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## Exploration of Conventional RAFT and SET-RAFT for Studies on Homopolymerization of Methyl Acrylate: Effect of CTA Structure on RAFT Polymerization.

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### ABSTARCT

Homo-polymerization of Methyl acrylate by SET-RAFT and RAFT using the three new CTA's (Z-C(=S)-S-R, dithio esters) CTA-A, CTA-B and CTA-C was carried out for comparison. These CTA's were easily synthesized from commercially available reagents and were characterized by spectroscopic techniques such as  $^1\text{H-NMR}$ ,  $^{13}\text{C-NMR}$  and IR spectroscopy. CTA-A and CTA-B have same R-group, but differ by the Z-group and CTA-B and CTA-C have similar Z-group and different R-group. The comparison study emphasize that homo-polymerization of methyl acrylate was better controlled by conventional RAFT using the new CTA's than the SET-RAFT polymerization. The later part of these work, was dedicated to study the influence of CTA's structure on the conventional RAFT homo-polymerization of MA from the kinetics of polymerization. This study also reveals that, under the given set of considerations the CTA's does not alter the polymerization rate or the control significantly.

**Keywords:** Reversible Addition Fragmentation chain Transfer (RAFT) polymerization, Single Electron Transfer (SET), Methyl acrylate (MA), Chain Transfer Agents (CTA) and Gel permeation chromatography (GPC).

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## INTRODUCTION

The prime requirement of the synthetic functional polymers is to have proper design with well-defined molecular properties for adapting to the needs of the application. These characteristic parameters are influenced by physical/chemical properties, such as molecular weight, poly dispersity index, composition and microstructure [1]. The living/controlled radical polymerization [2] holds the promise for providing a better synthetic tool to prepare polymers in controlled manner. Since, the molecular weight can be controlled by the stoichiometry of the reaction (the monomer: initiator ratio), block copolymers [3] can be prepared by sequential addition of monomer and chain-end functionalized polymers [4] can be prepared in quantitative yield.

During the last two decades, several controlled radical polymerization [5] (CRP) methodologies like ATRP [6], NMP [7], SET [8], RAFT [9] and TERP [10] were developed. Among the CRP methods available, RAFT [11] polymerization is the easiest and versatile due to the following reasons 1) is applicable wide range of monomers, 2) mild, 3) bulk, solution, suspension, emulsion [12], dispersion methods to polymerize the monomers and 4) tolerance of functional group [13] is excellent. In last decade, the synthesis of polymers via RAFT [14] method has gained importance, due to its compatibility with a wide range of monomers [15]. After the invention of SET-LRP in 2006 [8], it has become the most promising CRPs for synthesizing high molecular weight polymer with low poly-dispersity in room temperature. Literature reports [16] have demonstrated that both these techniques can be combined to form a new variety of CRP known as SET-RAFT polymerization. Since SET-RAFT is a combination of ultrafast polymerization at room temperature (SET-LRP) with the relatively slow and controlled polymerization due to chain transfer of active species (RAFT), it can be utilized to polymerize both fast propagating monomers like acrylates, methacrylates [17] and also slow propagating styrenic monomers [16].

Using SET-RAFT method, it has been demonstrated in the literature [16], that styrene polymerization can be initiated at the ambient temperature followed by the controlled propagation through the CTA via the RAFT mechanism [18], although not with appreciable rate. The general mechanism of SET-RAFT was also reported in the literature. In this work methyl acrylate has been polymerized using SET-RAFT and RAFT for comparison and the results are discussed in brief. The aim of this study is to understand the influence of RAFT methodology like SET-RAFT, conventional RAFT and influence of CTA's on the RAFT homo-polymerization of MA.

## EXPERIMENTAL SECTION

### Materials

Copper powder was purchased from SRL Chemicals India limited; all monomers (Methyl acrylate, cyclohexyl methacrylate, benzyl methacrylate and *iso*-bornyl methacrylate) were purchased from Aldrich at the highest purity, passed through the alumina column to remove the inhibitors and used without further purification. All the reagents carbon disulphide, 1-bromoethylbenzene, potassium phosphate, potassium iodide, iodine, potassium hydroxide, 2-mercaptoethanol and 3-mercaptopropionic acid and reagents were obtained from SRL chemicals, India, at the highest purity available and were used without further purification, unless and otherwise stated. Ethyl 2-bromopropionyl bromide, 1-bromo ethylbenzene were purchased from Aldrich and used without further purification. 2, 2-azobis(isobutyronitrile) (AIBN, 99%) was purchased from Aldrich and recrystallized before use. Solvents were purchased from SRL chemicals, India and purified according to the reported procedures [19].

