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Cite this: DOI: 10.1039/c0xx00000x

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ARTICLE TYPE

# Radical Coupling Polymerization (RCP) for Synthesis of Various Polymers

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Received (in XXX, XXX) Xth XXXXXXXXXX 20XX, Accepted Xth XXXXXXXXXX 20XX

DOI: 10.1039/b000000x

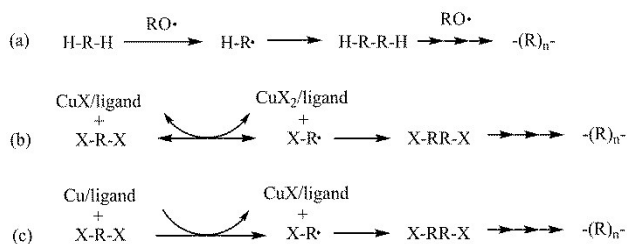
We report a general polymerization method involving direct radical coupling reaction of in-situ formed benzyl-type biradicals from dibromide in the presence of Cu(0)/ligand. The radical coupling polymerization can be employed to synthesize polyarene, polyester, polyether and polysulfone under mild condition and within a short time.

## Introduction

Radical is an active species employed in many kinds of organic reactions. It undergoes addition reaction to unsaturated bonds, self-reactions of disproportionation and coupling, and transfer reaction with the organic compound with abstractable hydrogen atom. Although radical addition reaction to carbon-carbon double bond is widely applied in chain polymerization of vinyl monomer,<sup>1</sup> the coupling reaction of radical, another extremely rapid reaction of radical, is scarcely used in polymerization. The main reason is that radical simultaneously undergoes redox, disproportionation and transfer reactions, which terminate the chain growth via radical coupling, and make it impossible to produce polymers with high molecular weight.

$$\frac{R_c}{R} = \frac{k_c[R_1\bullet]^2}{k_c[R_1\bullet]^2 + k_d[R_1\bullet]^2 + k_{tr}[R_1\bullet][R_2H] + k_x[R_1\bullet][X]} = \frac{k_c}{k_c + k_d + k_{tr}[R_2H]/[R_1\bullet] + k_x[X]/[R_1\bullet]} \quad (1)$$

If main reactions, such as coupling ( $k_c$ ), disproportionation ( $k_d$ ), chain transfer ( $k_{tr}$ ) and other reactions ( $k_x$ , such as redox, cyclization) of the radical, are considered, the ratio of coupling rate ( $R_c$ ) to the overall rate of radical reactions ( $R$ ) is given in **Equation 1**, where  $R_2H$  is the transfer agent,  $X$  is the nonspecific agent related to other reactions. The formation of carbon-carbon bond via radical coupling reaction depends on the value of  $R_c/R$ . According to **Equation 1**, high concentration of radical and large ratios of  $k_c$  to other kinetic parameters  $k_d$ ,  $k_{tr}$  and  $k_x$ , leads to the larger value of  $R_c/R$ , which is crucial for radical coupling reaction.



**Scheme 1.** Typical methods for generation of radical for its coupling polymerization.

Construction of the polymer chain by radical coupling reaction needs a continuous generation of radical. Earlier attempt is formation of radical by hydrogen atom transfer to alkoxy radical as route a shown in **Scheme 1**. In-situ formed radicals undergo coupling reaction to produce polymer.<sup>2</sup> Saturated hydrocarbons, such as diphenyl methane, esters, amine, and organometal compounds can be converted to polymer by this method.<sup>3-6</sup> No precise characterization of obtained polymer have been provided. Metal-catalyzed redox of organic halide,<sup>7, 8</sup> especially atom transfer method,<sup>9-15</sup> in which radical is generated by single electron transfer (SET) to organic halide and the decomposition of the alkyl halide, provides an efficient pathway to generate carbon radical under mild condition. The low active metals used in atom transfer redox reaction prevent further reduction of radical to anion, which make it a promising way for generation of radical.

