

# Synthesis of ‘living’ poly(2-dimethylaminoethyl methacrylate) and stimuli responsive/multifunctional block copolymers effective in fabrication of CdS ‘smart’ ‘Q-Particles’



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## HIGHLIGHTS

- Synthesis of ‘Living’ poly(2-dimethylaminoethyl methacrylate) by bulk ATRP using CuCl/PMDETA catalyst at ambient temperature.
- Polymerization occurs through soluble ATRP catalyst entrapped within reverse micelles of Aliquat<sup>®</sup>336.
- An adventitious role of water molecules during polymerization is noted.
- Stimuli responsive, multifunctional di and triblock copolymers are synthesized from living PDMAEMA macroinitiators.
- Fabrication of ‘Smart’ diblock copolymer/CdS ‘Q-particle’ hybrid materials is demonstrated.

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## ABSTRACT

Living poly[(2-dimethylamino)ethyl methacrylate] (PDMAEMA) has been synthesized by Atom Transfer Radical Polymerization (ATRP) of (2-dimethylamino)ethyl methacrylate in bulk at 30 °C using CuCl/*N,N,N',N',N''*-pentamethyldiethylenetriamine catalyst. Addition of catalytic amount of tricapyrylmethylammonium chloride (AQCl) keeps the deactivator cupric complex soluble throughout the polymerization resulting in controlled polymerization. The solubility of the charged copper complexes in bulk monomer is proposed through their entrapment within the ionic core of the reverse micelle like aggregates formed by AQCl, as observed from Cryo-TEM and dynamic light scattering analysis. An adventitious role of water molecules in respect of control over polymerization is noted when moist monomer or AQCl is used. Synthesized PDMAEMA molecules work efficiently as macroinitiators for the synthesis of different stimuli responsive, multifunctional di- or triblock copolymers through sequential polymerization. The diblock copolymer PDMAEMA-*b*-poly[di(ethyleneglycol) methyl ether methacrylate] stabilizes CdS quantum dots in aqueous medium which show stimuli dependent reversible switch between micelle ‘core-confined’ and ‘corona-embedded’ morphologies.

## 1. Introduction

Synthesis of functional polymeric materials with precise control over molecular weight, dispersity ( $\bar{M}_w/\bar{M}_n$ ) and architecture has been one of the major goals in the field of polymer synthesis since last two decades [1,2]. Advent of controlled radical polymerization has opened up avenues for polymer synthesis under less stringent conditions compared to cationic or anionic polymerization techniques. Ever since its discovery in mid 1990s [3,4], atom transfer radical polymerization (ATRP) has

been the most widely accepted method for carrying out reversible-deactivation radical polymerization (RDRP). In a typical mechanism of ATRP (Scheme 1), an alkyl halide initiator reacts with a metal complex in lower oxidation state to generate free radical which subsequently propagates and gets reversibly deactivated by the metal complex of higher oxidation state showing persistent radical effect. Copper based complexes have received maximum attention as ATRP catalysts [5,6] however, their contamination in the product polymer seriously limits the wide spread application of ATRP. Intensive research efforts to

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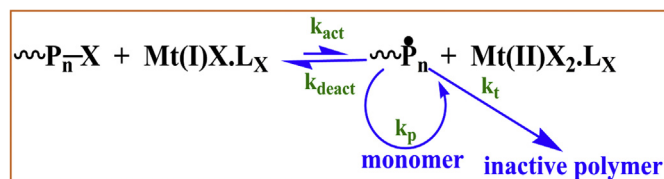
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**Scheme 1.** General Scheme for Atom Transfer Radical Polymerization (ATRP).

