Polymerization and Grafting onto Particle Surfaces via Continuous Flow Chemistry

INTRODUCTION

Polymer-grafted inorganic particles are attractive building blocks for numerous chemical and material applications.

Surface-initiated controlled radical polymerization (**SI-RAFT**) is one of the most feasible methods to fabricate these materials. However, conventional **in-batch approaches** still suffer from several disadvantages, such as **time-consuming purification** processes, **inefficient grafting**, and possible **gelation problems**.[1]

A facile continuous flow method was demonstrated to synthesize homopolymers and block copolymer-grafted inorganic particles in an environmentally friendly aqueous media, using the **Phoenix™ Flow Reactor**.[2]

Immobilization of the **initiator** (or chain transfer) agent and subsequent **polymerization** can be accomplished sequentially in this continuous flow system, avoiding in-between multi-step purification processes. The chain length (MW) of the grafted polymers is tunable by adjusting the flow rate or monomer concentration, and the narrower molar mass dispersity of the grafted polymers reveals the uniform polymer chains on the particles.

STATE OF THE ART:

A facile, controlled, and scalable method to fabricate **polymer-grafted particles** (PGP) in a continuous flow reactor system at a relatively **high temperature** in **water/ethanol** was reported. Utilization of surface-initiated reversible addition fragmentation and chain transfer **(SI-RAFT) polymerization** allowed grafted polymers with relatively **low molar mass dispersity**, and the length of the grafted polymers was adjustable by changing the reaction time or modifying the monomer concentration. Moreover, compared to the conventional **“grafting from” reaction** in a batch reactor, the in-solution “gelation” problem is avoided owing to the flow nature of the continuous system. *(Figure 1.)*.

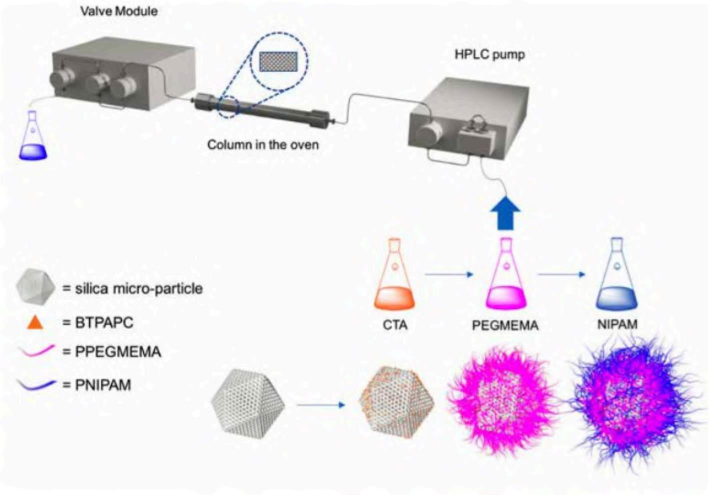

Figure 1. *Schematic diagram illustrating the grafting polymerization of particles (silica) packed in a column via SI-RAFT.*

INSTRUMENTATION

The **Phoenix™ Flow Reactor** is designed to perform reactions up to **450 °C**. The pressure range can reach up to **200 bar** by applying a back pressure regulator.

The reactor is equipped with a **stainless steel column** (99 mm length, 3.8 mm inner diameter), an HPLC pump, and a **Back Pressure Regulator Module** (controlling pressure of the whole system up to 200 bar), supplied by ThalesNano Inc. Both ends of the column were covered with a **stainless steel filter** (10 micron, Valco Instruments) to prevent the particles from being flushed out.

Risk assessment and hazards: Always use the system in a **well-ventilated fume hood** to avoid inhalation of solvent vapors. Never open it at high pressure or temperature, the overheated or pressurized solvents can cause injuries. Avoid contact with the heated parts.

