Ambient Temperature Copper-Mediated Living Radical Polymerization of Acrylonitrile with Me$_6$TREN as the Reducing Agent

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INTRODUCION

Transition metal-catalyzed living radical polymerization (LRP) is a powerful synthetic technique for synthesizing polymeric materials with a predetermined molecular weight, a low polydispersity index (PDI), and chain end functionality.[1–8] Among the family of transition metal catalysts, copper-based complexes are extremely appealing in view of high efficiency and relatively low cost. To date, many strategies have been developed for copper-mediated LRP, for example, atom transfer radical polymerization (ATRP) and single-electron-transfer (SET) LRP.[9–11]

Various ligands have been utilized to perform copper-mediated LRP. Among them, Tris[2-(dimethylamino)-ethyl] amine (Me$_6$TREN) has been widely used due to its higher activity, which stems from branched tertiary-amine-based structure.[12–15] Notably, the tertiary-amine group can serve as not only coordination site but also reducing agent (RA) according to the works of Shen's, Matyjaszewski's, Lai's, and Chen's groups in recent years. Moreover, Matyjaszewski et al. and Lai et al. respectively reported the copper-mediated LRP of MMA using an excess of nitrogen based ligands with tertiary-amine group in combination with CuBr$_2$ as catalytic systems, such as N,N,N′,N′-tetramethylethylenediamine, N,N,N′,N′,N-pentamethyldiethylenetriamine (PMDETA), and N,N,N′,N″, N‴,N‴′-hexamethyltriethylenetetramine (HMTETA).[16–17] More recently, Chen et al. extended this strategy to acrylonitrile (AN) using ethyl 2-bromoisobutyrate (EBiB)/HMTETA or PMDETA/CuBr$_2$ initiating system for the copper-mediated LRP in DMF or ionic liquid at 65 °C.[18–19] Totally, theses polymerizations were well controlled and displayed typical LRP characteristics. Considering the special structure of Me$_6$TREN (i.e., possessing four tertiary-amine groups), deeper investigations focusing on the use of CuBr$_2$/excess Me$_6$TREN catalytic system in LRP of vinyl monomers were needed. To the best of our knowledge, only one example of CuBr$_2$/Me$_6$TREN-catalyzed LRP of n-butyl acrylate at 60 °C was reported by Matyjaszewski et al.[20] Unfortunately, the loss of the control over the polymerization ($M_w/M_n = 1.83$ for a monomer conversion of 86%) was observed. Therefore, we envisioned that by optimizing the experimental parameters, the exploration of this ligand as the RA can provide a facile route to the LRP.

The present contribution first demonstrates that Me$_6$TREN can be successfully employed as the reducing agent for the ambient temperature copper-mediated of AN in dimethyl sulfoxide (DMSO). The LRP features have been confirmed by a combination of the polymerization kinetic studies and the detailed end-group analyses of the resultant polymer. Meanwhile, this study provides an insight into the mechanistic proposal, which allows for a comprehensive understanding of the CuBr$_2$/excess Me$_6$TREN catalytic system.

EXPERIMENTAL

Materials

AN (98%) was dried over anhydrous sodium sulfate and distilled before use. EBiB (98%, Aladdin), anhydrous cupric bromide (CuBr$_2$, 99%, Alfa Aesar) and ethylene carbonate (EC, 99%, Aladdin) were used as received. N,N-dimethylformamide (DMF, 99.5%), N-methyl-2-pyrrolidone (NMP, 98%), acetonitrile (MeCN, 98%), acetone (98%), toluene (98%), and DMSO (99.8%) were distilled at reduced pressure before use. Tris [2-(dimethylamino)-ethyl] amine (Me$_6$TREN) was prepared using a method adapted from the literature.[21]

Polymerization

AN, DMSO, Me$_6$TREN, CuBr$_2$, and EBiB were charged into a Schlenk tube equipped with a magnetic stir bar and the tube was tightly sealed with a rubber septum. The resulting solution was degassed with three freeze-pump-thaw cycles and then the tube was immersed in a thermostated oil bath at

Additional Supporting Information may be found in the online version of this article.