overcome this have resulted in the development of techniques like Activator Generated by Electron Transfer (AGET) [7], Activator Regenerated by Electron Transfer (ARGET) [8,9], Supplemental Activation Reducing Agent (SARA) [10], Initiators for Continuous Activator Regeneration (ICAR) [11], etc. which require the use of ppm level of copper complexes during polymerization. These techniques work quite successfully with relatively less polar styrenes or (meth)acrylate monomers [12]. However, with more polar, water soluble monomers having pendant reactive functional groups like DMAEMA, (2-diethylamino)ethyl methacrylate (DEAEMA), 2-hydroxyethyl methacrylate (HEMA), Di(ethyleneglycol) methyl ether methacrylate (DEG), poly(ethyleneglycol) methyl ether methacrylate (PEGMA) etc., lowering in concentration of copper complexes often fails to produce polymers with desired level of yield and control [6,12]. This is attributed to the catalyst deactivation due to monomer coordination. Therefore use of strongly coordinating and costly ligand systems like 1,1,4,7,10,10-Hexamethyltriethylenetetramine (HMTETA) [13], tris[(2-pyridyl)methyl]amine (TPMA) [12,14], tris[(2-dimethylamino)ethyl]amine ( $\text{Me}_6\text{TREN}$ ) [15,16] or polymerization in protic/aqueous based medium [17–20] have been typically reported in this purpose. Nevertheless, polymerization in aqueous based medium suffers from unique problems due to hydrolysis of the catalyst complexes [21] leading to inferior control over the polymerization.

Functional polymers produced from the above monomers are very useful in biomedical applications. In particular PDMAEMA has received significant attention owing to its aqueous solubility and dual responsive (pH & temperature) character [22]. PDMAEMA based polymer systems find significant applications in bioseparation [22], drug delivery [23–25], as antimicrobial or antibacterial agents [26–30] and gene delivery area [31–35] due to lower cytotoxicity with improved gene transfection efficiency compared even to typically used poly(ethyleneimine) (PEI) [36,37]. Therefore, exploration of cost effective methods for ATRP of DMAEMA under modest conditions is very much desirable. Matyjaszewski and co workers were first to report the successful ATRP of DMAEMA in 1998 using  $\text{CuCl}/\text{HMTETA}$  complex at elevated temperature [13] After this, several reports have claimed successful ATRP of DMAEMA either using expensive tetradentate ligand systems or with  $\text{CuCl}/\text{bpy}$  complex in aqueous medium [6,12,17,20,22,38–40]. However, the polymers produced failed to undergo successful chain extension reactions except in some cases only in aqueous based medium [40,41]. Furthermore, it may be mentioned here that ATRP of DMAEMA in aqueous based medium reportedly suffers from the problem of trans-esterification [20,42].

Pentamethyldiethylenetriamine (PMDETA) has been a satisfactory tridentate ligand for copper based ATRP. Besides supporting reasonably fast activation by  $\text{Cu}^I/\text{PMDETA}$  complex, it is less expensive and commercially available [43]. However, the issue of monomer coordination and hence catalyst deactivation due to relatively lower formation constant of  $\text{CuCl}$  complex with tridentate PMDETA ligand [44] probably limits its applications in the ATRP of DMAEMA or other similar reactive monomer systems [12]. The literature gives a few reports claiming well defined PDMAEMA synthesis with  $\text{CuBr}/\text{PMDETA}$  catalyst system [45,46]. Cordeiro et al. [47]. have given a detailed account of ATRP of DMAEMA using  $\text{CuBr}/\text{PMDETA}$  catalyst system in aqueous *iso*-propanol medium giving emphasis over the kinetics of polymerization in different conditions using much reduced amount of copper

complex. However, the polymerization has shown significant amount of termination reactions leading to only partial re-initiation by the PDMAEMA macroinitiators during chain extension experiments.

