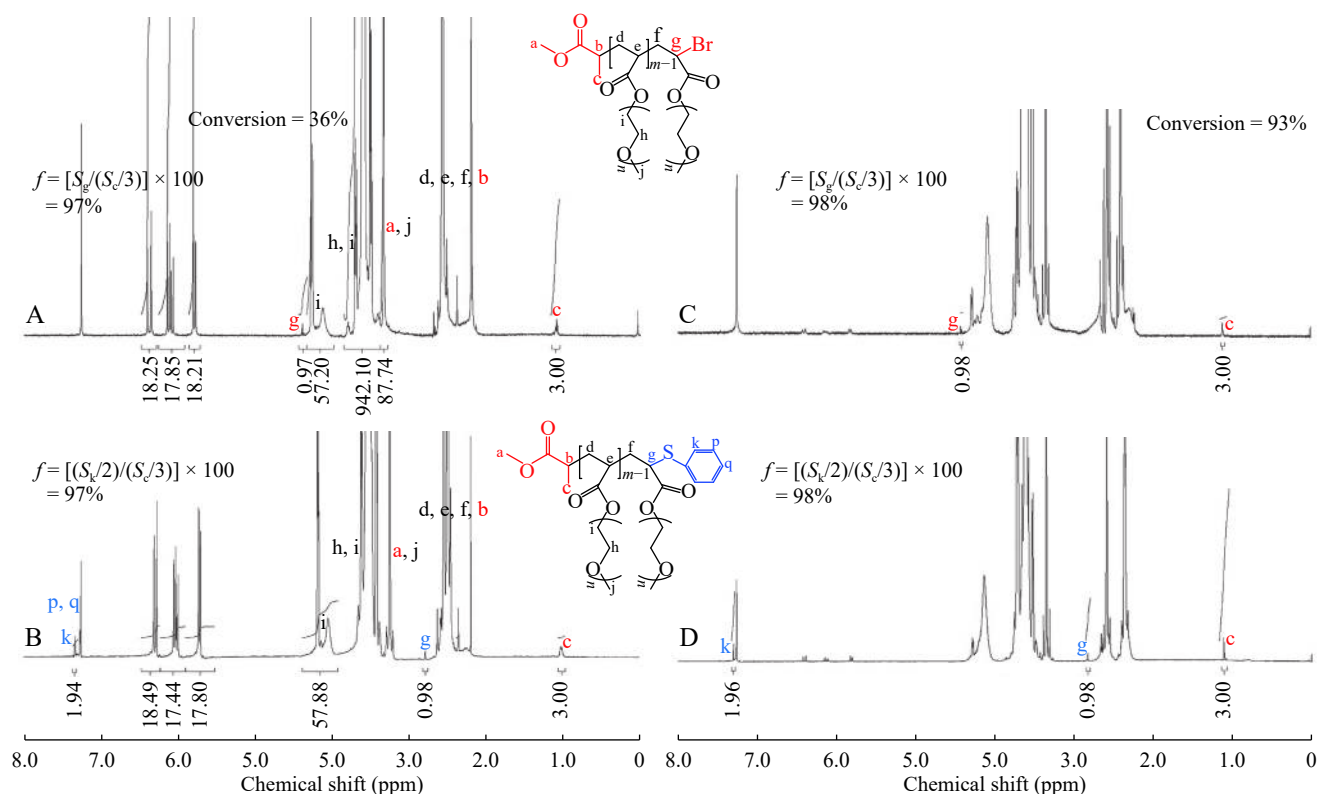


Fig. 7 ¹H-NMR spectra for PEOMEA-Br isolated at (A, B) 36% and (C, D) 93% conversion from SET-LRP of OEOMEA without inhibitor (A, C) before the “thio-bromo click” reaction and (B, D) after the “thio-bromo click” reaction

Chain Extension of PEOMEA-Br with MA by SET-LRP Catalyzed by Cu(0) Wire/TREN in an DMSO/H₂O Mixture

Further evidence for the high chain-end fidelity of PEOMEA-Br was experimentally provided by chain extension with MA to afford block copolymer. To analyze the chain extension by ¹H-NMR spectroscopy more precisely, a low ratio

of [Monomer]₀/[Initiator]₀ was used first to prepare a suitable PEOMEA-Br sample with relatively low molecular weight.^[29] Therefore, PEOMEA-Br sample was synthesized under the condition of [OEOMEA]₀/[MBP]₀/[TREN]₀ = 25/1/0.1. Fig. 8(a) shows the evolution of conversion and ln([M]₀/[M]) versus time throughout this biphasic fast reaction. The polymerization of OEOMEA under the similar