TABLE 1 Copper-Mediated LRP of AN Using Me_6TREN as the Reducing Agent[a]

Entry	Solvent	$[AN]_0$ (mol/L)	Time (h)	Conv. (%)	$M_{n,th}$ (Da)	$M_{n,GPC}$ (Da)	M_w/M_n
1	DMF	10.12	5	9.19	1,170	4,725	1.46
2	NMP		5	15.42	1,831	3,307	1.15
3	EC		2	9.17	1,168	2,905	1.13
4	EC		5	24.31	2,775	4,610	1.22
5	EC		7	33.75	3,777	6,015	1.34
6	DMSO		5	24.89	2,836	5,067	1.13
7	DMSO		12	53.35	5,857	10,530	1.32
8	DMSO	7.60	5	21.92	2,521	4,255	1.30
9	DMSO		12	63.50	6,933	9,413	1.22
10	DMSO		17	78.64	8,540	10,130	1.19
11	DMSO	5.06	12	60.02	6,564	8,023	1.19
12	DMSO		17	71.87	7,822	9,754	1.13

[a] $[AN]_0/[EBiB]_0/[Me_6TREN]_0/[CuBr_2]_0 = 200:1:0.5:0.05$, $T = 25\ °C$.

25 °C. After the desired polymerization time, the resulting solution was dissolved in DMSO and then precipitated into large amounts of methanol/HCl (v/v, 100/0.1). The resultant polymer was filtered and dried under vacuum until a constant weight at 50 °C. The monomer conversion was determined gravimetrically.

Chain Extension of PAN

A predetermined quantity of obtained PAN with $CuBr_2$, Me_6TREN, and AN were dissolved in DMSO. The polymerization temperature was then stabilized at 25 °C. The rest of the procedure was identical to that described above.

Characterization

The number-average molecular weights ($M_{n,GPC}$) and polydisperisity indexes of the obtained PANs were determined by gel permeation chromatography (GPC) system, which consisted of a Waters 510 HPLC pump, three Waters Ultrastyragel columns (500, 10^3, and 10^5), and a Waters 2414 RI detector with a flow rate of 1.0 mL/min. The universal calibration can be used to correct the molecular weights obtained for PMMA to PAN using Mark–Houwink–Sakarada (MHS) equation between PMMA and PAN with MHS parameters: $K_{PMMA} = 1.32 \times 10^{-4}$ dL/g and $\alpha_{PMMA} = 0.674$,[22] and $K_{PAN} = 3.17 \times 10^{-4}$ dL/g and $\alpha_{PAN} = 0.746$.[23] Theoretical molecular weights ($M_{n,th}$) of the resulting PAN was calculated by the following equation:

$$M_{n,th} = \frac{[AN]_0 \times Conv. \times M_{AN}}{[EBiB]_0} + M_{EBiB}$$

where $[AN]_0$ and $[EBiB]_0$ are the initial concentrations of AN and EBiB, respectively, M_{AN} and M_{EBiB} correspond to the molecular weight of AN and EBiB, $Conv.$ is the monomer conversion.

^{1}H NMR spectra of PAN were recorded on a Bruker 300 MHz Spectrometer using DMSO-d_6 as the solvent and tetramethylsilane as the internal standard.

RESULTS AND DISCUSSION

Copper-Mediated LRP of AN with Me_6TREN as the Reducing Agent at 25 °C

As PAN is not soluble in AN monomer and most organic solvents, the choice of suitable solvent is crucial to the copper-mediated LRP of AN with Me_6TREN as the reducing agent at 25 °C.[24–28] Therefore various solvents (DMF, NMP, EC, and DMSO) were first examined and the representative results are summarized in Table 1. Obviously, for the resultant polymers obtained within 5 h, low PDI values are observed for all cases (PDI = 1.13–1.22, entries 2, 4, and 6) except DMF (PDI = 1.46, entry 1). In addition, the polymerization in NMP gradually became cloudy after 1h, probably due to the poor solubility of PAN in this solvent. Important, compared with DMF and NMP, EC and DMSO exhibited relatively higher rates of polymerization (entries 4 and 6). However, EC is a solid at ambient temperature and would complicate the reaction.[29] Consequently, DMSO bearing a lower melting point was chosen for the medium of the subsequent reactions.

