Synthesis of Controlled Polymer Nanospheres by a Reversible Addition-Fragmentation Chain Transfer (RAFT) Miniemulsion Polymerization

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Objectives

- To apply a RAFT agent bearing carboxyl acid group to miniemulsion polymerization
- To obtain stability-enhanced functionalized polymer nanospheres with narrow PDI via RAFT method

Introduction

Synthetic methods of functionalized particles

- Copolymerization with ionic monomers
- Polymerization with charge endowing surfactants or initiators
- Multi-step process in which functional groups are introduced after the colloid synthesis

Applications

- Colloidal drug carrier, detoxification
- Solid-phase supports in biomedical and biochemical fields
- Information technology
- Materials for humidity sensors ….

Living Free-Radical Polymerizations

LRP Methods

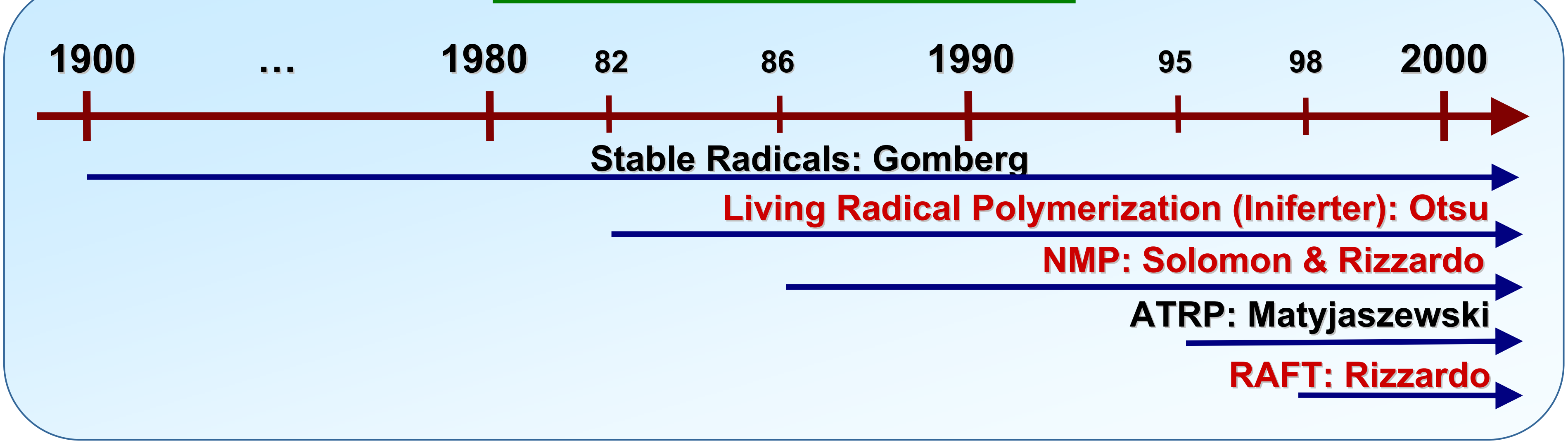
- Reversible Addition-Fragmentation Chain Transfer Polymerization (RAFT)
- Nitroxide-Mediated Polymerization (NMP)
- Atom-Transfer Radical Polymerization (ATRP)

Characteristics of LRP

- Precise control of M_n & PDI
- Precise control of stereostructure
- Synthesis of highly functional block copolymers
- Tailor-made polymer products
- Advanced materials applicable to IT, BT, and NT

Trend in LRPs

Timeline of LRP

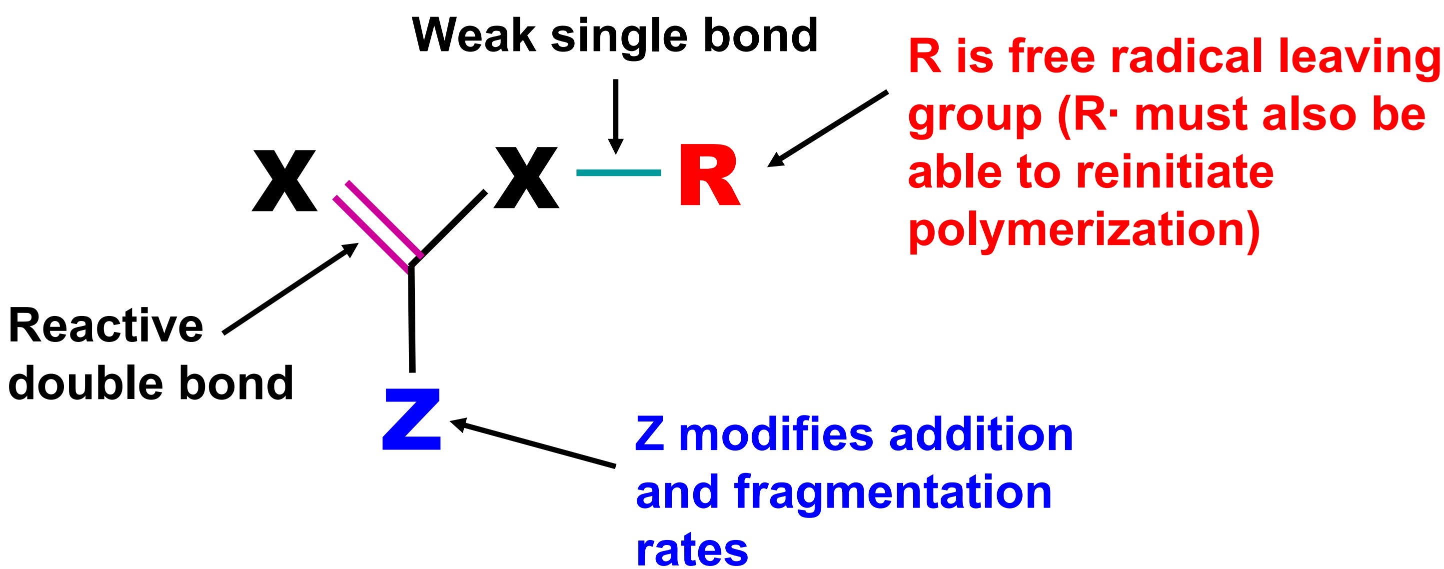


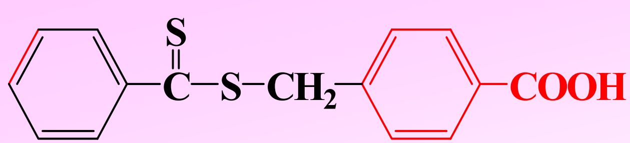
Research Interest in LRPs

1. Homogeneous: Bulk / Solution → Heterogeneous: Miniemulsion → Heterogeneous: Emulsion
2. Molecular Design in Homogeneous Polymerization

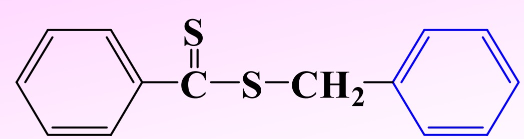
RAFT Polymerization

◈ Generic RAFT Agent Structure





(4-Toluic acid) dithiobenzoate, TADB



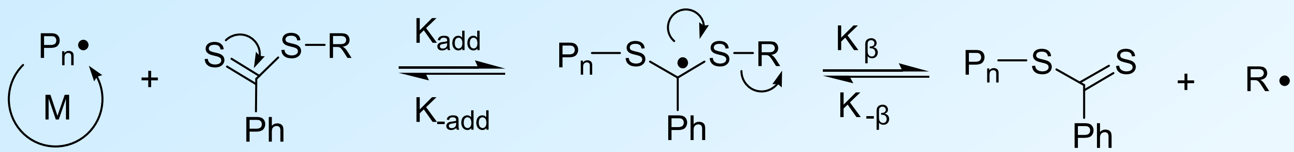
Benzyl dithiobenzoate, BDB

Mechanism of RAFT Polymerization

Initiation

$$\text{Initiator} \longrightarrow I\bullet \xrightarrow{M} P_n\bullet$$

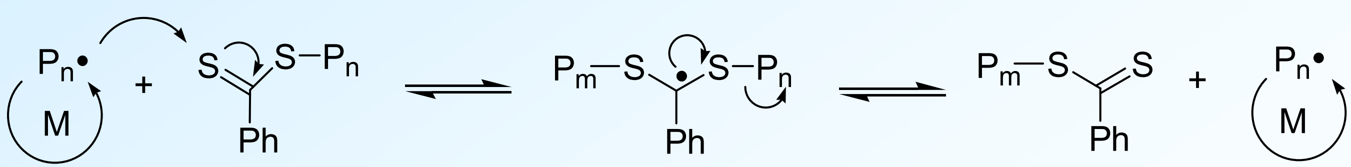
Chain transfer



Reinitiation

$$R\bullet \xrightarrow[k_i]{M} R{-}M\bullet \xrightarrow[k_p]{M} P_m\bullet$$

Chain equilibration



Termination

$$P_n\bullet + P_m\bullet \xrightarrow{k_t} \text{dead polymer}$$

RAFT Polymerization

◈ Problems in conventional emulsion polymerization

- Lack of colloidal stability
- Retardation of polymerization rate
- Formation of a conspicuous red layer at the beginning of polymerization
- Broad molecular weight distribution (higher than 1.5)