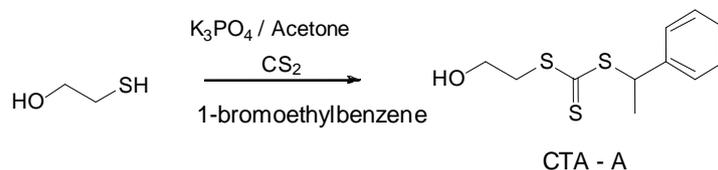
### Measurements

For IR measurements, JASCO Fourier Transform Infrared Spectrometer 410 (Japan) was used. For NMR measurements, Bruker AV400 (400 MHz for  $^1\text{H}$ ) was used. Waters GPC system was used for the determination of number average molecular weight ( $M_n$ ) and polydispersity index (PDI). THF was used as the eluent (flow rate - 1 mL/min) and polystyrene standards with narrow molecular weight were used for calibration. All the measurements were made at room temperature.

## Synthesis of Chain Transfer Agent - (CTA's)

The CTA-A was prepared using modified literature procedure (Scheme 1) [20]. The CTA-B synthesis and crystal data has been published [21]. The synthesis of CTA-C was similar to that used for CTA-A and CTA-B with necessary modifications.

**Scheme 1: Synthesis of CTA-A.**

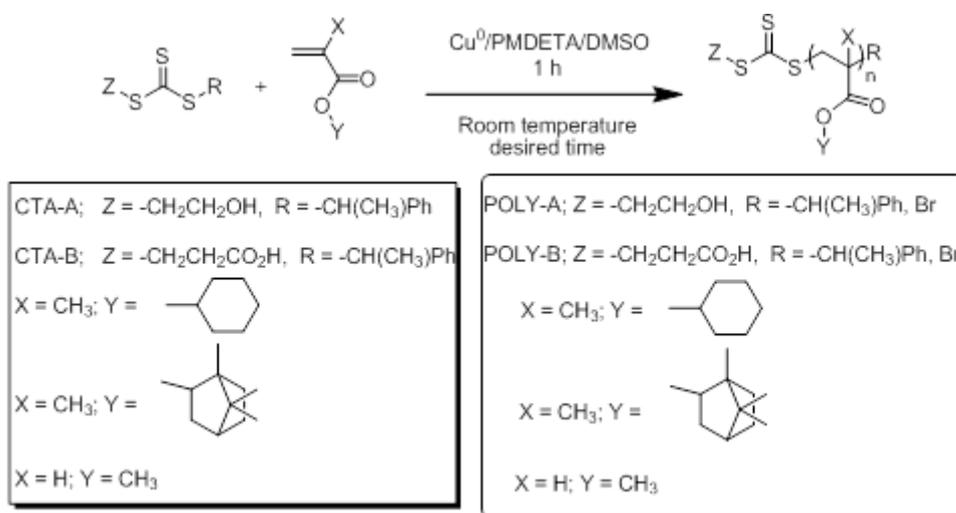


## Polymerization Procedure

### Polymerization of Few Acrylate and Methacrylate by SET-RAFT at Room Temperature Using the New CTAs without Alkyl halide Initiator.

A typical procedure for the homo-polymerization of acrylates and methacrylates by SET-RAFT polymerization at room temperature using the new CTAs is as follows (Scheme 2): The required amount of the copper powder, CTA, and the monomer were mixed in a glass ampoule. It was then degassed by freeze-evacuate-thaw cycles (three times). Calculated amount of ligand ( $\text{Me}_6\text{TREN}$ ), DMSO (if needed) were added to the sealed ampoule and placed in a water bath maintained at room temperature for the desired time. At the end, the glass ampoules were opened and the contents were diluted with THF, followed by precipitation into a large excess of a non-solvent. It was then dried under vacuum to constant mass for determining the percentage monomer conversion. The polymer samples were subsequently analyzed by GPC and other spectroscopic tools.

