

# **Application of the Supercritical Fluid Technology for the Synthesis of a Temperature and pH-Sensitive Copolymer**

*Muoi Tang, Department of Chemical and Materials Engineering, Chinese Culture University, Taipei, Taiwan; Sheau-Ling Ho, Department of Chemical and Materials Engineering, Chinese Culture University, Taipei, Taiwan; Yan-Ping Chen, Department of Chemical Engineering, National Taiwan University, Taipei, Taiwan*

This study presents our experimental results for the synthesis of an environmentally sensitive copolymer using the supercritical fluid technology. The physical behaviors of this thermo- and pH-sensitive copolymer change in response to the stimulations. The major target of this study is to demonstrate the feasibility for the green reaction process by employing supercritical carbon dioxide.

A core-shell copolymer is synthesized in this study. N-isopropylacrylamide (NIPAM) as a base material is copolymerized with the hydrophilic monomer N-vinyl-2-pyrrolidinone (VPL) to form the temperature sensitive core, P(NIPAM-co-VPL). Poly(dimethylsiloxane) grafted poly(acrylic acid) (PDMS-g-PAA) contributes as the pH-sensitive shell. The initiator and cross-linker in this reaction are AIBN and Bis, respectively. The final product, P(NIPAM-co-VPL) / PDMS-g-PAA, is a biodegradable core-shell composite. Various analyses using FTIR, SEM, TEM, TGA, UV-Vis spectrometer are reported to confirm the successful synthesis of this core-shell copolymer. The optimal reaction conditions such as the reaction temperature, pressure and the concentrations of the reactants and cross-linker are also reported. Furthermore, the environmental response characteristics of this copolymer product are reported by the in vitro release of a drug compound.

Supercritical fluids (SCF) have versatile properties for the synthesis and processing of various materials. The use of supercritical carbon dioxide (scCO<sub>2</sub>) as a medium in the fields of polymerization, extraction, and micronization has received much attention recently [1]. We demonstrate a one-step copolymerization to synthesize multi-responsive hydrogels with core-shell structures using scCO<sub>2</sub> as reaction medium. PDMS-based materials, which have high chain flexibility are soluble in CO<sub>2</sub>, and offer extra properties such as physiological inertness, good blood

compatibility, thermal and oxidative stability, and mechanical integrity to the composites. The assistance of PDMS-g-PAA stabilizes the polymer particles sterically in the dispersion polymerization, and contributes to additional functionality to the final product.

During the copolymerization, the clear appearance became opaque after 1 hour, and then the precipitate formation was observed immediately. Primary radicals were formed from thermally promoted fragmentation of AIBN, which initiated the copolymerization of NIPAM and VPL in the presence of BIS cross-linker. As the first polymer chains were produced, the system became heterogeneous. Generally, the surfactant sterically stabilized the dispersion of solid particles in scCO<sub>2</sub> phase. It was postulated that PDMS-g-PAA was effective amphipathic stabilizer because it contained CO<sub>2</sub>-phobic graft anchoring onto the insoluble polymer chains and the CO<sub>2</sub>-philic backbone stretching into continuous scCO<sub>2</sub> phase [2].

A typical TEM analysis of the reaction products is presented in Fig. 1. The formation mechanism can be postulated that the thermo-sensitive copolymers formed as the cores and the pH-sensitive material, PDMS-g-PAA, acted as stabilizer to emulsify CO<sub>2</sub>-insoluble cores and prevent polymer particles from coagulation.

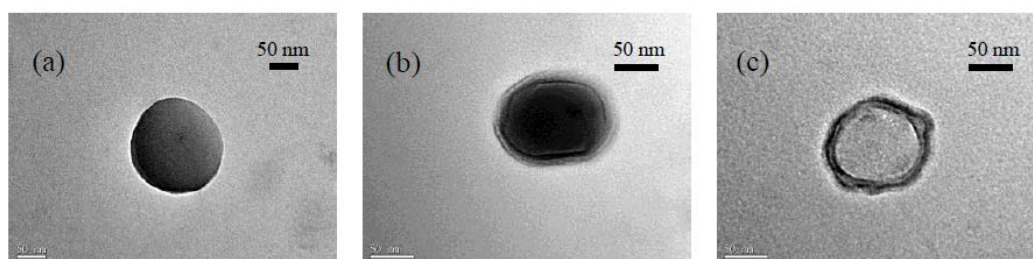


Fig. 1. TEM images of (a) P(NIPAM-co-VPL), (b) P(NIPAM-co-VPL)/PDMS-g-PAA at room temperature, (c) P(NIPAM-co-VPL)/PDMS-g-PAA at 60°C.

## References

- [1] W. Wang, S. M. Howdle, D. Yan, *Chemical Communication*, **31**, 3939-3941 (2005).
- [2] Q. Zhao, E. Samulski, *Polymer*, **47**, 663-671 (2006).