◈ Techniques utilized to overcome the problems

- Semi-batch process
- Seeded emulsion polymerization
- *Miniemulsion polymerization*

Experimental

Recipe

- Reaction medium : double distilled de-ionized (DDI) water
- Monomer : Methyl methacrylate, Styrene
- Surfactant : Sodium dodecyl sulfate (SDS)
- Cosurfactant : Hexadecane
- Initiator : 2,2' – Azobis(isobutyronitrile) (AIBN)
- RAFT agent : (4-Toluic acid) dithiobenzoate, Benzyl dithiobenzoate

Conditions

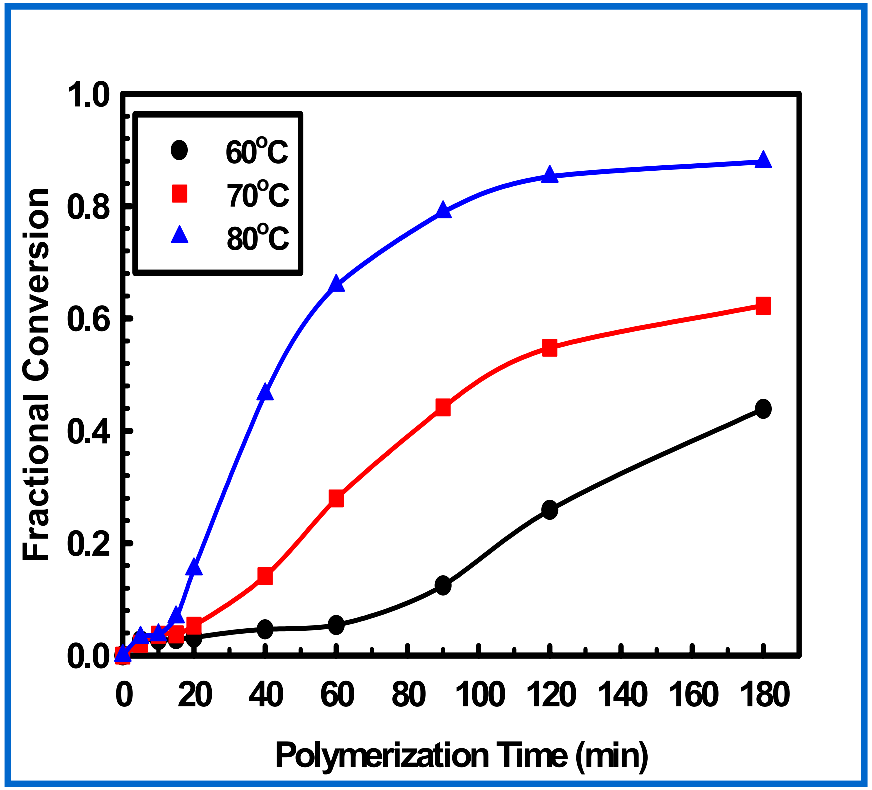
- 60 – 80°C, 220 rpm
- [RAFT]/[AIBN] = 0, 1, 2, 5

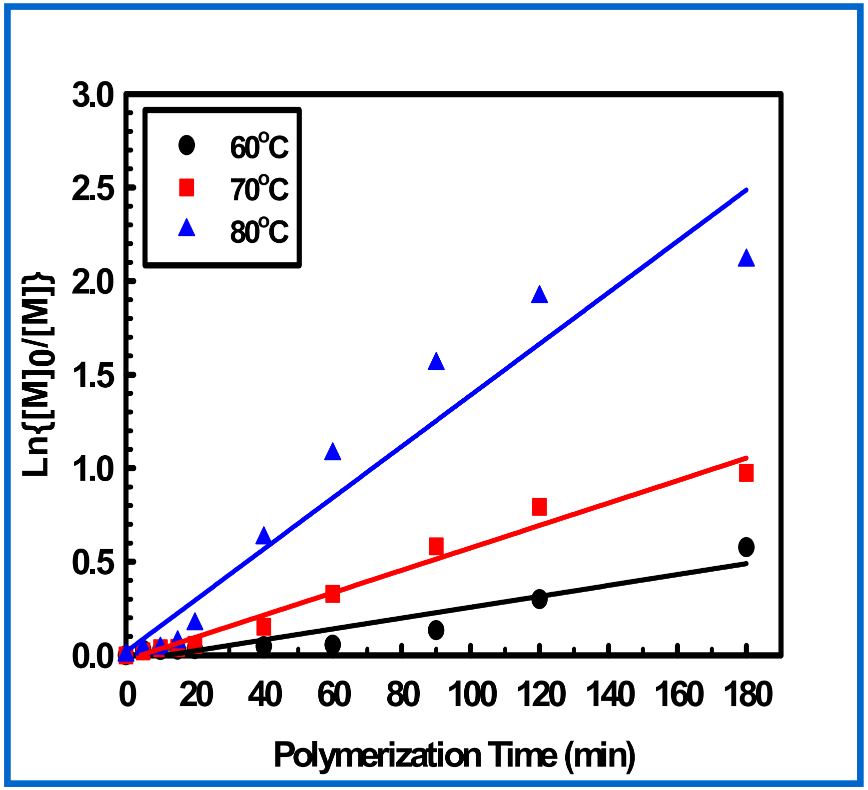
Characterizations

- Molecular weight measurement : GPC
  HPLC pump (WATERS 510), Viscometer (Viscotex)
- Particle size and Zeta potential : Zetasizer (Malvern, Zetasizer 4000)
- Conductivity measurement : Conductivity meter (*KEM*, GM - 115)
- Analysis of particle size & morphology : SEM (Hitachi, S - 4300)

Experimental Results

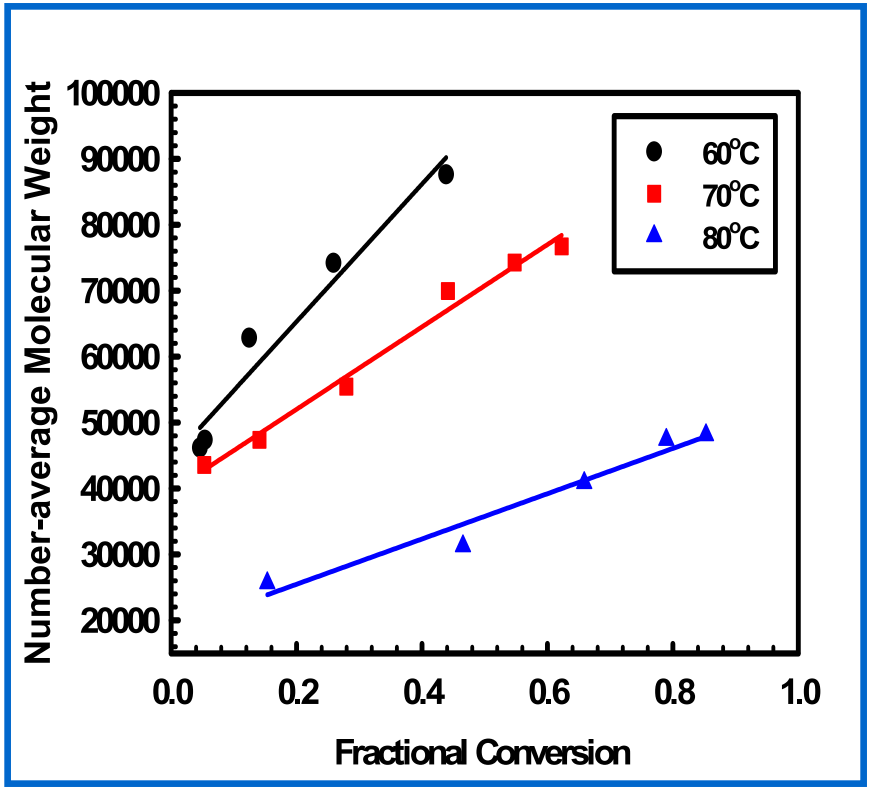
◆ **Polymerization Kinetics : Effect of Reaction Temperature ([TADB]/[AIBN]=1), PMMA**