**Scheme 2: SET-RAFT polymerization of acrylate and methacrylates at room temperature using the new CTAs.**

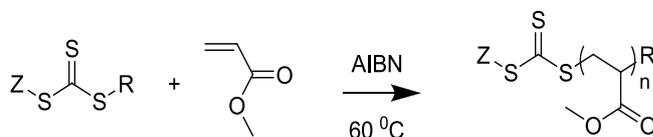


### Homopolymerization of Methyl Acrylate Using the Three New CTAs

A typical preparation of poly(methyl acrylate) is as follows (Scheme 3): The required amount of the CTA and the initiator (in cases where it is used) was mixed with the required quantity of monomer in a glass ampoule. It was degassed by freeze-evacuate-thaw cycles (three times). It was then placed in an oil bath maintained at the required temperature for the desired time. At the end, the glass ampoules were removed, cooled down to room temperature, opened and the contents were diluted with THF followed by precipitation into a large excess of a non-solvent. It was then dried under vacuum to constant mass for determining the

percentage monomer conversion. The polymer samples were subsequently analyzed by GPC and other spectroscopic tools.

**Scheme 3: RAFT synthesis of poly(methyl acrylate) using the newly synthesized CTAs**



CTA-A; Z = -CH<sub>2</sub>CH<sub>2</sub>OH, R = -CH(CH<sub>3</sub>)Ph  
 CTA-B; Z = -CH<sub>2</sub>CH<sub>2</sub>COOH, R = -CH(CH<sub>3</sub>)Ph  
 CTA-C; Z = -CH<sub>2</sub>CH<sub>2</sub>COOH, R = -CH(CH<sub>3</sub>)COOEt

PMA-A; Z = -CH<sub>2</sub>CH<sub>2</sub>OH, R = -CH(CH<sub>3</sub>)Ph  
 PMA-B; Z = -CH<sub>2</sub>CH<sub>2</sub>COOH, R = -CH(CH<sub>3</sub>)Ph  
 PMA-C; Z = -CH<sub>2</sub>CH<sub>2</sub>COOH, R = -CH(CH<sub>3</sub>)COOEt

**RESULTS AND DISCUSSION**

The success of results obtained with SET-RAFT [16] and ATRP initiated by adventitious oxygen [22] present in the solvent for polymerizing few monomers using ATRP encouraged us to extend the SET-RAFT polymerization of few monomers without the alkyl halide initiator. The SET-RAFT polymerization of Methyl acrylate (MA), cyclohexyl methacrylate (CHMA), benzyl methacrylate (BzMA) and *iso*-bornyl methacrylate (IBMA) mediated by synthesized CTA's was studied with various RAFT conditions. In order to investigate the influence of the RAFT methodology, the polymerization was conducted by varying the conditions like with or without DMSO and without initiator.

The results from the polymerization of acrylates and methacrylates by SET-RAFT polymerization at room temperature using the new CTAs were tabulated in the Table 1.

**Table 1: Molecular Weight and Conversion Data for Homopolymerizations by SET-RAFT Polymerization at Room Temperature Using the New CTAs**

| S. No | Monomer | CTA | Solvent | Temp. (° C) | Time (h) | M <sub>n</sub> (GPC) | PDI  |
|-------|---------|-----|---------|-------------|----------|----------------------|------|
| 1     | IBMA    | B   | DMSO    | 30          | 2        | 9600                 | 2.3  |
| 2     | CHMA    | A   | DMSO    | 30          | 2        | 3200                 | 2.8  |
| 3     | CHMA    | B   | DMSO    | 30          | 30 (min) | 12800                | 2.9  |
| 4     | CHMA    | B   | -       | 60          | 2        | 10800                | 3.2  |
| 5     | CHMA    | B   | DMSO    | 30          | 7        | 18400                | 3.1  |
| 6     | MA      | B   | DMSO    | 30          | 1        | 2800                 | 1.5  |
| 7     | MA      | A   | DMSO    | 30          | 1        | 3200                 | 1.6  |
| 8     | BzMA    | B   | DMSO    | 30          | 1        | 54000                | 1.88 |

The typical reactant ratio of SET-RAFT polymerization is Monomer : CTA : Cu<sup>0</sup> : PMDETA = 200 : 1 : 2 : 2 (Entry 4 the polymerizations is carried out for 30 minutes and entry 5 the polymerizations is carried at 60 °C).

From the PDI values in the Table 1 it is clear that the polymerizations of CHMA, IBMA, BzMA and MA were not proceeding in a controlled manner. In the absence of the alkyl halide initiator the adventitious oxygen present in the solvent initiate the polymerization. The reason for the uncontrolled polymerizations by SET-RAFT polymerization initiated by oxygen in the solvent (DMSO) at room temperature (30 °C) is the CTA is not getting cleaved at that temperature. When the polymerization was done at 60 °C (entry 4 in the Table 1) the CTA may get cleaved to generate the reinitiating radical which is initiating the polymerization of CHMA since there is no oxygen (DMSO is not added during polymerization) to initiate the polymerization. But the polymerization still proceeds in uncontrolled manner indicating the essential of DMSO to control the polymerization via SET-RAFT conditions.