We report a method for carrying out solvent free ATRP of DMAEMA using less expensive  $\text{CuCl}/\text{PMDETA}$  catalyst system at 30 °C in presence of catalytic amount of AQCl under homogeneous condition. A significant control over molecular weight and dispersity ( $\text{Đ}$ ) of the synthesized PDMAEMA is observed even when different higher molecular weights are targeted. PDMAEMA has been successfully chain extended with different methacrylate monomers for the synthesis of various stimuli responsive, multifunctional di- or triblock copolymers. Appreciably high reactivity of the catalyst system allows synthesis of high molecular weight PDMAEMA using much reduced amount of cupric complex in the presence of excess tin(II) 2-ethylhexanoate [ $\text{Sn}(\text{EH})_2$ ]. A significant role of the presence of moisture is also observed on the quality of polymerization which has also been reported previously [48]. A probable explanation for this adventitious role of water has been proposed from UV/VIS analysis of the  $\text{CuCl}_2/\text{PMDETA}$  complex considering literature reported structures of  $\text{CuCl}/\text{PMDETA}$  and  $\text{CuCl}_2/\text{PMDETA}$  from EXAFS analysis. Preparation of 'Smart' hybrid nano structures containing CdS quantum dots stabilized with synthesized dual stimuli responsive diblock copolymer have been successfully demonstrated.

## 2. Experimental

### 2.1. Materials

2-(Dimethylamino)ethyl methacrylate (DMAEMA, 98%), Di(ethylene glycol) methyl ether methacrylate (DEG, 95%), 2-hydroxyethyl methacrylate (HEMA, 97%), Butyl methacrylate (BMA, 99%), *tertiary*-butyl methacrylate (*t*BMA, 98%) and Furfuryl methacrylate (FMA, 97%) all are purchased from Sigma-Aldrich chemicals. DMAEMA is freshly distilled under reduced pressure before use and all other monomers are passed through basic alumina column and stored under nitrogen atmosphere at  $-15^\circ\text{C}$ .  $N,N,N',N'',N''$ -pentamethyldiethylenetriamine (PMDETA, 99%), tricaprylmethylammonium chloride (Aliquat<sup>®</sup> 336, AQCl), ethyl 2-bromoisobutyrate (EBiB, 97%), 2-bromoisobutyryl bromide (BiB, 98%) and tin(II) 2-ethylhexanoate [ $\text{Sn}(\text{EH})_2$ , 92.5–100%] all Sigma-Aldrich products are used as received. The difunctional initiator 1,2-bis(bromoisobutyroxy)ethane (BiBE) is synthesized using a literature reported method [49]. Acetone (GR, E-Merck, India), Tetrahydrofuran (THF) (GR, E-Merck, India & HPLC grade Spectrochem, India), Methyl alcohol (GR, E-Merck, India) Petroleum benzene (GR, E-Merck, India),  $\text{Cd}(\text{OAc})_2$  (E-Merck, India) are also used as received.  $\text{CuCl}$  (98%, BDH) is purified by washing with 10% aqueous HCl followed by methanol and diethyl ether in a Schlenk tube under nitrogen atmosphere.

### 2.2. Bulk polymerization of DMAEMA with a target DP 64

In all polymerization reactions, ultra high pure (UHP) nitrogen gas after bubbling through about 150 ml of Fieser solution (aqueous) is purged to remove oxygen from the reaction systems. In a nitrogen-purged test tube ( $8 \times 2.5$  cm) provided with a B-14 standard joint, AQCl (0.076 gm, 0.186 mmol),  $\text{CuCl}$  (0.0093 gm, 0.093 mmol) and a magnetic bar are added. Nitrogen purging is continued for 10 min and the tube is septum sealed. After this, previously nitrogen purged (for about 25 min) DMAEMA (1 ml, 5.92 mmol) is injected into it with a nitrogen-purged gas-tight syringe and the tube is thoroughly shaken for about 30 min. In the next, PMDETA (0.02 ml, 0.093 mmol) is injected into the polymerization mixture and the admixture is shaken manually until the solution becomes transparent. Finally EBiB (0.014 ml, 0.093 mmol) is injected into it and the polymerization is started with stirring at 30 °C. During determination of polymerization kinetics, the septum is opened after suitable time intervals, polymerization is

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