Radical coupling reaction promoted by transition-metal complex, which is termed as atom transfer radical coupling (ATRC) (route b shown in **Scheme 1**) was widely applied to prepare block polymer by using mono- or dihalogenated polymer as precursor. Coupling efficiency of ATRC normally does not exceed 95%.<sup>16-18</sup> Only a few papers reported synthesis of polymer from small organic molecules by ATRC. Direct radical coupling of  $\alpha, \alpha'$ -dibromo *p*-xylene<sup>19</sup> and propane-1,3-diyl bis(2-chloro-2-phenylacetate) (PDBCP)<sup>20</sup> under ATRC condition were reported. ATRC of monomer sequence unit generated periodic vinyl polymer with high molecular weight and broad polydispersity.<sup>21</sup> The limitation of ATRC is that polymerization time is very long, e.g. more than 24 hours, due to the low concentration of the radical derived from the equilibrium between  $RX + Cu(I)X$  and  $R\bullet + Cu(II)X_2$ .

Carbon-carbon bond formation by reductive coupling of alkyl halide catalyzed by various metals or its salts has extensively investigated for decades. The mechanism of carbon-carbon formation is correlated with the kind of metal employed. For example, the Wurtz reaction<sup>22</sup> consists of a halogen-metal exchange involving the radical species and then the carbon-carbon bond formation in a nucleophilic substitution reaction between alkyl anion and alkyl halide. Although radical is proved to be intermediate species, the formation of carbon-carbon bond

is not via direct radical coupling reaction. Low molecular weight copolymers have been prepared by coupling of  $\alpha$ ,  $\alpha'$ -dibromo-*m*- and -*p*-xylene catalyzed by chromous chloride for several days and evidence was given for the occurrence of free radicals in the decomposition of the intermediate organochromium complex.<sup>23</sup>

Synthesis of the polymer with high molecular weight by direct radical coupling polymerization (RCP) from small organic molecules is still not carefully studied. In principle, nearly 100% coupling efficiency and high concentration of the radical are prerequisite based on kinetic consideration. In this paper, we report RCP of benzyl-type biradicals in-situ generated by redox reaction between dibromo compound and Cu(0)/ligand (route c in **Scheme 1**) as a potential route for the synthesis of some new kinds of polymers under mild condition and within a short time.

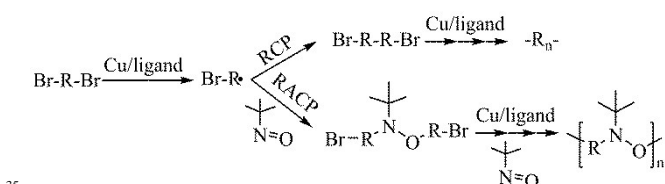
## Experimental Section

All dibromides were synthesized by bromination of corresponding substrates with N-bromosuccinimide and characterized by <sup>1</sup>H-NMR and elementary analysis.

Typical polymerization procedure. 29.2 mg of BBEB (0.1 mmol), 58.0 mg of TPMA (0.2 mmol) and 14.1 mg of copper powder (0.22 mmol) were added to an ampule equipped with a stir bar. The ampule was degassed, backfilled four times with N<sub>2</sub>. 1 mL of deoxygenated THF was then added. The ampule was heated at 60 °C for 2 hours. The ampule was immersed in liquid nitrogen and the mixture was diluted with THF and purified by passing through a neutral alumina column. The solution was concentrated, precipitated with methanol and dried under vacuum at 40 °C to yield polymer. The yield was determined gravimetrically and the conversion was calculated by  $W_{\text{polymer}}/(W_{\text{monomer}} \times \text{weigh fraction of carbon and hydrogen of monomer})$ .

Experimental details can be found in the supporting information.