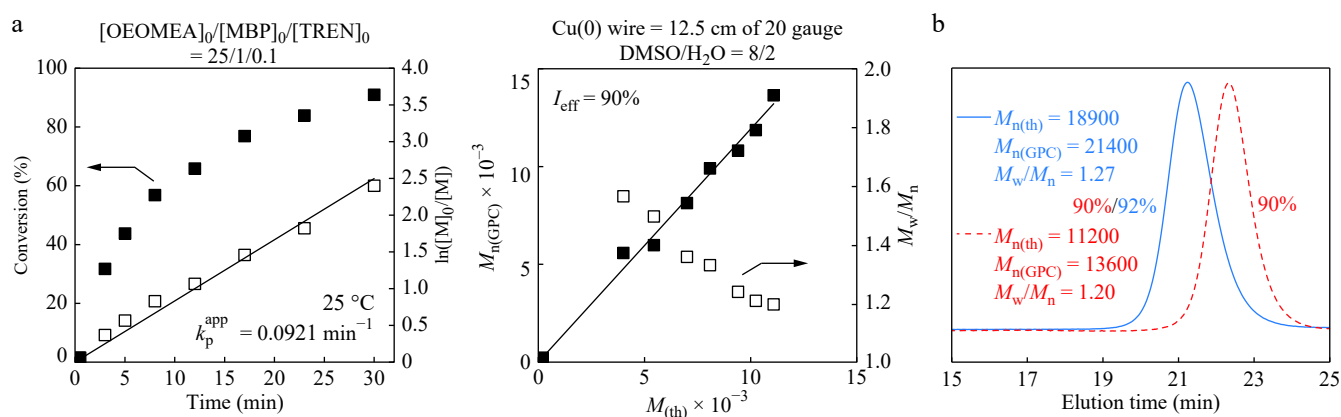


Fig. 8 (a) Kinetic plot, molecular weight, and dispersity evolution for 12.5 cm hydrazine-activated Cu(0) wire/TREN catalyzed SET-LRP of OEOMEA without inhibitor in DMSO/H₂O (8/2, *V/V*) with 25/1/0.1 molar ratio of monomer, initiator, and ligand; (b) GPC traces of POEOMEA-Br obtained in (a) and chain extension of POEOMEA-Br with MA at high conversions

conditions exhibited a linear first order kinetic plot, suggesting a constant concentration of growing species up to high conversion. The linear evolution of molecular weight and the progressive decrease of dispersity also support the livingness of the system. Finally, chain extension was realized upon addition of a deoxygenated aliquot of MA when the homopolymerization had completed and reached high conversion (90%). The resulting block copolymer was obtained in high conversion (92%, Fig. S6 in ESI) with relatively narrow molecular weight distribution (1.27, Fig. 8b). The complete shift to higher molecular weight is indicative of minimal loss of the α -Br end group during homopolymerization, even at the high conversion.^[30,31]

CONCLUSIONS

Cu(0) wire-mediated SET-LRP of OEOMEA was successfully performed in a diversity of biphasic water/water soluble organic solvents. The effects of Cu(0)-wire length, ligand, and solvent on SET-LRP have been evaluated. When hydrazine-activated Cu(0) wire/Me₆-TREN was first used as the catalyst, SET-LRP of OEOMEA in DMSO and the mixture with 20% H₂O gifted the “living” character to the polymerization system, producing polymers with high conversion and relatively narrow molecular weight distribution. The addition of increased H₂O (40%–60%) to DMSO resulted in the reduced rate constant considering that OEOMEA could self-assemble in water-rich mixtures of DMSO. Subsequently, TREN was used as a ligand in hydrazine-activated Cu(0) wire catalyzed SET-LRP under identical conditions; the polymerization still exhibited linear kinetics, linear dependence of the experimental molecular weight on conversions, and narrow molecular weight distributions. The presence of 20% H₂O in the organic solvents also led to higher rate of polymerization than that in pure organic solvents, and nearly quantitative chain end fidelity of POEOMEA was checked *via* post-polymerization modification by thiol-Michael addition reaction. The high end-group fidelity of POEOMEA was also experimentally verified by chain extension with MA to furnish the block copolymers.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://dx.doi.org/10.1007/s10118-019-2263-7>.

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