In general, an ideal LRP process should display the following characteristics including pseudo first-order kinetics of polymerization, a linear increase of the number average molecular weight with monomer conversion, low PDIs, and controlled molar mass.[30] To follow the polymerization kinetics and the evolution of MW and PDI values, copper-mediated LRP of AN initiated with $EBiB/CuBr_2/Me_6TREN$ in DMSO at 25 °C was detailedly investigated.[31] As shown in Figure 1, a pseudo first-order kinetic was clearly observed, indicating an approximately constant concentration of active species throughout the polymerization. Noticeably, there did exist a significant induction period (ca. 2 h), which was probably attributed to the presence of trace oxygen or an excess of the deactivators Cu(II) relative to the radicals due to the slow reduction from Cu(II) to Cu(I) by Me_6TREN at the initial stage of the polymerization. Furthermore, the M_n values obtained by GPC technique linearly increase with the monomer conversions (Fig. 2). However, the experimental results are higher than the theoretical ones, which possibly might originate from the unsuitable PMMA
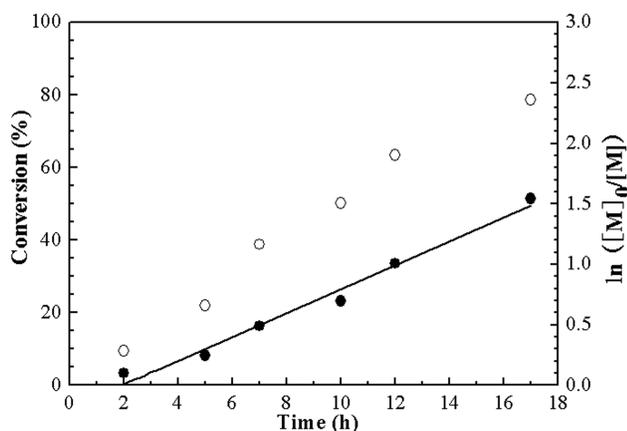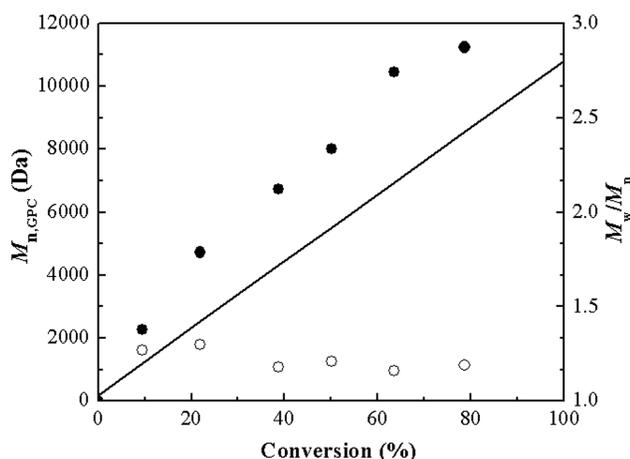
FIGURE 1 Plots of monomer conversion (○) and ln ([M]$_0$/[M]) (●) versus reaction time for copper-mediated LRP of AN using Me$_6$TREN as the reducing agent in DMSO. Reaction conditions: [AN]$_0$/[EBiB]$_0$/[Me$_6$TREN]$_0$/[CuBr$_2$]$_0$ = 200:1:0.5:0.05, [AN]$_0$ = 7.60 M, T = 25 °C.

standard for PAN. Concerning the PDI values, they progressively decrease with the polymerization process, maintaining a level of 1.16–1.30. The rules are also accurately mirrored in the GPC curves of the obtained PAN samples (Fig. 3). The traces shift completely and cleanly to the high MW regions with the increase of the monomer conversions. Additionally, all traces are always narrow during the whole reaction. Therefore the results confirm that the copper-mediated LRP of AN with Me$_6$TREN as the reducing agent possessed typical CRP characteristics and proceeded in a living manner.