The GPC traces of poly(methyl acrylate) formed by SET-RAFT polymerization without added alkyl halide initiator is shown in the Figure 1 (SI). The peaks are broad resulting in high PDI values. The GPC traces of poly(cyclohexyl methacrylate), poly (benzyl methacrylate) and poly (isobornyl methacrylate) were shown in the Figure 2 (SI). The broadness of the peaks suggests that polymerization is not controlled under given set of conditions.

### Homopolymerization of Methyl Acrylate

The homo-polymerization results of few acrylates and methacrylates by SET-RAFT polymerization (Table 1) is not encouraging, The PDI values of all the polymers synthesized by SET-RAFT polymerization were high. Among the polymers, the PDI values of Methyl acrylate were closer to the PDI values of controlled polymerization. The PDI values of MA suggest that the homo-polymerization of methyl acrylate might be controlled with the synthesized CTA's by altering the polymerization condition. Hence the polymerization of Methyl acrylate was carried out by conventional RAFT polymerization using the CTA's in the presence of radical initiator AIBN.

**Table 2: Comparison of Homopolymerization of Methyl Acrylate, using synthesized CTA's**

| S. No | Time (min) | CTA | Solvent | Temp.(° C) | M <sub>n</sub> (GPC) | PDI  |
|-------|------------|-----|---------|------------|----------------------|------|
| 1     | 60         | A   | DMSO    | 30         | 3200                 | 1.6  |
| 2     | 60         | A   | -       | 60         | 1500                 | 1.28 |
| 3     | 60         | B   | DMSO    | 30         | 2800                 | 1.5  |
| 5     | 60         | B   | -       | 60         | 2400                 | 1.32 |
| 7     | 60         | C   | -       | 60         | 1800                 | 1.22 |

Polymerization conditions: Polymerization at 60 °C with AIBN; Degree of polymerization (DP) = [M<sub>0</sub>] / [CTA<sub>0</sub>] = 250; [CTA : AIBN = 20 : 1]; (conditions except entry 1 and 3)

Table 2 shows the homo-polymerization data of methyl acrylate using newly synthesized CTA's CTA-A, CTA-B and CTA-C. Entry 1 and 3 were extracted from the previous table 1, polymerization done in the SET-RAFT conditions (added for comparison). Conventional RAFT conditions provide better control than the SET-RAFT, because the radical generated from the initiator (AIBN) alone initiates the polymerization. These results also reveal that the polymerization control does not alter much by changing the CTA's. The PDI values of homopolymerization of methyl acrylate by thermal RAFT using the new CTA's are in the range of 1.2 – 1.35, which indicates the all the polymerizations were controlled.

Kinetics of polymerization of methyl acrylate were done by all the three new CTA's for studying the influence of R-group and Z-group structure over the polymerization rate and control. The kinetic data of polymerization of methyl acrylate using CTA-A and CTA-B were included in the supporting information SI.

### Kinetics of Homopolymerization of Methyl Acrylate, at 60 °C, with AIBN

**Table 3: Molecular Weight and Conversion Data for Homopolymerization of Methyl Acrylate at 60 °C, in the Presence of CTA-C**

| S. No | Time (h) | Conversion (%) | M <sub>n</sub> (calc) | M <sub>n</sub> (GPC) | PDI  |
|-------|----------|----------------|-----------------------|----------------------|------|
| 1     | 60       | 12.1           | 2700                  | 1800                 | 1.22 |
| 2     | 135      | 29.2           | 6400                  | 6000                 | 1.22 |
| 3     | 175      | 38.7           | 9500                  | 7900                 | 1.23 |
| 4     | 230      | 51.4           | 12300                 | 9500                 | 1.26 |
| 5     | 312      | 61.6           | 13400                 | 10100                | 1.19 |
| 6     | 405      | 71.6           | 14700                 | 12000                | 1.24 |
| 7     | 585      | 76.5           | 16700                 | 13800                | 1.25 |
| 8     | 720      | 89.1           | 19200                 | 17700                | 1.24 |

Polymerization conditions: Polymerization at 60 °C in the presence of AIBN; Degree of polymerization (DP) = [M<sub>0</sub>] / [CTA<sub>0</sub>] = 250; [CTA : AIBN = 20 : 1]; MA = 3 ml (33 mmol), CTA-C= 0.0375 g (0.13 mmol) and AIBN = 10x10<sup>-4</sup> g (0.0065 mmol)

The newly synthesized CTAs CTA-A, CTA-B and CTA-C were used for the homo-polymerization of methyl acrylate. Monomer conversion was determined gravimetrically. Polymerizations were stopped at different time in order to determine the kinetics of the polymerizations and the development of the molecular weight distribution. The results from the polymerization using CTA's were summarized in Table 2 for comparison.