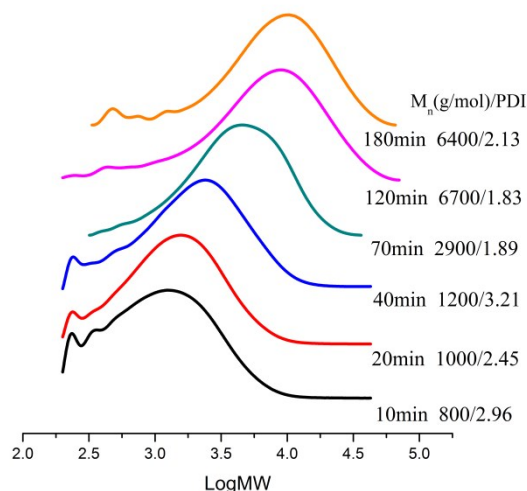
## Results and Discussion



**Scheme 2.** Mechanisms of radical coupling polymerization (RCP, top) and radical addition coupling polymerization (RACP, bottom).

Benzyl-type radicals are stable intermediate radical involved in many organic reactions. The self-reactions of benzyl,  $\alpha$ -methylbenzyl and cumyl radicals give predominant coupling products.<sup>24</sup> In radical polymerization of styrene, more than 80% of the chain termination is radical coupling reaction.<sup>1</sup> We consider benzyl-type radicals as a class of suitable candidates for RCP. Two dibromides, such as 1,4-bis(bromomethyl)benzene (BBMB) and 1,4-bis(1-bromoethyl)benzene (BBEB) were prepared and used for polymerization. The polymerization of two dibromides was conducted in the presence of Cu(0)/tris[(2-pyridyl)methyl]amine (TPMA) in THF. No soluble polymer was obtained for BBMB while soluble polymer was obtained for BBEB.

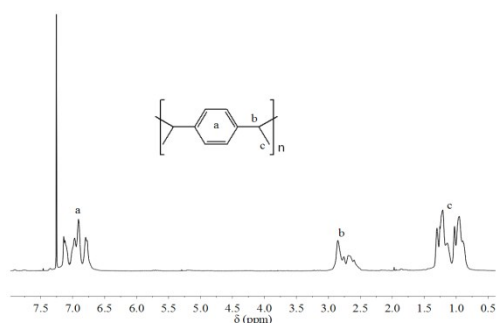
To confirm the radical mechanism, both BBMB and BBEB were polymerized with the equivalent amount of spin-trapping agent, 2-methyl-2-nitroso propane (MNP) in the presence of Cu(0)/TPMA in THF. Polymers with high molecular weight and alternative unit sequence (BBMB/BBEM-MNP)<sub>n</sub> were obtained from both dibromides, which follow the radical addition coupling polymerization (RACP, shown in **Scheme 2**) mechanism previously reported by us.<sup>25</sup> (Figure S23, S24) This reveals the success of in-situ generation of radicals via SET redox reaction promoted by Cu(0)/TPMA for both dibromides. ATRC of BBMB catalyzed by Cu(I)Br/PMDETA was reported without full characterization due to insolubility of the poly(*p*-xylene) (PPX).<sup>19</sup> Although BBMB can undergo RACP, no soluble product was obtained in RCP. After careful removal of the copper complex from the product obtained from BBMB, bright yellow solid was obtained. The IR spectrum (Figure S25) of the solid is nearly the same as reported PPX.<sup>26</sup> Elementary analysis shows it contains 81.02 % of carbon and 7.10% of hydrogen, which indicates molar ratio of C/H is 0.95, close to theoretical value 1.0. The left 12% is probably bromine derived from the end group of oligomer.



**Fig. 1** Variation of GPC curves of polymers produced by RCP of BBEB with time.

The variation of molecular weight of the polymer was monitored by GPC at different polymerization times. The polymerization was conducted under [BBEB]/[TPMA]/[Cu(0)]=1/2/2.2, [BBEB]=0.1 M, at 60 °C in THF. As shown in **Fig. 1**, a clear shift of the GPC curve towards high molecular weight was observed. The polydispersity index varied between 1.8 to 3.2. The evolution of molecular weight distribution clearly demonstrates that the polymerization follows the step-growth mechanism. The polymer could be obtained within 2 hours, which is much faster than normal ATRC.<sup>19-21</sup>

The <sup>1</sup>H-NMR spectrum of polymer obtained at 2 hours is shown in **Figure 2**. No -CH<sub>2</sub>Br was found in the spectrum suggested that full conversion of the functional group. Three groups of the peaks at 0.75-1.3 ppm, 2.48-3.0 ppm and 6.7-7.2 ppm corresponded to the methyl, methine and benzenic protons of polymer respectively.