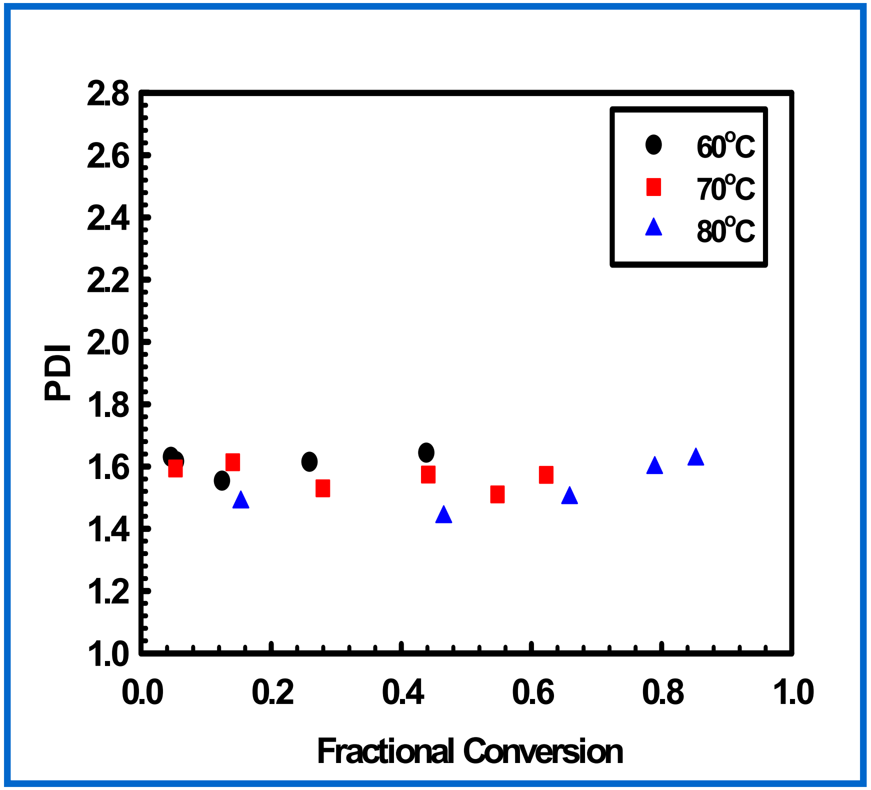




Experimental Results

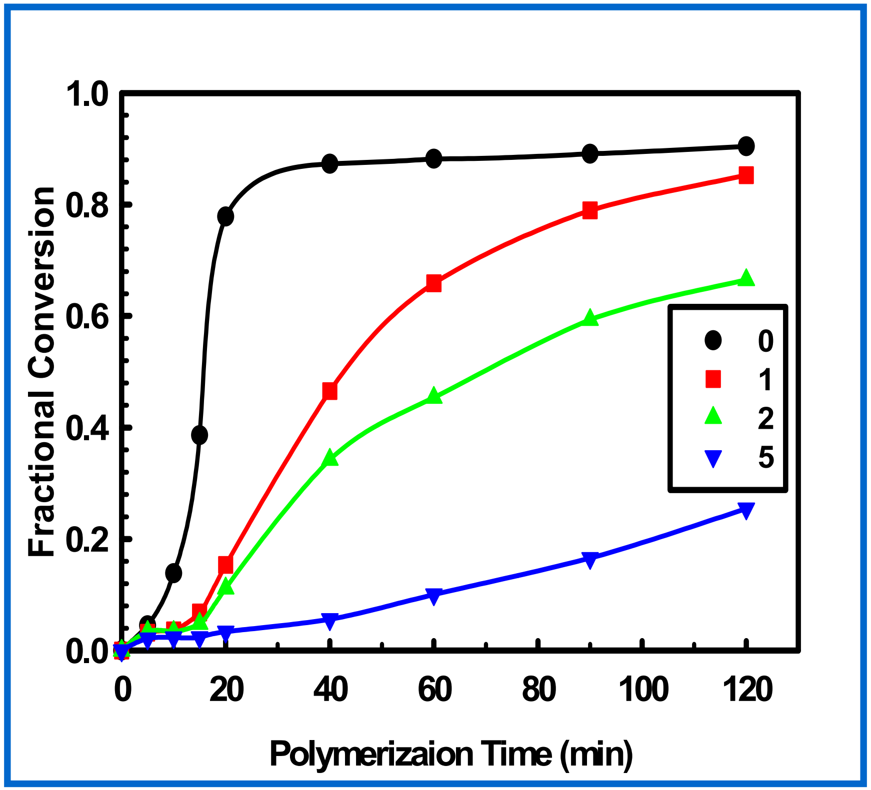
◆ **Molecular Weight Evolution : Effect of Reaction Temperature ([TADB]/[AIBN]=1), PMMA**