The kinetics of polymerization by these new CTA's reveals, that the polymerization rate and control was not altered significantly by changing the CTA. Since the rate of polymerization using CTA-C is the highest and the control also slightly better (PDI values 1.19-1.26), the kinetics of polymerization of methyl acrylate using CTA-C is high-lightened here.

The increase in the  $M_n$  with monomer conversion and the relatively narrow PDI suggests the typical controlled radical polymerization is in operation. The  $M_n$  (GPC) is found to be lower than the  $M_n$  (calc) value. This is probably due to the hydrodynamic radius of a PMA being different from that of the corresponding polystyrene standard used for obtaining the calibration and hence a calibration curve based on polystyrene standards may not reflect the actual molecular weight of the PMA. From the plot of  $M_n$  (GPC) vs. conversion (%) (Fig. 1) it is seen that the  $M_n$  (GPC) varies linearly with conversion, which indicates that these polymerizations are reasonably controlled.

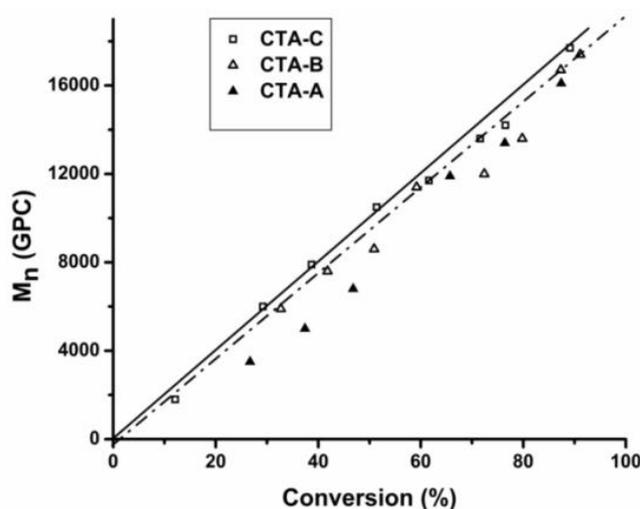


Figure 1 Number-average molecular weights ( $M_n$  obtained from GPC) as a function of monomer conversion, for CTA-A, CTA-B and CTA-C mediated polymerization of Methyl acrylate, at 60 °C, in bulk.

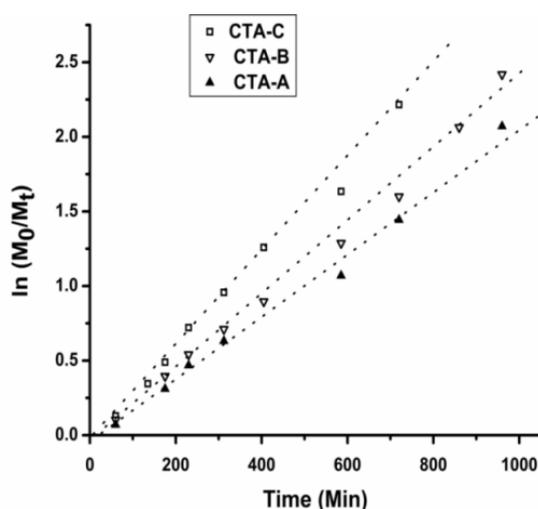


Figure 2  $\ln \{[M]_0/[M]_t\}$  vs. time (min) plot for RAFT polymerization of methyl acrylate using CTA-A, CTA-B and CTA-C, at 60 °C.