Effect of Monomer Concentration

The homogeneity of the reaction mixtures considerably influences the controllability of the polymerization due to the limited solubility of PAN.[32] Thus, it is indispensable to investigate the effect of monomer concentration on the ambient temperature copper-mediated LRP of AN with Me$_6$TREN as the reduc-

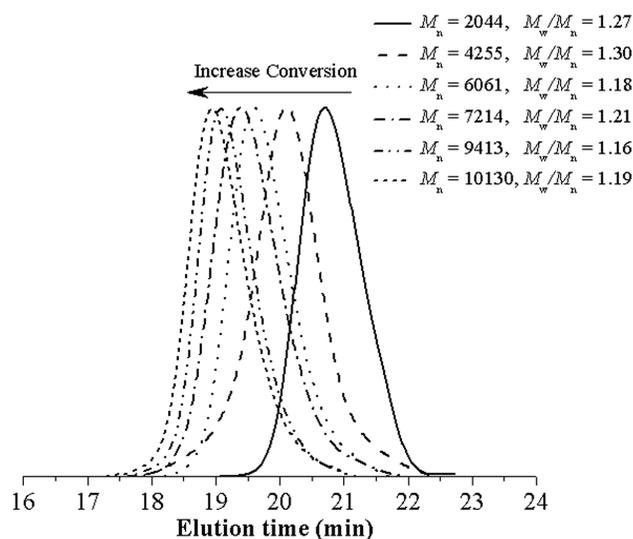**FIGURE 2** Evolution of $M_{n,GPC}$ (●) and PDI (○) with monomer conversion for copper-mediated LRP of AN using Me$_6$TREN as the reducing agent in DMSO. Reaction conditions: [AN]$_0$/[EBiB]$_0$/[Me$_6$TREN]$_0$/[CuBr$_2$]$_0$ = 200:1:0.5:0.05, [AN]$_0$ = 7.60 M, T = 25 °C.

ing agent. Three experiments (entries 6–12 in Table 1) were conducted by only varying the monomer conversions, that is, [AN]$_0$ = 5.06, 7.60, and 10.12 M. As expected, for the polymerization with a higher [AN]$_0$ of 10.12 M, the reaction mixture exhibited cloudy at the middle-to-later polymerization stage, and the monomer conversions limited 53.35% even further lengthening the reaction time. The corresponding kinetic plot shows a curvature after 10.5 h (49.88% monomer conversion, see Supporting Information Fig. S1). In contrast, a pseudo first-order kinetic curve was obtained for a lower [AN]$_0$ of 5.06 or 7.60 M, suggesting that the improved homogeneity of reaction mixtures did contribute to maintain constant concentration of active centers during the polymerization. Moreover, the PDI values of PAN samples at high monomer conversions for a [AN]$_0$ of 5.06 M or 7.60 M were about 1.20, whereas that at a monomer conversion of 53.35% for a [AN]$_0$ of 10.12 M was 1.32. In summary, the optimized monomer concentration can facilitate a high level of both the degree of living and the rate of polymerization.

Chain-End Functionality

An important criterion of LRP is that the resultant polymer possesses high chain-end functionality. ^{1}H NMR technique can be very useful for the analysis of the structure of PAN synthesized via copper-mediated LRP of AN using Me$_6$TREN as the reducing agent at 25 °C, as shown in Figure 4. Signals at 5.1–5.3 ppm were attributed to the methine proton of AN unit adjacent to the bromine atom at ω-end. The chemical shifts at 4.05–4.15 ppm corresponded to the methylene protons of the ethyl ester unit at the α-end in the initiator EBiB. Moreover, the integration ratios of H_b/H_g close to 2 and H_{a+c}/H_g near 9 verified the high chain-end functionality of the PAN obtained. The molecular weight of PAN sample determined from the ^{1}H NMR spectrum ($M_{n,NMR}$) was 3528,