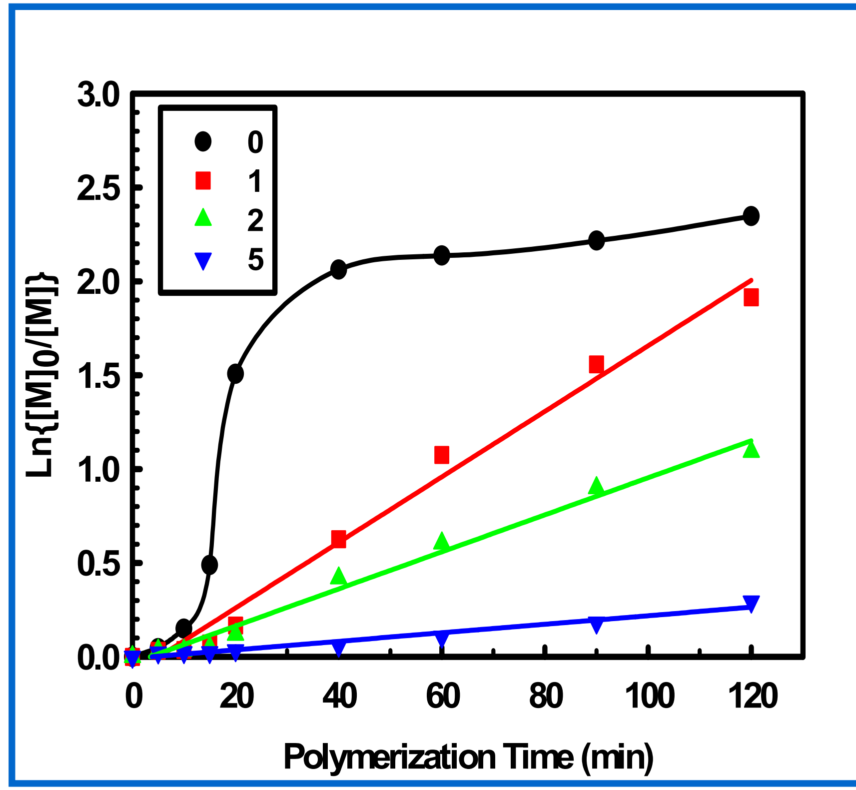




Experimental Results

◆ **Polymerization Kinetics : Effect of [TADB]/[AIBN], 80°C PMMA**





Experimental Results

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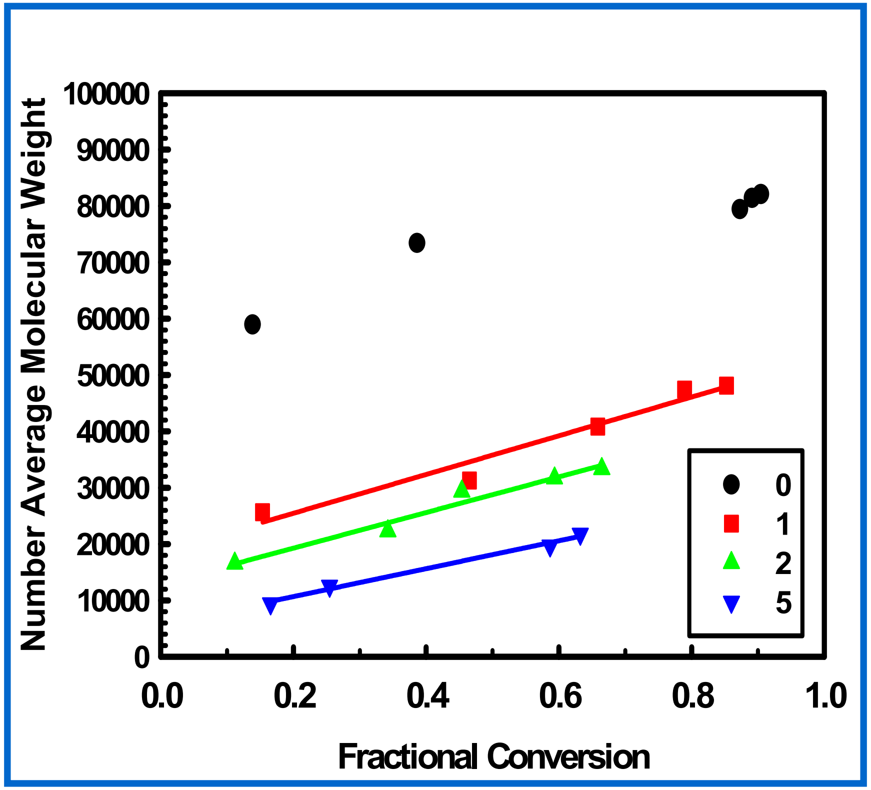
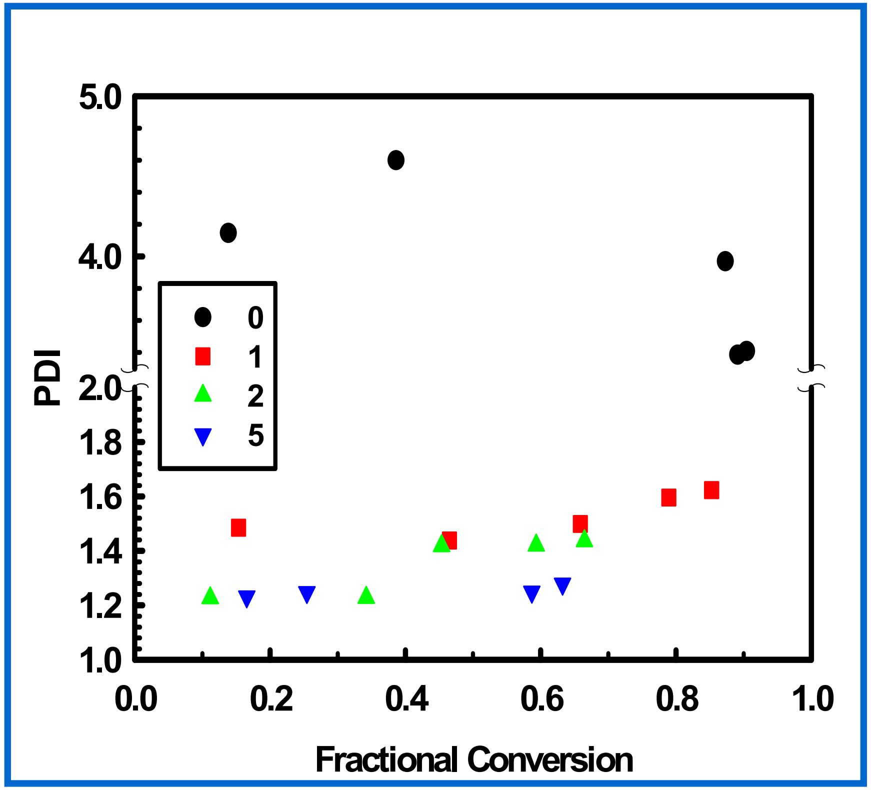
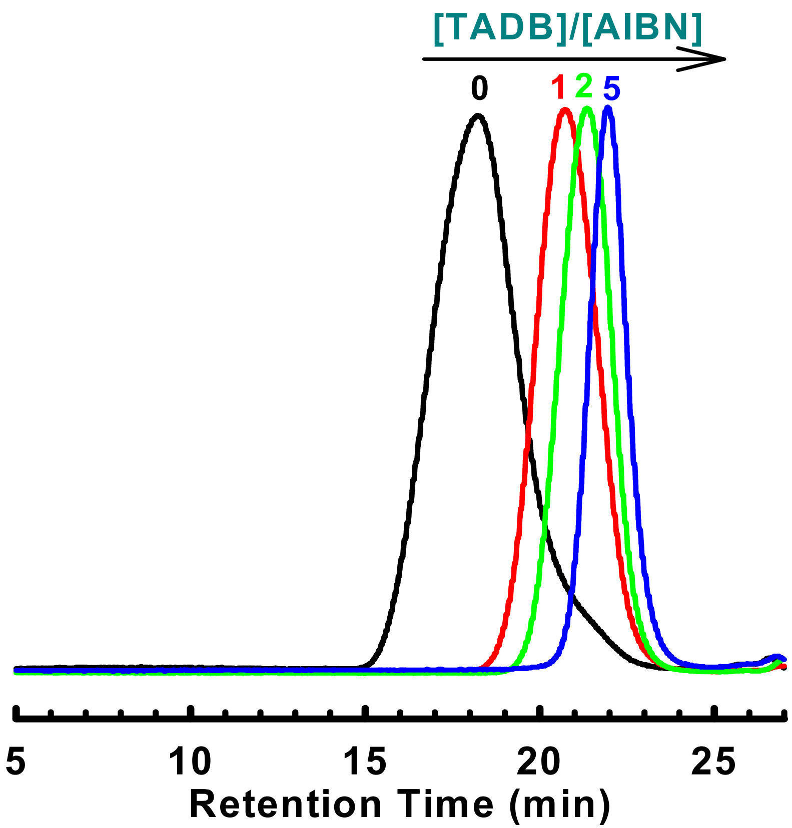
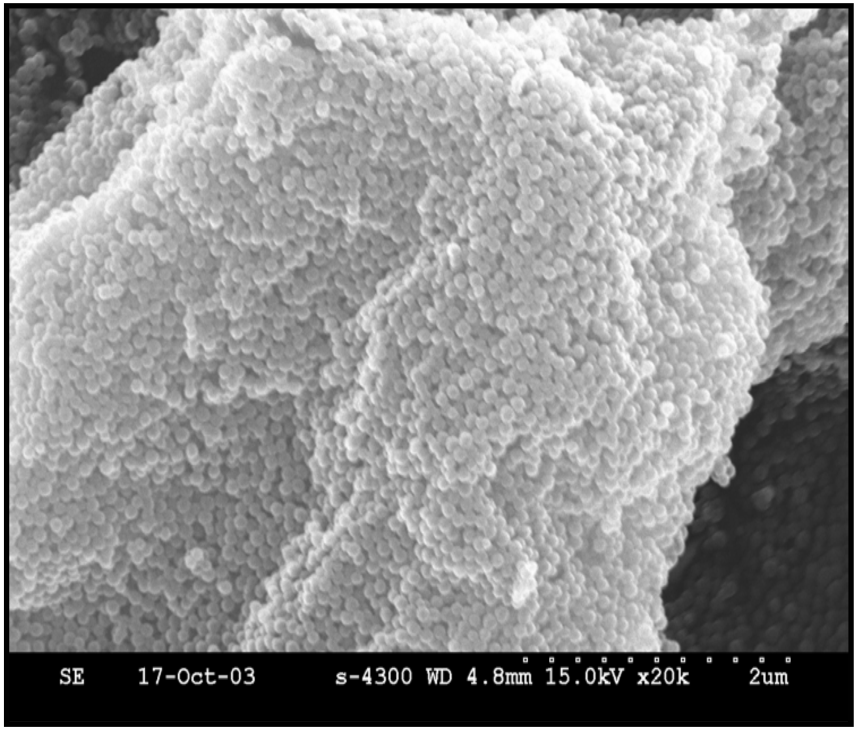