**Fig. 2**  $^1\text{H-NMR}$  spectrum of product of polymerization of BBEB in  $\text{CDCl}_3$ .

**Table 1.** Radical coupling polymerization of 1,4-bis(1-bromoethyl) benzene (BBEB) promoted by Cu/ligand.<sup>a</sup>

| Run | [BBEB] (M) | Temp (°C) | [Cu]/[BBEB] | Ligand                   | $M_n^b$ (g/mol) | PDI <sup>b</sup> |
|-----|------------|-----------|-------------|--------------------------|-----------------|------------------|
| 1   | 0.1        | 30        | 2.2         | TPMA                     | 500             | 1.57             |
| 2   | 0.1        | 40        | 2.2         | TPMA                     | 1000            | 2.28             |
| 3   | 0.1        | 50        | 2.2         | TPMA                     | 1900            | 2.64             |
| 4   | 0.1        | 60        | 2.2         | TPMA                     | 6700            | 1.83             |
| 5   | 0.1        | 60        | 2.2         | PMDETA                   | 3700            | 1.70             |
| 6   | 0.1        | 60        | 2.2         | $\text{Me}_6\text{TREN}$ | 4300            | 1.96             |
| 7   | 0.05       | 60        | 2.2         | TPMA                     | 4100            | 1.74             |
| 8   | 0.3        | 60        | 2.2         | TPMA                     | 4500            | 1.89             |
| 9   | 0.5        | 60        | 2.2         | TPMA                     | 3200            | 2.12             |
| 10  | 0.1        | 60        | 4.4         | TPMA                     | 6300            | 1.87             |
| 11  | 0.1        | 60        | 11          | TPMA                     | 6300            | 2.13             |

<sup>a</sup> General condition: [BBEB]:[ligand]=1:2, THF=1mL, 2 hours. <sup>b</sup>

Number-averaged molecular weight ( $M_n$  in g/mol) and polydispersity index (PDI) were measured by gel permeation chromatograph (GPC) with polystyrene as standard.

The influence of temperature, concentration of monomer, type of ligand and amount of Cu(0) were studied and the results were summarized in **Table 1**. As runs 1-4 given in Table 1, when the temperature varied from 30 °C to 60 °C, the  $M_n$  of the polymer greatly increased. Among three ligands, the  $M_n$  of polymer decreased in the order TPMA> $\text{Me}_6\text{TREN}$ >PMDETA as shown by run 4-6. As the concentration of monomer increased from 0.05M to 0.5M (runs 4, 7-9), the highest  $M_n$  was obtained when the concentration was 0.1 M, lower or higher concentration led to slight decrement of  $M_n$ . The amount of Cu used was also varied (runs 4, 10-11) and it was found that excess Cu powder has slight influence on the  $M_n$  of the polymer.

As shown in **Scheme 2**, the mechanism of RCP is not complicated. Radical is in-situ generated by SET redox reaction of alkyl dibromide and Cu(0)/ligand in the polar solvent, which subsequently undergoes coupling reaction continuously. As manifested in polymerization kinetics, RCP follows step-growth polymerization mechanism. The average molecular weight of the polymer prepared by step-growth polymerization depends on the extent of reaction. The extent of reaction in RCP is determined by two factors. One is the conversion of bromide to radical, and the other is the non-coupling reactions of radical leading to chain termination.