FIGURE 3 GPC traces of PANs formed via copper-mediated LRP of AN using Me$_6$TREN as the reducing agent in DMSO at different conversions: 9.51, 21.92, 38.78, 50.19, 63.50, 78.64%. Reaction conditions: [AN]$_0$/[EBiB]$_0$/[Me$_6$TREN]$_0$/[CuBr$_2$]$_0$ = 200:1:0.5:0.05, [AN]$_0$ = 7.60 M, T = 25 °C.
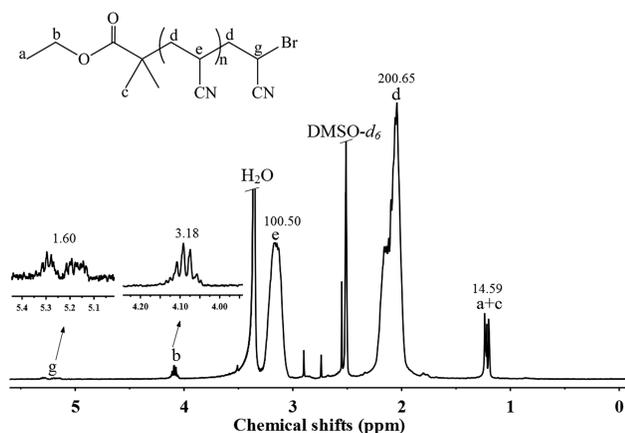
FIGURE 4 ^{1}H NMR spectrum of PAN ($M_{n,GPC}$ = 2044 g/mol, M_w/M_n = 1.27) obtained by copper-mediated LRP of AN using the reducing agent. Reaction conditions: [AN]$_0$/[EBiB]$_0$/[Me$_6$T-REN]$_0$/[CuBr$_2$]$_0$ = 200:1:0.5:0.05, [AN]$_0$ = 7.60 M, T = 25 °C, reaction time = 2 h, monomer conversion = 9.51%.

which was very close to the theoretical one ($M_{n,th}$ = 4310). The ^{1}H NMR analyses showed that the PAN was mainly capped by the EBiB moieties.[24–26,33,34]

An additional efficient way for confirming the high chain-end functionality of the resultant polymer is to perform chain-extension reaction by employing the same polymerization approach, that is, the ambient temperature copper-mediated LRP using Me$_6$TREN as reducing agent. As expected, an obvious peak shift from the original PAN-Br ($M_{n,GPC}$ = 5067, M_w/M_n = 1.13) macroinitiator to the chain-extended PAN ($M_{n,GPC}$ = 21939, M_w/M_n = 1.20) was observed in Figure 5. The monomodal and symmetrical GPC curve and low PDI value of the latter indicated the successful chain-extension reaction. The results confirm the living features of copper-mediated LRP of AN with Me$_6$TREN as the reducing agent.

Mechanism for Copper-Mediated LRP of AN Using Me$_6$TREN as the Reducing Agent

To gain more insights into the present CuBr$_2$/Me$_6$TREN-mediated LRP of AN, two sets of experiments were conducted. First, the influence of different ligand concentrations on the reaction was examined (Supporting Information Fig. S1) and the molar ratio of [AN]$_0$/[EBiB]$_0$/[CuBr$_2$]$_0$ = 200:0.5:0.05 was used. Clearly, No polymer can be detected with lower Me$_6$T-REN loadings (1or 2 equiv with respect to CuBr$_2$), indicating all Me$_6$TREN was almost engaged in coordinating CuBr$_2$ and there no external Me$_6$TREN could be used to reduce CuBr$_2$ to CuBr. In contrast, increasing the Me$_6$TREN amount (Supporting Information Table S1, entries 3–5) led to the gradual increase of rate of polymerization. Importantly, the polymerization in presence of the excess Me$_6$TREN possessed typical living polymerization characteristics. The improvement can be attributed to that a large excess of Me$_6$TREN to CuBr$_2$ facilitates the reduction of CuBr$_2$ to CuBr. However, when too high a concentration of Me$_6$TREN (40 or 60 equiv. with respect to CuBr$_2$) was used, lower polymerization rate and larger PDI value (Supporting Information Table S1, entries 6–7) was