Experimental Results

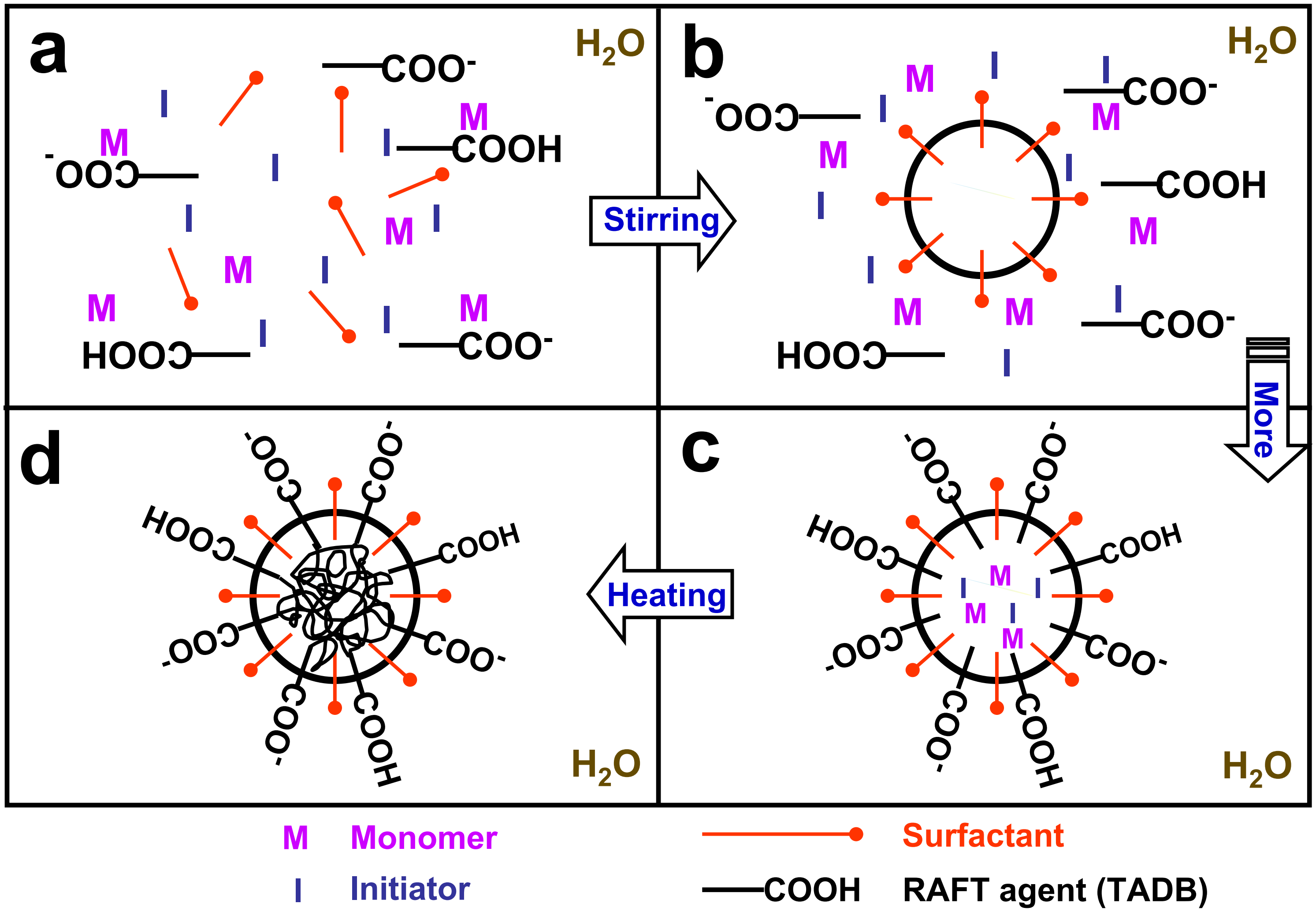
◈ GPC Traces & SEM Photograph of PMMA : 2hr, 80^{o}C





