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# Activators Regenerated by Electron Transfer Atom Transfer Radical Polymerization in Miniemulsion with 50 ppm of Copper Catalyst

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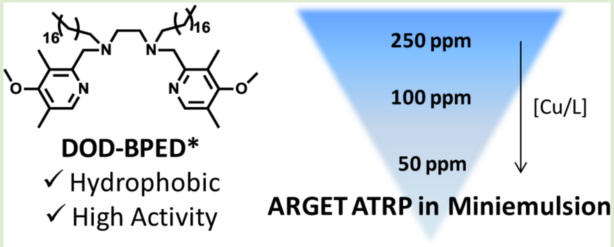
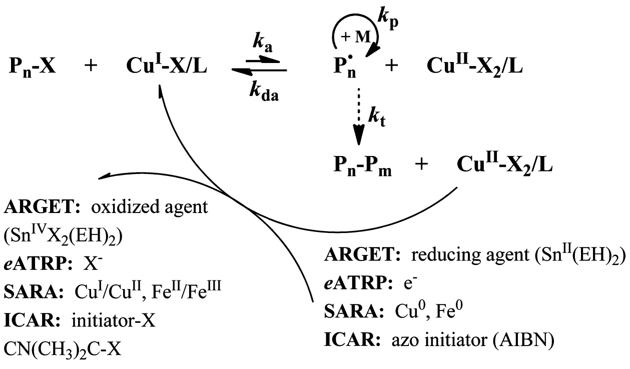
*Supporting Information*



**ABSTRACT:** The design and synthesis of a powerful ligand is reported for use in activators regenerated by electron transfer atom transfer radical polymerization (ARGET ATRP) in miniemulsion. The structure of *N′*,*N″*-dioctadecyl-*N′*,*N″*-bis[2-(4-methoxy-3,5-dimethyl)pyridylmethyl]ethane-1,2-diamine (DOD-BPED*) was formulated to produce a tetradentate ligand which was both hydrophobic and highly active. Studies in homogeneous ARGET ATRP with $CuBr_2$/DOD-BPED* demonstrated a high degree of control, similar to those ligands traditionally used. $CuBr_2$/DOD-BPED* also proved itself to be extremely useful in ARGET ATRP miniemulsion systems, at concentrations of catalyst as low as 50 ppm while maintaining control over the polymerization of butyl methacrylate (BMA). Additionally, the catalyst was tested over a range of degrees of polymerization, DP = 2000−10 000, all of which resulted in successful polymerizations. Most notably, high molecular weight polymers with $M_{n,exp} > 700\,000$ and $M_w/M_n < 1.4$ were prepared with only 50 ppm of $CuBr_2$/DOD-BPED* catalyst under miniemulsion conditions.

Polymerization in aqueous dispersed media is recognized to be a mild, environmentally benign technique and therefore widely considered for use on an industrial scale. Water as a reaction medium not only affords greater heat dissipation during polymerization but also eliminates the necessity of using volatile organic solvents.[1−4] Atom transfer radical polymerization (ATRP)[5−9] has been successfully extended to aqueous dispersed media including microemulsion,[10,11] miniemulsion,[12−15] and emulsions,[16−20] all of which resulted in well-defined polymers and latexes.

### Scheme 1. Low Parts per Million Catalyst ATRP Mechanisms



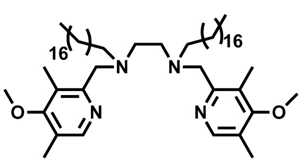


**Figure 1.** Structure of DOD-BPED*.

### Table 1. ARGET ATRP of BMA with TPMA and DOD-BPED*

| entry[a] | *t* (h) | conv.[b] | $M_{n,th}$ | $M_{n,GPC}$ | $M_w/M_n$ |
|---|---|---|---|---|---|
| TPMA | 8 | 0.35 | 9800 | 11000 | 1.12 |
| DOD-BPED* | 7.5 | 0.27 | 7700 | 7600 | 1.38 |
| BPMODA | 7 | 0.30 | 8600 | 10500 | 1.42 |

[a]All polymerizations were conducted with [BMA]:[EBPA]:[$CuBr_2$]:[Ligand]:[$Sn^{II}(EH)_2$] = 200:1:0.01:0.03:0.1, 20% (v/v) anisole, $T$ = 60 °C. [b]Determined by $^1$H NMR.