observed. The results revealed that the coordination of the ligand to the metal center may lower catalytic activity and poison catalytic system when the ligand concentration was further increased. That is to say, the appropriate molar ratio of CuBr$_2$/Me$_6$TREN (i.e., 1:10) favors the achievement of the rapid equilibrium between dormant species and active radicals. Second, the effects of various non-disproportionating solvents on the reaction were also studied (Supporting Information Table S2 and Fig. S2). After 12 h, <15% monomer conversions in all cases (12.00, 13.65, and 0% for MeCN, acetone, and toluene, respectively), which were far less than the conversion in disproportionating solvent (63.50% for DMSO). One reason for the low polymerization rates might ascribe to the poor solubility of PAN or the slow disproportionation of CuBr in these solvent. In the meantime, the PDI values were higher than 1.50 for MeCN and acetone, suggesting chain termination or other side reaction pathways were not negligible in these solvents. Based on our findings, we propose the mechanism to explain polymerization of AN initiated by EBiB/CuBr$_2$/Me$_6$TREN. The original reaction starting with CuBr$_2$ and an excess of Me$_6$TREN gave the CuBr *in situ*. Subsequently, two possibilities are considered. Conversely, CuBr in conjunction with EBiB would initiate the normal ATRP process.[6] On the other hand, further disproportionation of CuBr to Cu(0) and CuBr$_2$ in DMSO would contribute the control of the polymerization according to Percec et al.[35–47] Therefore, under the SET-LRP mechanism, Cu(0) triggers activation of EBiB for generating radical species and CuBr$_2$ serves as a deactivator to capture propagating radical species. Consequently, it is possible that both ATRP and SET-LRP mechanisms contribute to the ambient temperature LRP of AN initiated from EBiB/CuBr$_2$/Me$_6$TREN in DMSO.
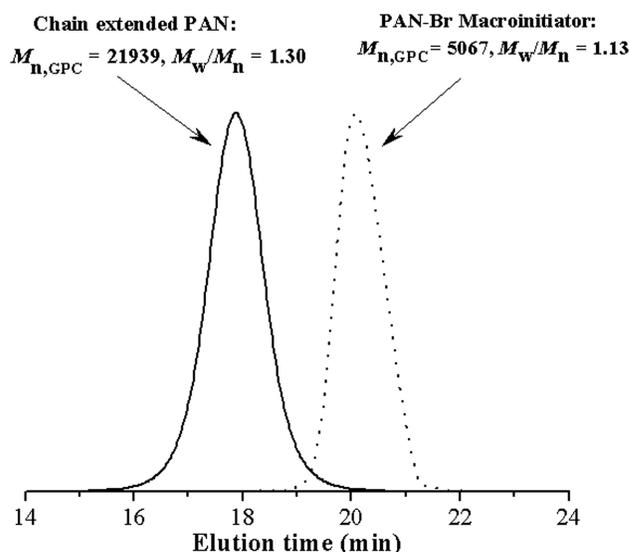
FIGURE 5 GPC traces of PAN-Br macroinitiator before (dot) and after (solid line) chain extension with AN. Reaction conditions: Original PAN: [AN]$_0$/[EBiB]$_0$/[Me$_6$TREN]$_0$/[CuBr$_2$]$_0$ = 200/1/0.5/0.05, [AN]$_0$ = 10.12M, T = 25 °C, reaction time = 5 h, monomer conversion = 24.89%; Chain extended PAN: [AN]$_0$/[PAN-Br]$_0$/[Me$_6$TREN]$_0$/[CuBr$_2$]$_0$ = 400/1/1/0.1, [AN]$_0$ = 7.60M, T = 25 °C, reaction time = 12 h, monomer conversion = 60.86%.

CONCLUSIONS

A universal high reactive ligand, Me$_6$TREN, was successfully explored as the reducing agent for the ambient temperature copper-mediated LRP of AN. The key to success is ascribed to the optimized Me$_6$TREN amount and reaction conditions employed, producing ideal living free radical polymerization characteristics as evidenced by pseudo first-order kinetic plots of polymerization, the molecular weights linearly increase with the monomer conversions, and low PDI values of the resultant polymers. Choosing the proper reaction medium (DMSO) and monomer concentration (7.60 mol/L) significantly improve the rate of the polymerization and the control over the molecular weight and PDI results. The very high chain-end functionality of the resultant polymer has been detailedly confirmed by GPC and ^{1}H NMR analyses as well as the chain-extension reaction.

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