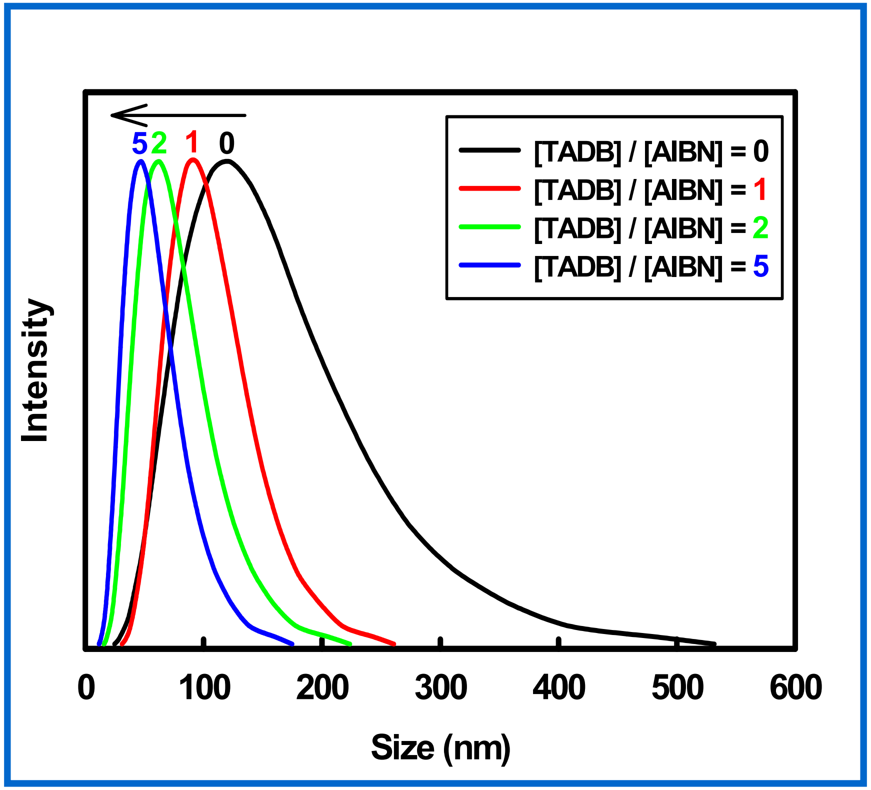
[TADB]/[AIBN]=1, 90nm

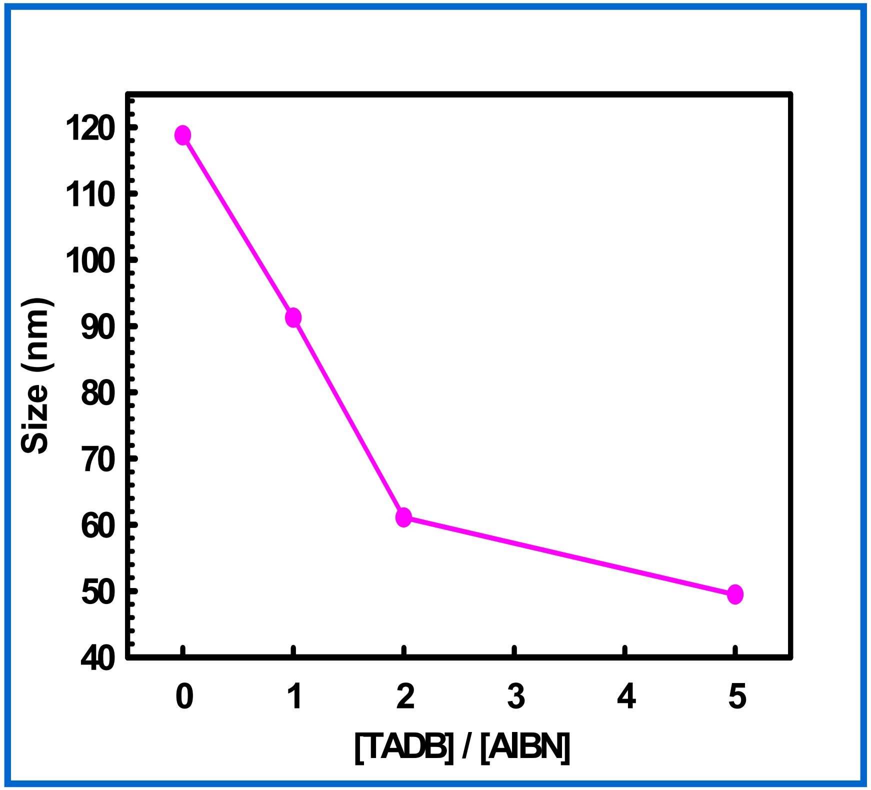
Synthetic Mechanism



Experimental Results

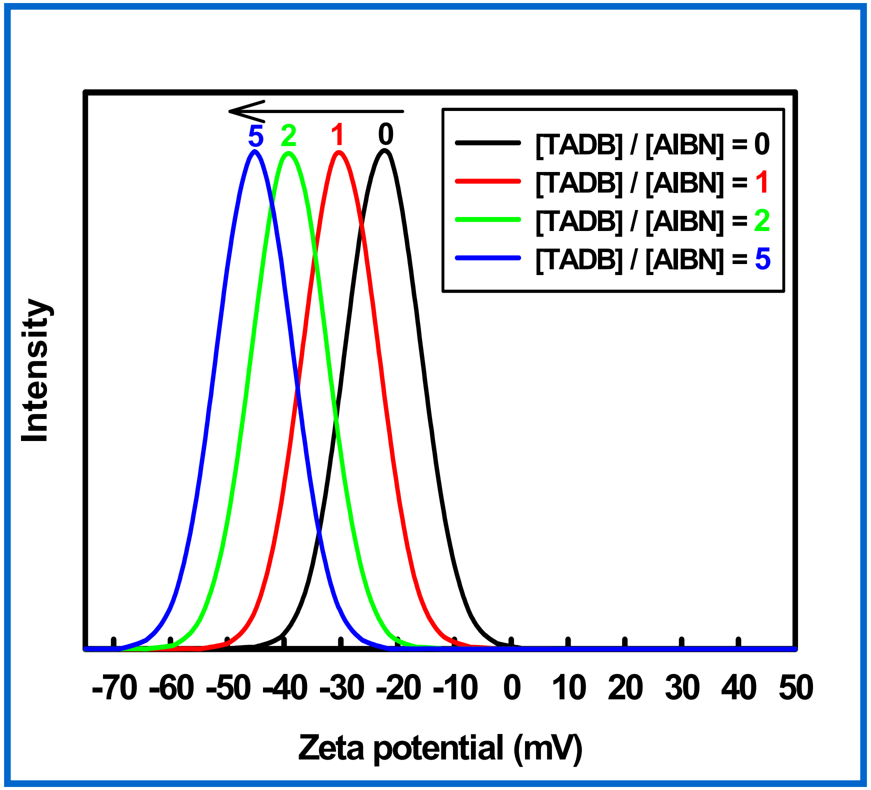
◈ Particle Size Distribution of PMMA Latex : 2hr, 80°C

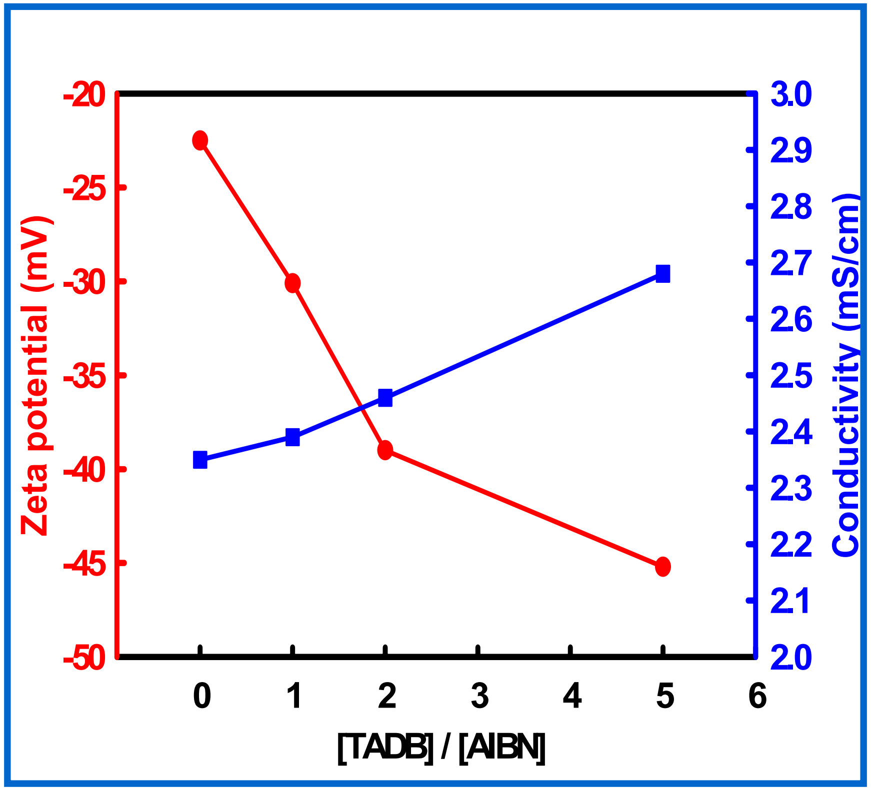




Experimental Results

◈ Zeta Potential & Conductivity of PMMA Latex : 2hr, 80^{o}C

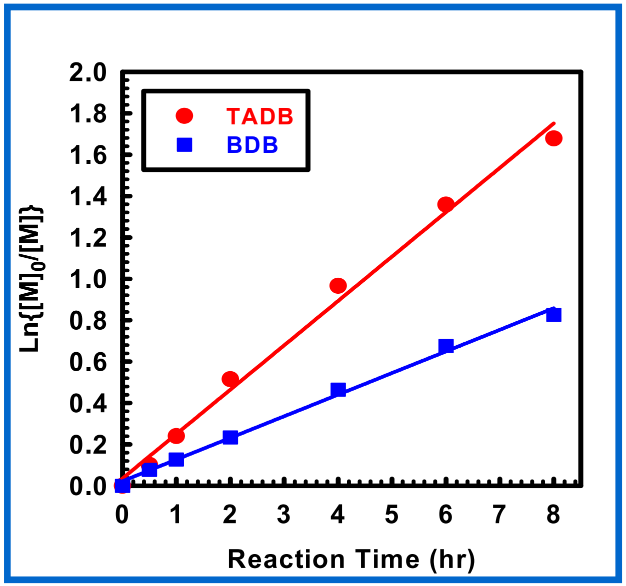


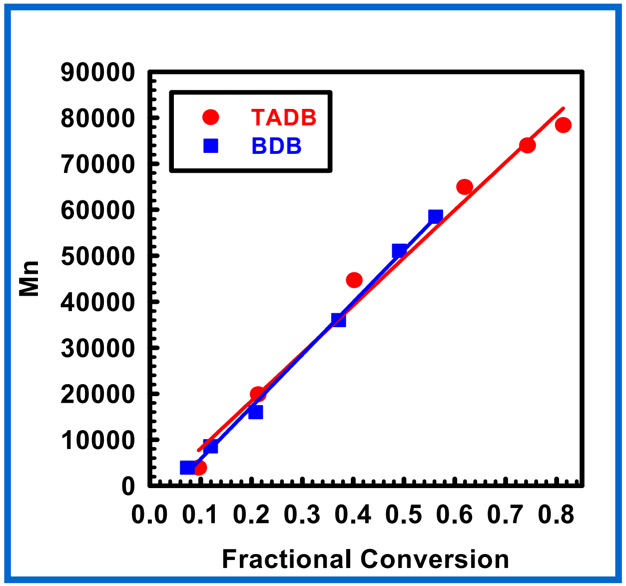


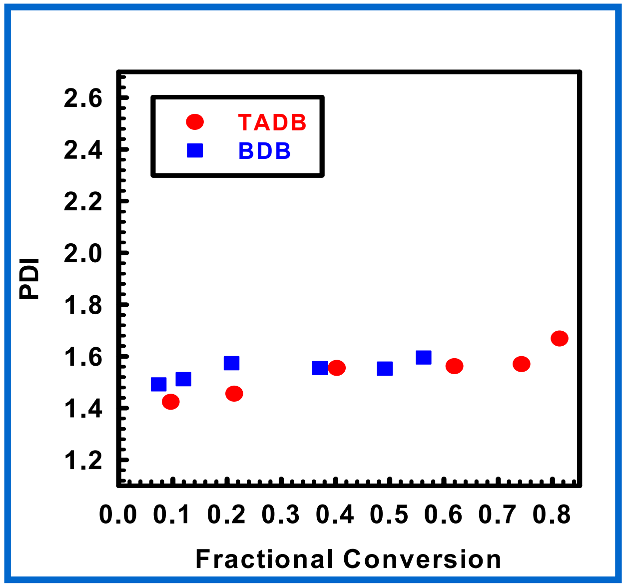
Experimental Results

◈ Polymerization Characteristics : Effect of carboxyl acid

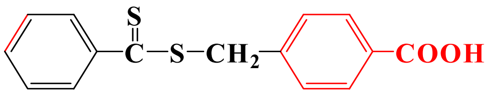
[RAFT]/[AIBN] = 1.3, 80℃, PS



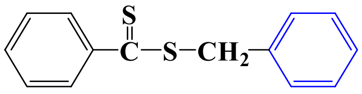




TADB :