Control in ATRP relies on the dynamic equilibrium between propagating ($P_n^\bullet$) and dormant species ($P_n$−X, X = Cl or Br). Through reversible activation of the alkyl halide by the lower oxidation state catalyst complexes ($Cu^IX$/L, L = Ligand) the macroradical species, $P_n^\bullet$, is formed and then deactivated by the high oxidation state catalyst complex ($Cu^{II}X_2$/L). The ratio of activation ($k_a$) and deactivation ($k_{da}$) rate constants is defined as the equilibrium constant of ATRP, $K_{ATRP}$, and determines the number of radicals present in the polymerization. As the equilibrium of ATRP favors the deactivated state, the number

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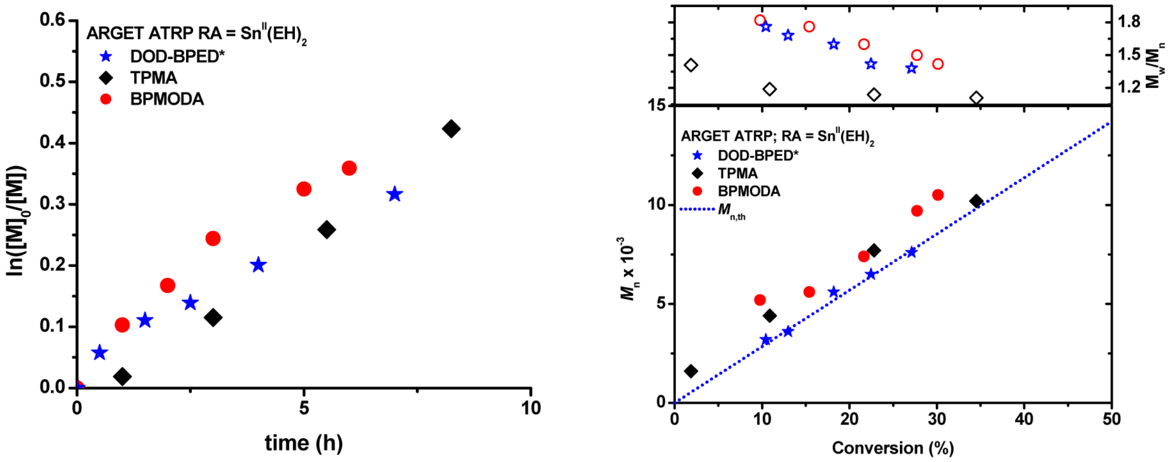

**Figure 2.** First-order kinetic plots (left) and evolution of $M_n$ and $M_w/M_n$ with monomer conversion (right) for the ARGET ATRP of BMA with DOD-BPED*, TPMA, or BPMODA. All polymerizations were conducted with [BMA]:[EBPA]:[$CuBr_2$]:[Ligand]:[Sn$^{II}$(EH)$_2$] = 200:1:0.01:0.03:0.1, 20% (v/v) anisole, $T$ = 60 °C.

**Table 2. ARGET ATRP of BMA in Miniemulsion with DOD-BPED*$^a$**

| entry | BMA | EBPA | $CuBr_2$ (ppm) | ligand | AA | conv$^b$ | $M_{n,th}$ | $M_{n,GPC}$ | $M_w/M_n$ |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 2000 | 1 | 0.5 (250) | 0.5 | 0.25 | 0.54 | 152 800 | 173 700 | 1.23 |
| 2 | 2000 | 1 | 0.2 (100) | 0.2 | 0.1 | 0.44 | 124 700 | 124 900 | 1.24 |
| 3 | 2000 | 1 | 0.1 (50) | 0.1 | 0.05 | 0.28 | 80 600 | 78 200 | 1.33 |
| 4 | 5000 | 1 | 0.5 (50) | 0.5 | 0.25 | 0.37 | 261 300 | 248 900 | 1.33 |
| 5 | 10000 | 1 | 1 (50) | 1 | 0.5 | 0.37 | 527 700 | 755 500 | 1.39 |

$^a$[Brij 98]/[hexadecane] = 2.3/3.6 wt % vs BMA, $T$ = 80 °C. $^b$Determined by gravimetry.

of active radials ($P_n^\bullet$) available for propagation ($k_p$) and termination ($k_t$) is well controlled.