EXPERIMENT

The synthesis of the initiator: **butyl (1-oxo-1-((3-(trimethoxysilyl)propyl)amino)prop-an-2-yl) carbonotrithioate** (BTPAPC) is reported in the publication. The grafting of the BTPAPC initiators to the **Silica microparticles** (SiMP) was done in situ via flow reactor procedures. The synthesis and grafting of **PPEGMEMA-grafted SiMPs** (PPEGMEMA-g-SiMPs) was done via flow reactor procedures and is reported in the publication. Finally, the synthesis and grafting of the block copolymer: **PPEGMEMA-b-PNIPAM-grafted SiMPs** (PPEGMEMAb-PNIPAM-g-SiMPs) via flow reactor was also reported in the publication. Further characterization of the products was done by Size Exclusion Chromatography (SEC), NMR, IR, and thermogravimentric analysis (TGA).

Chemicals and Reagents: (3-Aminopropyl)trimethoxysilane (APSi, 97%), N-(3-Dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride (EDC, commercial grade), Poly(ethylene glycol) methyl ether methacrylate (PEGMEMA, Mn=300), N-Isopropylacrylamide (NIPAM, 97%), 4,4'-Azobis(4-cyanovaleric acid) (ACVA, >=98%), and hydrofluoric acid (HF, 48%) were purchased from Sigma-Aldrich and used as received.

N-Hydroxysuccinimide (NHS, 97%) was purchased from Alfa Aesar. Unless otherwise specified, the purity and chemical structures of the chemical reagents were verified by ^{1}**H NMR**. Hydrochloric acid (HCl) solution (37%) was purchased from British Drug Houses (BDH). Anhydrous ethanol (EtOH) was purchased from Millipore. Deionized (DI) water was produced using a Milli-Q water system. Silica micro-particles were purchased from BDH (BDH9000, 40-63 μm diameter, 60 Å pore size). The carboxylic acid terminated RAFT-CTA, i.e., 2-(((butylthio)carbonothioyl)thio)propanoic acid (BCPA), was synthesized according to the previous literature.

RESULTS AND DISCUSSION

The synthesis of the initiator (or **chain transfer agent**) (CTA) was based on a previously reported procedure. This CTA was then grafted in situ to the **microparticles** (SiMP) packed in the column. After removal of the excess initiators with flushing, the first homopolymer, **PPEGMEMA-gSiMPs**, was grafted via activation of the CTA with the introduction of the free radical initiator **ACVA**. Controlling the temperature and pressure allowed for the **shorter half-life** for activation. By controlling the flow rate, residence time (circulation time) or the monomer feed ratio, it is possible to **control** the **MW** *(Figure 2)*.

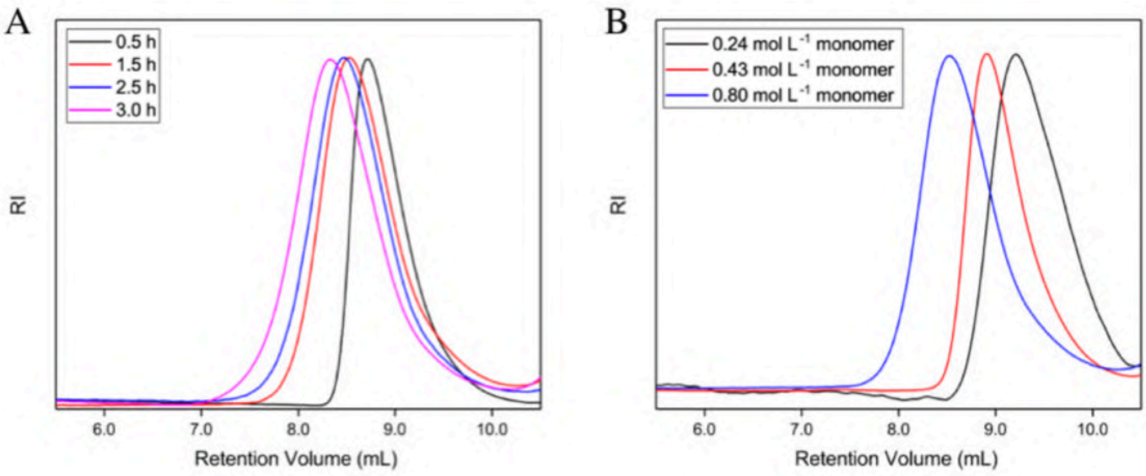

Figure 2. *SEC Data of PEGMEMA Homopolymers grafted on the particle surace: A) Residence time control (longer time, higher MW), B) Monomer feed control (higher Monomer ratio, higher MW). Lower Retention volume = higher MW.*