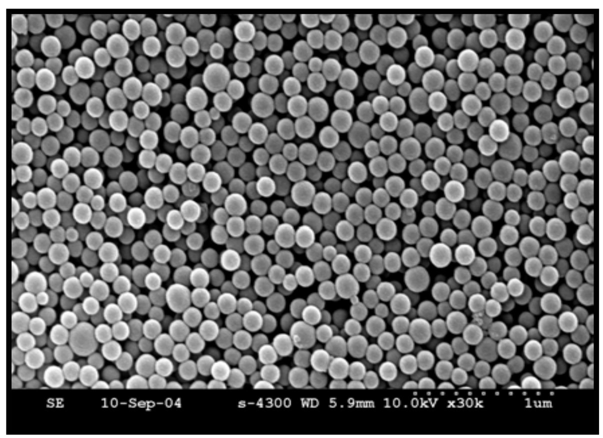
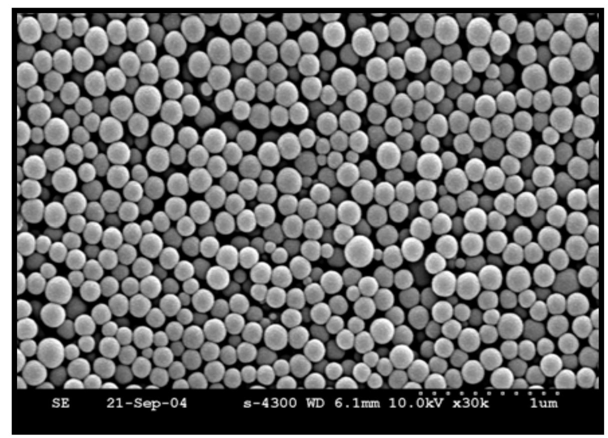


BDB :



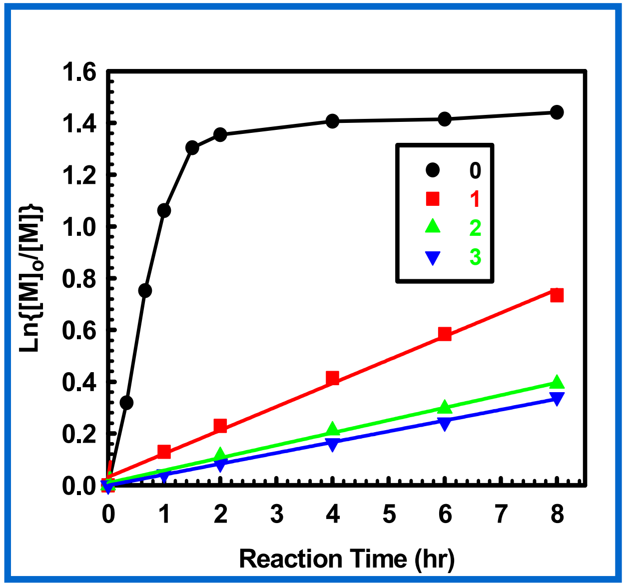
Experimental Results

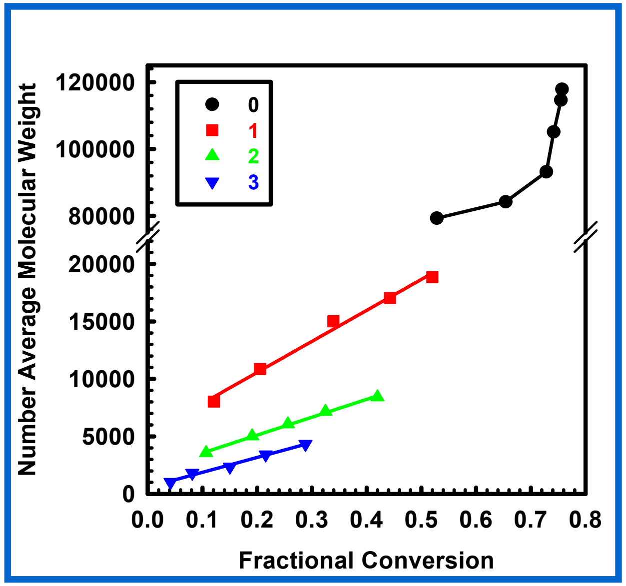
Influence of RAFT agents : Particle size, Zeta potential, and Conductivity (8hr), PS

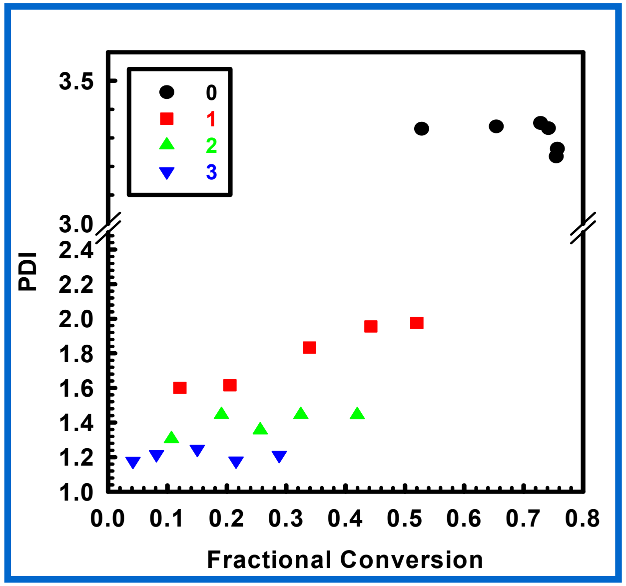
[RAFT]/[Initiator] = 1.3	TABD	BDB
Particle Size (nm)	125.1	135.7
Zeta potential (mV)	-48.2	-44.5
Conductivity (mS/cm)	2.60	2.48
SEM images		