Several advances have been made to homogeneous ATRP, which allow for the use of parts per million levels of catalyst, affording more environmentally friendly and industrially viable systems.[21,22] The addition of a reducing agent, such as tin(II) 2-ethylhexanoate, glucose, ascorbic acid, or hydrazine in activators regenerated by electron transfer (ARGET) ATRP,[23,24] application of a potential as in electrochemically mediated ATRP (*e*ATRP),[25] light in the photochemical process,[26] addition of copper wire as in supplemental activators and reducing agent (SARA) ATRP,[27] or addition of thermal initiators as in initiators for continuous activator regeneration (ICAR) ATRP[23] are all proven methods. In each case, the activator, Cu$^I$X/L, is resorted through the reduction of accumulated Cu$^{II}X_2$/L species during irreversible termination (Scheme 1).

The key to successful ARGET ATRP in aqueous dispersed media systems lies with the ligand as it must be both hydrophobic and highly active. Hydrophobicity prevents the catalyst from diffusing to the aqueous phase,[11] while high activity, or $K_{ATRP}$ value, affords well-controlled polymerizations at low catalyst concentrations. The most commonly employed ligand in emulsion-based ATRP is *N*,*N*′-bis(2-pyridylmethyl)-octadecylamine (BPMODA).[28] Due to a relatively low $K_{ATRP}$ value, this ligand is successful under normal ATRP conditions in dispersed media; however, it is unable to perform well at low catalyst concentrations as in ARGET ATRP. Conversely, ligands with high $K_{ATRP}$ values such as tris[2-(dimethylamino)-ethyl]amine ($Me_6$TREN)[29] and tris(2-pyridylmethyl)amine (TPMA),[5] which perform well in low catalyst homogeneous ARGET ATRP,[21−24] show much higher affinity toward water than the oil phase. Therefore, these ligands are not useful in aqueous dispersed media.

A new ligand for ARGET ATRP in miniemulsion, *N*,*N*′-bis[2-(4-methoxy-3,5-dimethyl)pyridylmethyl]octadecylamine (BPMODA*), was recently reported[30] which resulted in well-controlled heterogeneous polymerizations conducted with as low as 250 ppm of $CuBr_2$/BPMODA* catalyst. The success of this catalyst was attributed to increased ligand activity from the addition of six electron-donating groups to the tridentate BPMODA-based structure. It is the goal of this paper to expand the previously reported work through the design and synthesis of a new tetradentate ligand for ARGET ATRP in miniemulsion systems, *N*′,*N*″-dioctadecyl-*N*′,*N*″-bis[2-(4-methoxy-3,5-dimethyl)pyridylmethyl]ethane-1,2-diamine (DOD-BPED*), whose structure is given in Figure 1.

When considering the design of the new ligand, hydrophobicity and $K_{ATRP}$ value were increased through the number of aliphatic chains present as well as the denticity of the ligand. The structure of DOD-BPED*, whose detailed synthetic procedure may be found in the Supporting Information, was based on *N*,*N*′-dimethyl-*N*,*N*′-bis(2-pyridylmethyl)ethane-1,2-diamine (BPED), a tetradentate ligand known to have a $K_{ATRP}$ value similar to that of TPMA.[31] Two octadecyl chains were incorporated into the BPED-based structure affording increased hydrophobicity over BPMODA* which contains only one aliphatic chain. In addition to being tetradentate, as compared to the less active tridentate structure of BPMODA*, six electron-donating groups were also included on two pyridine rings to further increase activity.[31−33]

It has been reported that half-wave potentials ($E_{1/2}$ values) measured by cyclic voltammetry (CV) are correlated to $K_{ATRP}$, thereby providing insight into the activity of a catalyst complex.[31,34,35] DOD-BPED*, when complexed with $CuBr_2$,