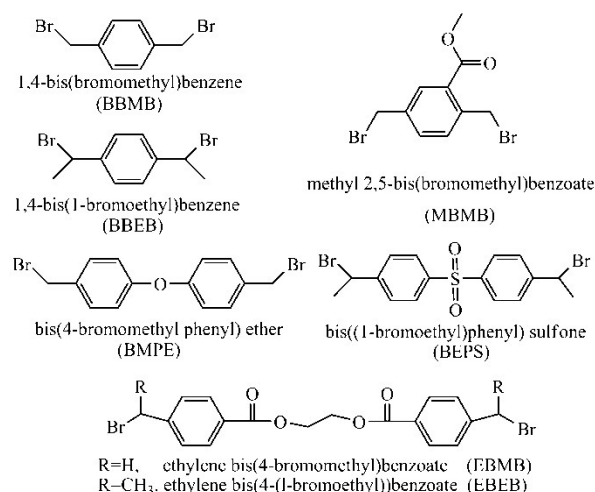
The SET is a very efficient pathway to produce radical from organic halide. Successful RACP of two dibromides in the presence of MNP gave polymers with high molecular weight. This demonstrates both dibromides are efficiently reduced to corresponding radicals by Cu(0)/Ligand. In reduction reaction of alkyl halide by metal or its salt, the in-situ generated intermediate

radical can be further reduced to anion if the metal is very active, which is proved in the Wurtz reaction.<sup>22</sup> Due to the reactivity of anion, the side reactions are so common that affects the coupling efficiency. Even for other Wurtz-type reactions catalyzed by less active metals, the yields of carbon-carbon bond are far from 100%. In the ATRA, ATRP and ATRC reaction, the redox equilibrium between  $\text{RX}+\text{Cu(I)X}$  and  $\text{R}\cdot+\text{Cu(II)X}_2$  results in the low concentration of radical, which greatly reduces the rate of the coupling reaction. This results in long reaction time (more than 24 hours) and low conversion of the monomer (~30%) for RCP under ATRC condition.<sup>19-21</sup>

For various benzyl-type small radicals, the values of  $k_d/k_c$  are typically in the range 0.05-0.16.<sup>24</sup> The trend of the temperature dependencies of  $k_d/k_c$  for the small organic radicals is uniformly to decreasing  $k_d/k_c$  ratios with increasing temperature.<sup>24</sup> Therefore, high temperature favours radical coupling reaction.

Values of  $k_{tr}$  and  $k_x$  are much smaller than  $k_c$ . The concentration of radical species in conventional radical addition polymerization is about  $10^{-6}$ - $10^{-8}$  M, and it was much lower in ATRP.<sup>14</sup> Low concentration of radical reduces the chain termination rate through radical self-reaction in radical addition polymerization,<sup>1</sup> and the radical coupling rate as well. In contrast, the relatively high concentration of the radical is required for RCP. In order to achieve high concentration, the monomer concentration (0.05 - 0.5 M) used in RCP was in the same range as in RACP<sup>25</sup> and was much higher than that in ATRC of bromo-polystyrene.<sup>19</sup> SET redox of alkyl halides is a fast way to generate high concentration of radical under mild condition. According to **Equation 1**, the high concentration of radical leads to the larger value of  $R_c/R$ , and results in high extent of reaction required for high average molecular weight, which is the difference between RCP in this work and reported ATRC.

The activation ability of the three ligands in ATRP decreases in the order  $\text{Me}_6\text{TREN}$ >TPMA>PMDETA,<sup>27</sup> while the best polymerization result was obtained by using TPMA as ligand. This is due to the quaternization reaction between alkyl bromide/monomer and ligand. Both PMDETA and  $\text{Me}_6\text{TREN}$  reacts with BBEB slowly and produces white solid in THF at room temperature within 4 hours, while no reaction occurs between TPMA and BBEB overnight.