Secondly, after removing the excess monomers, the block copolymer **PPEGMEMA-b-PNIPAM-g-SiMPs** was prepared. Again, by controlling the flow rate, residence time (circulation time) or the monomer feed ratio, it is possible to control the MW of the second block. The successful grafting of block copolymer with **low molar mass dispersity** was confirmed by **IR spectra**, **SEC curve** and ^{1}**H NMR spectra.** TGA measurements confirmed the change in weight composition upon grafting of the successive blocks of polymers. Because of the thermo-sensitivity of the outer **PNIPAM block**, the surface of **PPEGMEMA-b-PNIPAM-g-SiMPs** became more **hydrophobic** when raising the temperature above the lower critical solution temperature (LCST). This was proven by doing **contact angle–wetting experiments** on the modified particles *(Figure 3)*.

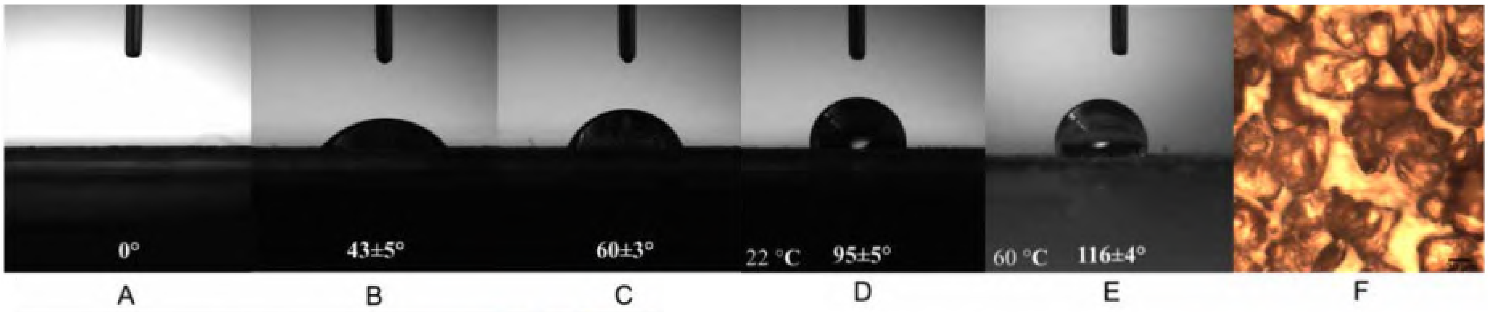

Figure 3. *Contact angle measurement on the particles at various stages of the surface modification, A) unmodified particle, B) SiMP, C) PPEGMEMA, D) PPEGMEMA-b-PNIPAM at room temperature, E) PPEGMEMA-b-PNIPAM at higher temperature, and F) Optical Micrograph of modified particles.*

CONCLUSION

In conclusion, a **facile**, **controlled**, and **scalable** method to fabricate **PGPs** in the Phoenix™ Flow Reactor system at relatively high temperature in water/ethanol was demonstrated. Utilization of **SI-RAFT polymerization** allows to synthesize **grafted polymers** with relatively **low molar mass dispersity**, and the length of grafted polymers is adjustable by changing the reaction time or modifying the monomer concentration.

Moreover, compared with the conventional **"graft from"** reaction in a **batch reactor**, the in-solution "gelation" problem is avoided due to the flow nature of the continuous system. Fabrication of **block copolymer-grafted SiMPs** was also demonstrated due to the living nature of the RAFT polymerization.

Compared with the cumbersome and time-consuming batch fabrication of PGPs and possible gelation problem, the continuous flow chemistry approach allows a **facile fabrication** of **PGP** in a continuous manner with a **more environmentally friendly solvent.** This should open the possibility for more **process control** in actual commercial applications.

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