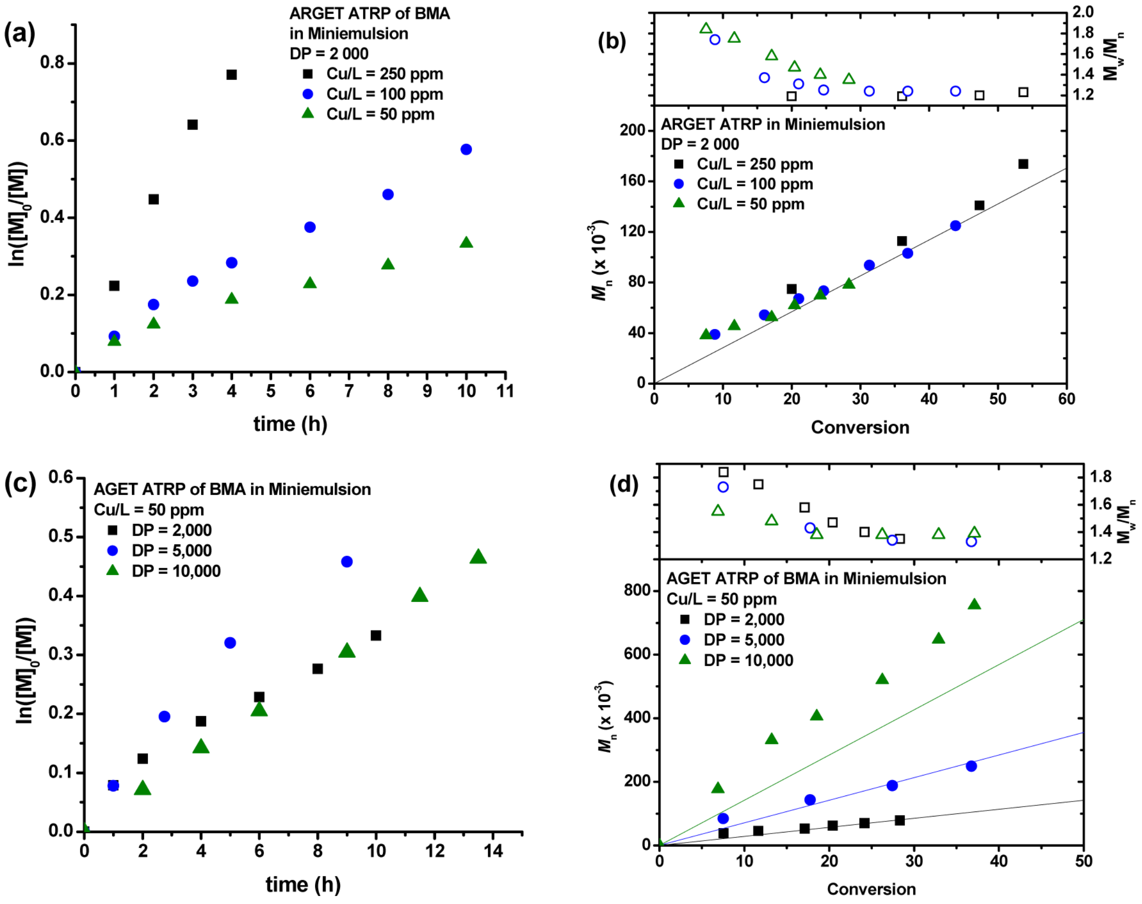

**Figure 3.** First-order kinetic plots (a,c) and evolution of $M_n$ and $M_w/M_n$ with monomer conversion (b,d) for the ARGET ATRP of BMA DOD-BPED* under miniemulsion conditions. All polymerizations were conducted with [Brij 98]/[hexadecane] = 2.3/3.6 wt % vs BMA, $T$ = 80 °C. Specific reaction conditions are in Table 2.

is insoluble in aceteonitrile preventing the measurement of the $E_{1/2}$ and $K_{\mathrm{ATRP}}$ values by CV. Utilizing a solvent other than acetonitrile for CV will provide a trend in $E_{1/2}$ value changes with ligand structure. For example, the $E_{1/2}$ value of BPMODA* is more negative, indicating a more active ligand than BPMODA due to the presence of electron-dontating groups on BPMODA*. When measured in DMF, a similar trend for the BPMDOA to BPMODA* structure change was observed: −0.07 and −0.14 V (vs SCE), respectively. Comparison of the cyclic voltammograms of *N′*,*N″*-dioctadecyl-*N′*,*N″*-bis(2-pyridylmethyl)ethane-1,2-diamine (DOD-BPED) ($E_{1/2}$ = −0.13 V vs SCE) with that of DOD-BPED* ($E_{1/2}$ = −0.17 V vs SCE) resulted in more negative $E_{1/2}$ values for DOD-BPED* due to the electron-donating groups within the structure. This shift toward a more negative $E_{1/2}$ value indicates a higher $K_{\mathrm{ATRP}}$ value for DOD-BPED* than for DOD-BPED.