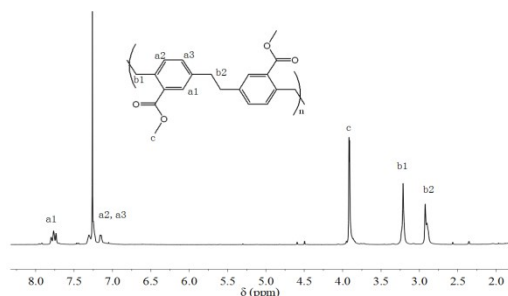
**Scheme 3.** Various dibromides as monomers used in radical coupling polymerization.

**Table 2.** Radical coupling polymerization of various monomers<sup>a</sup>

| run | Monomer           | M <sub>n</sub> <sup>b</sup> (g/mol) | PDI <sup>b</sup> | Conversion (%) |
|-----|-------------------|-------------------------------------|------------------|----------------|
| 1   | BBMB <sup>c</sup> | -                                   | -                | 83             |
| 2   | BBEB <sup>d</sup> | 6700                                | 1.83             | 93             |
| 3   | MBMB              | 4700                                | 1.90             | 91             |
| 4   | BMPE              | 5400                                | 2.15             | 79             |
| 5   | BEPS <sup>e</sup> | 4700                                | 1.74             | 58             |
| 6   | EBEB              | 13100                               | 9.57             | 89             |
| 7   | EBMB              | 4500                                | 2.76             | 71             |

<sup>a</sup> General conditions: [monomer]:[TPMA]:[Cu]=1:2:2.2, [monomer]=0.1 M, 4 hours, 60 °C, in THF. <sup>b</sup> Number-averaged molecular weight (M<sub>n</sub>) and the polydispersity index (PDI) was measured by gel permeation chromatograph (GPC). <sup>c</sup> Insoluble product was obtained. <sup>d</sup> Reaction time was 2 h. <sup>e</sup> [monomer]=0.025 M.

More dibromides were designed and synthesized by routine methods, which are shown in **Scheme 3**. The polymerization results were summarized in **Table 2**. GPC data and <sup>1</sup>H-NMR spectra all confirm the chain structure of the product generated by radical coupling mechanism (see SI). Normally, polyether and polysulfone are synthesized under harsh condition and polyester with long time. RCP can be applied to synthesize polyarene, polyester, polyether and polysulfone under mild condition within a short time. Soluble polymers produced by BBEB and MBMB are modified PPXs with substitution of aliphatic and aromatic carbons respectively. RCP provides a novel pathway of synthesis of soluble modified PPX.

**Fig. 3** <sup>1</sup>H-NMR spectrum of product of polymerization of MBMB in CDCl<sub>3</sub>.

The <sup>1</sup>H-NMR spectrum of polymer prepared by MBMB, which is an asymmetrical monomer, is shown in **Fig. 3**. Only two types of methylene protons are identified in the polymer, which suggests the monomer coupled in head-head and tail-tail mode. This also demonstrates the RCP is a suitable method to synthesize the periodic polymer as other step-growth polymerization methods.

Compared with ATRC and reductive coupling, the current polymerization is termed as radical coupling polymerization, which represents the repeating reaction involved. The generation of radical involves irreversible "atom transfer" from halide to metal corresponding to reduction of alkyl halide to alkyl radical. In ATRA<sup>7</sup> and ATRP,<sup>10</sup> the halogen atom is reversibly transferred between organic halide and metal complex.

## Conclusions

We report radical coupling polymerization of various dibromides promoted by Cu(0)/ligand. High radical concentration in the polymerization media is obtained via reduction of benzyl bromide

by Cu(0)/ligand which favors radical coupling reaction kinetically. This method provides a fast and efficient approach to the synthesis of the polymer via direct radical coupling polymerization under the mild condition and within a short time. The monomer can be well designed, which leads to some novel polymers that cannot be prepared by current polymerization methods.

## Acknowledgments

Financial support from National Natural Science Foundation of China (21174123) is appreciated.

## Notes and references

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<sup>†</sup> Electronic Supplementary Information (ESI) available: GPC and the <sup>1</sup>H NMR spectra of obtained polymers. See DOI: 10.1039/b000000x/

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## GRAPHICAL ABSTRACT

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