Experimental Results

Polymerization Characteristics : Effect of [TADB]/[AIBN], 80℃, PS

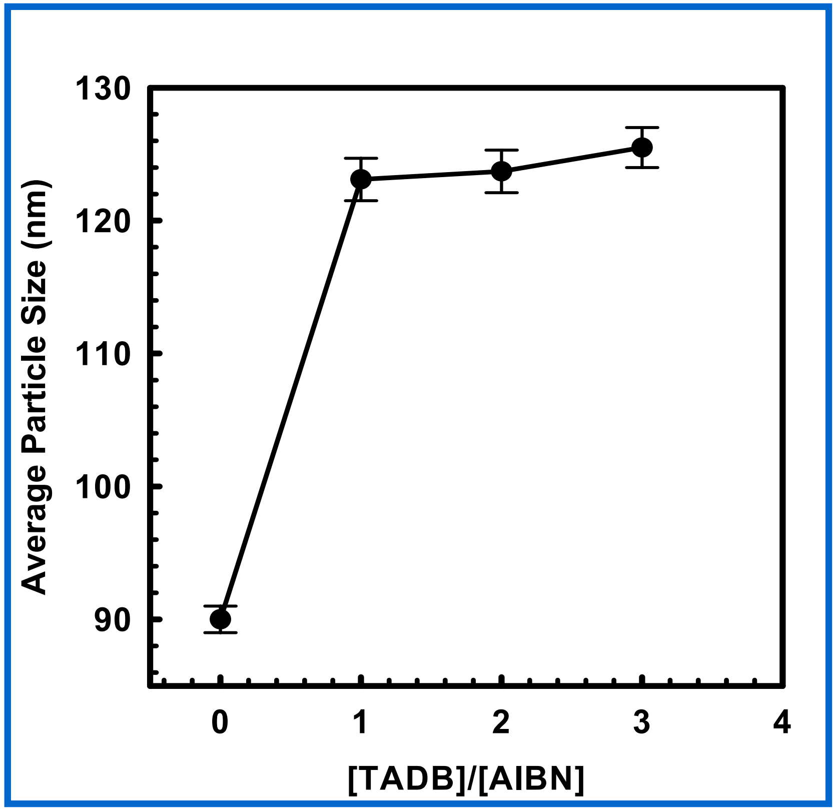


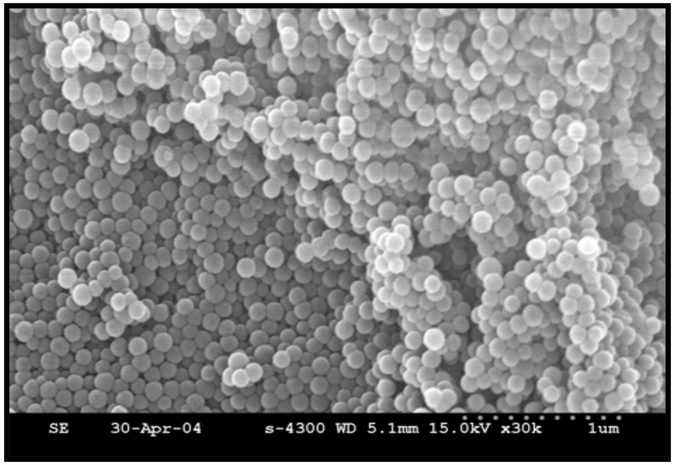




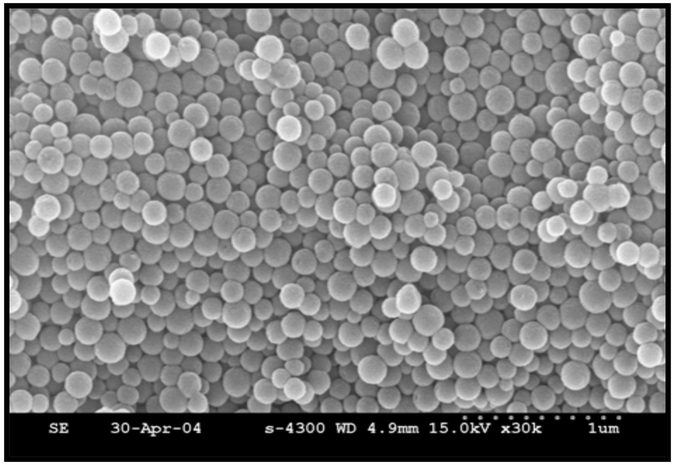
Experimental Results

Average Particle Size & SEM Photographs of PS : 8hr, 80^{o}C





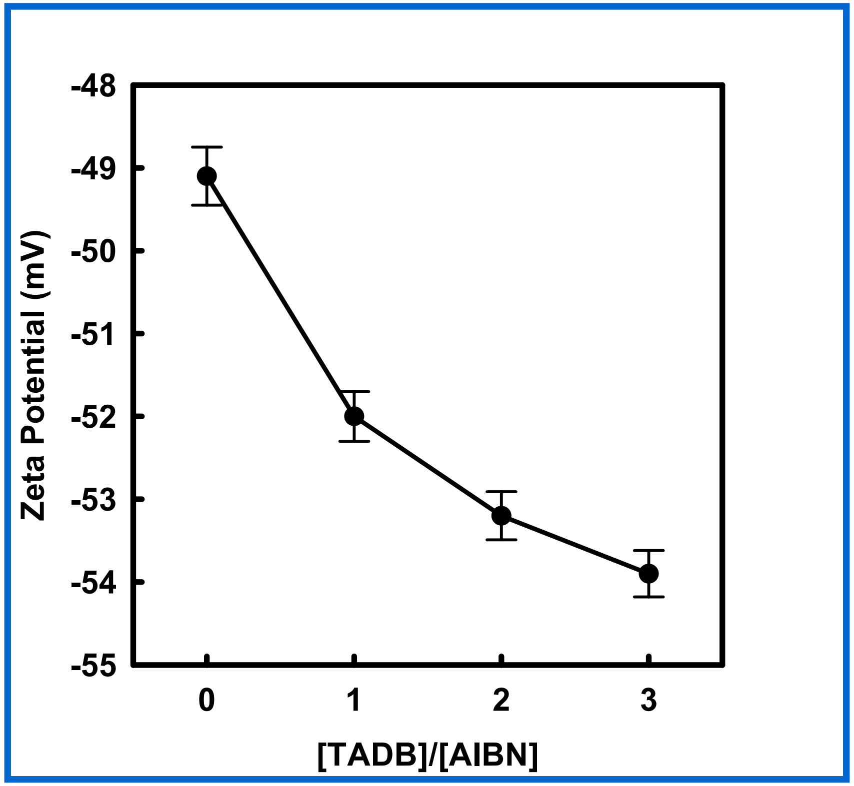
[TADB]/[AIBN]=0, 90nm

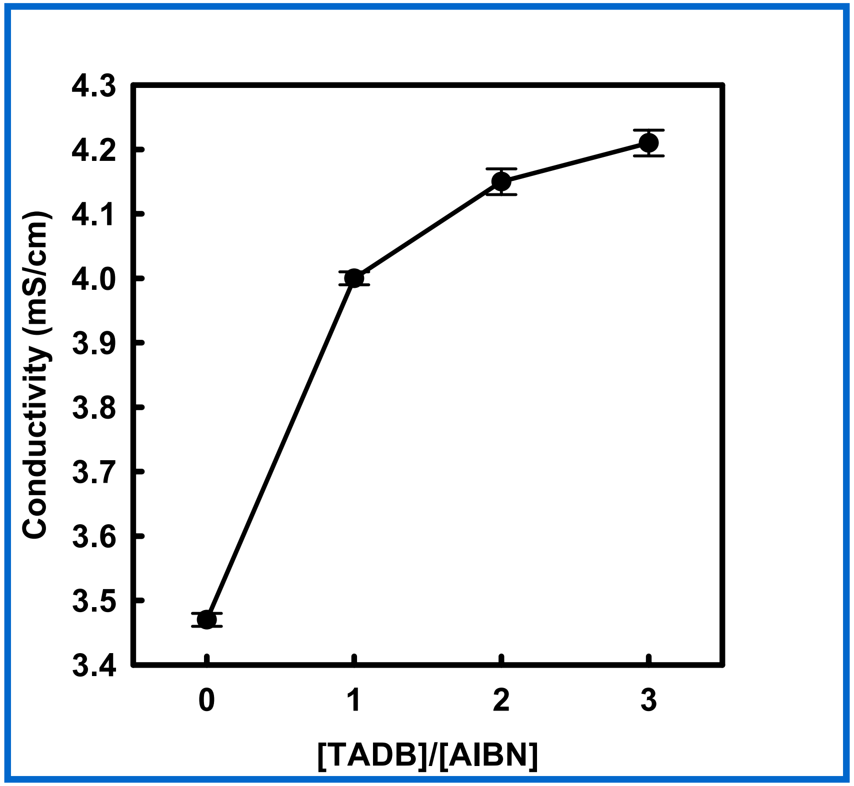


[TADB]/[AIBN]=3, 125nm

Experimental Results

◈ Zeta Potential & Conductivity of PS Latex : 8hr, 80^{o}C





Conclusions

- A linear increase in M_n with respect to the conversion is observed, indicating the nature of living (controlled) radical polymerization.
- The PMMA-system

  - The higher the temperature, the faster conversion, the lower M_n and PDI are obtained.

  - As the ratio of [TABD]/[AIBN] increases, the conversion, molecular weight, molecular weight distribution, and particle size decrease.

  - With the ratio of [TABD]/[AIBN], the zeta potential & conductivity increase, i.e. the stability of the PMMA latex is enhanced.

Conclusions

- The PS-system

  - A BDB (w/o carboxyl acid functionalized)-added system leads to slower conversion, similar M_n and PDI, and larger particle size, however, decreases the zeta potential and conductivity.

  - As the ratio of [TABD]/[AIBN] increases, the conversion, molecular weight, and molecular weight distribution decrease, however, particle size increases.

  - With the ratio of [TABD]/[AIBN], the zeta potential & conductivity increase, i.e. the stability of the PS latex is enhanced.

- The polymer nanospheres functionalized with carboxylic acid group can be prepared by a novel mechanism.