$CuBr_2$/DOD-BPED* was first tested as a catalyst under homogeneous ARGET ATRP conditions and compared with $CuBr_2$/TPMA and $CuBr_2$/BPMODA. Butyl methacrylate (BMA) was polymerized at a targeted DP = 200 with 50 ppm of $CuBr_2$/L catalyst and $Sn^{II}(EH)_2$ as the reducing agent (RA). Specific reaction conditions and results are summarized in Table 1 and Figure 2. Linear first-order kinetics as well as similar rates of polymerization ($R_p$) were observed for all ligands. While all polymerizations demonstrated good correlation between experimental ($M_{n,\mathrm{exp}}$) and theoretical ($M_{n,\mathrm{th}}$) molecular weights, the final $M_w/M_n$ values of 1.12, 1.38, and 1.42 for TPMA, DOD-BPED*, and BPMODA, respectively, signify that the polymerization with BPMODA was the least controlled. ARGET ATRPs conducted with $CuBr_2$/TPMA are established and known to offer a high degree of control at catalyst concentrations as low as 10 ppm, and such was the case in this work. While the polymerization with DOD-BPED* resulted in a larger $M_w/M_n$ value as compared to TPMA, the linear first-order kinetics and good correlation of $M_{n,\mathrm{exp}}$ and $M_{n,\mathrm{th}}$ values confirm successful heterogeneous polymerizations with low catalyst concentrations.

Polymerizations under heterogeneous miniemulsion conditions were conducted with $CuBr_2$/DOD-BPED* catalyst whose concentration was systematically decreased from 250 to 50 ppm at a targeted DP = 2000 as detailed in Table 2 (entries 1−3) and Figure 3a,b. Although lower catalyst concentrations resulted in a decreased rate of polymerization ($R_p$), linear first-order kinetics was observed for each polymerization. All polymerizations demonstrated linear growth of molecular weight with monomer conversion in addition to good correlation between $M_{n,\mathrm{exp}}$ and $M_{n,\mathrm{th}}$ values. When 250 or 100 ppm (entries 1 and 2) of $CuBr_2$/DOD-BPED* catalyst was employed, $M_w/M_n$ values were low (ca. 1.23 and 1.24, respectively). Only a slight increase of the final $M_w/M_n$ value (ca. 1.33) was observed when a mere 50 ppm (entry 3) of catalyst was utilized.

Maintaining the catalyst concentration at 50 ppm, the targeted degrees of polymerizations were systematically increased from DP = 2000 to DP = 10 000 while keeping monomer conversion below 50% to avoid any particle aggregation. Table 2 (entries 3−5) and Figure 3c,d summarize these results. All polymerizations demonstrated linear first-order kinetics as well as linear growth of molecular weight with monomer conversion. $M_w/M_n$ values decreased with monomer conversion reaching final $M_w/M_n$ values = 1.35, 1.33, and 1.39 for DP = 2000, 5000, and 10 000, respectively. The synthesis of high MW polymers with low $M_w/M_n$ values may be attributed to the more active ligand, DOD-BPED*, which allows for low catalyst concentrations during the polymerization, thereby reducing the $Cu^IX/L$-induced catalytic radical termination effect.[36] However, this may also be due to compartmentalization where radical−radical termination is limited due to the separation of radicals in the miniemulsion system.[37] The generation of a polymer with $M_{n,exp}$ > 700 000 and narrow MWD values while utilizing only 50 ppm of catalyst (Table 2, entry 5) is an extraordinary advancement of ATRP in aqueous dispersed media.

In summary, careful ligand design is an important tool for the improvement and expansion of ATRP success. A series of polymerizations were presented in this work which clearly illustrate the utility of DOD-BPED* for ATRP in miniemulsion. Well-controlled polymerizations were achieved with as low as 50 ppm of catalyst. Moreover, while maintaining this level of catalyst concentration, it was shown that DOD-BPED* can successfully polymerize BMA at a targeted DP = 10 000. Most significantly, very high molecular weight polymers of $M_{n,exp}$ > 700 000 with low $M_w/M_n$ values were achieved using only 50 ppm of $CuBr_2$/DOD-BPED* catalyst.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

Experimental section. 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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