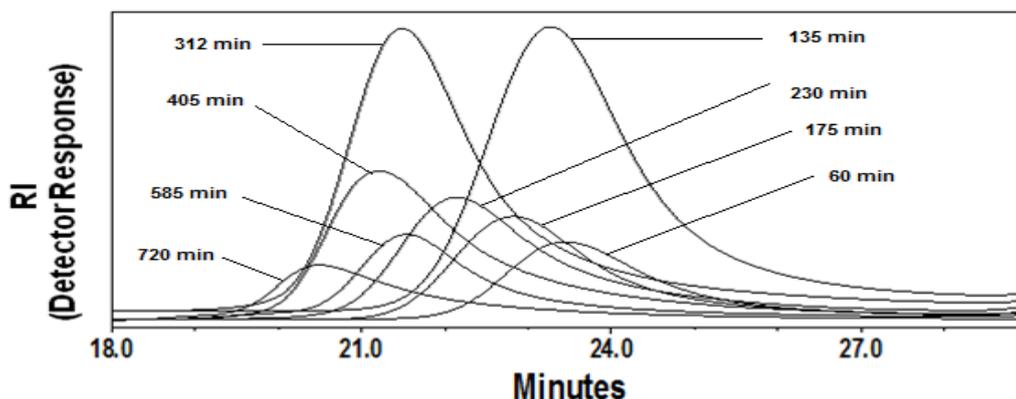


Figure 3: GPC traces for the PMA obtained using CTA-C, at 60 °C with AIBN.

The logarithmic plots of monomer concentration vs. time are shown in Figures 2. The straight line passing through the origin suggests that the polymerization is first order with respect to the monomer concentration. The GPC traces for the polymethylacrylate obtained from the polymerization are in Figures 3. This shows the important features such as, i) the  $M_n$  (GPC) increasing with time suggesting that the polymerization is deviating from the conventional free radical polymerization and ii) the peaks are broader, particularly at the lower molecular weight region (tail). All these polymerizations were carried out at 60 °C and  $t_{1/2}$  of AIBN at that temperature is 10 hours. In the given period of polymerization, sufficient amount of initiator remain un-dissociated, this might initiate the polymerization later, resulting in the lower molecular weight tail. Hence the PDI values of the polymers are relatively higher than that in the literature reports [23].

#### SET-RAFT Vs Conventional RAFT

Under the given set of conditions, there might be two systems present i.e., SET and RAFT mechanisms both co-exist independently in the given circumstances. Hence the system gets deviated from the control manner. The bimodal distribution of molecular weight curve in the GPC traces (Figure 1 & 2, SI) emphasizes the above inference. The above mentioned effect becomes pronounced as the temperature is raised 30 °C to 60 °C. The higher molecular weight peak proportion on the left side of the curve is grown to notable ratio at 60 °C. The comparison of various initiating system for methyl acrylate homopolymerization using three new CTAs (Table 2) shows that conventional polymerization is best method among the three systems.

#### Influence of R/Z group structure in the CTA

The RAFT polymerization kinetics of methyl acrylate (MA) was studied by CTA's CTA-A, CTA-B and CTA-C. The homo-polymerization of MA using all the three synthesized CTA's are controlled. Even though the Z group has changed (R group remains the same), while going from CTA-A to CTA-B, there is no significant change in the control of the polymerization. Hence both the Z group were efficient in controlling the polymerization. In the process of using CTA-B in place of CTA-C the R changes but with minor changes in the rate of polymerization. The polymerization of methyl acrylate using CTA-C is the fastest among the polymerization while that with CTA-A was the slowest. This is expected from the similarity in the structure of the radicals generated from CTA-C and polymeric radical.

#### CONCLUSION

SET-RAFT provides us the new technique to synthesize wide variety of polymers at room temperature, but at the given set of conditions here in this work, it does not seem to be efficiently controlling the polymerization of CHMA, IBMA and BzMA. The various initiating system for methyl acrylate homo-polymerization using three new CTAs (Table 2) were compared. The prime disadvantage in the SET-RAFT method, might be the two initiating system existing independently, at same instant. From the studies, it has been established, that the homo-polymerization of methyl acrylate was better controlled by conventional RAFT using the new CTA's than the SET-RAFT polymerization. To make use of SET-RAFT to synthesize required homo and block copolymer, then necessarily the conditions are to be adjusted to favour the process.

The homo-polymerization of MA using all the three synthesized CTA's by conventional RAFT was controlled. There is no significant change in the control of the polymerization by changing the CTA's. The polymerization of methyl acrylate using CTA-C is the fastest among the polymerization while that with CTA-A was the slowest. The PDI values of the homopolymerization of methyl acrylate using CTA-C were marginally low, when compared to other CTA's, the reason might be due to the similarity in the structures of propagating radical from polymeric species and reinitiating radical generated from CTA.

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