Synthesis of new carbon fiber precursors using AGET ATRP in microemulsion

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Three precursor materials are used for manufacturing of carbon fibers such as rayon, polyacrylonitrile (PAN) and mesophase. Among these, PAN has been the most widely used material for carbon fiber precursors because of its outstanding chemical and mechanical properties. Approximately, 90% of the global production of carbon fibers originates from PAN precursors [1]. Through the incorporation of several co-monomers, such as methyl acrylate, in PAN structure is used to improve the processability and mechanical properties of PAN-based precursor fiber. Acidic co-monomer such as acrylic or itaconic acid catalyzes the cyclization of nitrile groups during the heat treatment of PAN precursors in stabilization step. PAN copolymer architecture, which defines the location of co-monomer along PAN chain, is an important factor for controlling the final properties of the resulting carbon material.

High molecular weight and narrow polydispersity index are essential requirements for PAN synthesis in order to fulfill the need for high performance PAN fibers. Controlled/ “living” radical polymerization is a suitable tool for synthesis of the desirable PAN copolymer with various co-monomers. Atom transfer radical polymerization (ATRP) leads to polymers with predefined molecular weights, narrow polydispersity index and preferred molecular architectures [2]. However, normal ATRP is difficult to handle due to its air and humidity sensitivity since the use of low valent transition metal as catalyst is required. The newly AGET (activator generated by electron transfer) ATRP technique is used to overcome the limitations of normal ATRP and provide a more convenient method to initiate ATRP via using a reducing agent.

In recent years, research is interested in more environmental and economic synthetic techniques of products. In the case of PAN-based precursor fiber, to date, conventional radical polymerization in organic dispersed media is used for the synthesis of PAN copolymers [3]. Water based methods have attracted interest lately; because of their well-known properties and pollution free to environment [4]. The AGET technique is the most convenient method for initiating an ATRP in a microemulsion system. The technique ”one-pot”, “two-step” (Fig. 1) was first performed by Matyjaszewski’s group to carry out ATRP in a microemulsion system resulting in the preparation of stable translucent microlatexes [5].

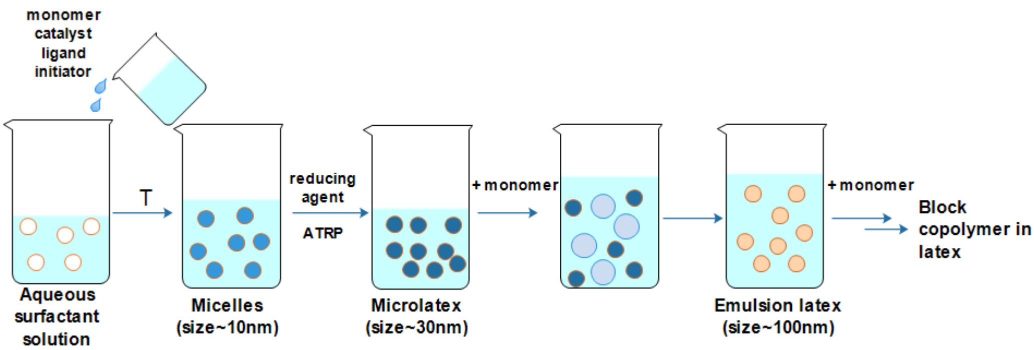

Figure 1: Schematic illustration of ATRP in an emulsion by using the two-step procedure [5].

In this study, the technique ”one-pot”, “two-step” based on microemulsion was used to conduct PAN copolymers with a variety of co-monomers. Specifically, diblocks PAN-b-PMMA, PAN-b-PIA and triblock PAN-b-PMMA-b-PIA were synthesized via AGET ATRP in microemulsion. The investigation of controlled/ “living” polymerization character was demonstrated by kinetic data. Gel permeation chromatography (GPC) and ^{13}C NMR analyses were used to monitor the polymerization process and to evaluate the living character. For instance, in the case of biblock PAN-b-PMMA, the

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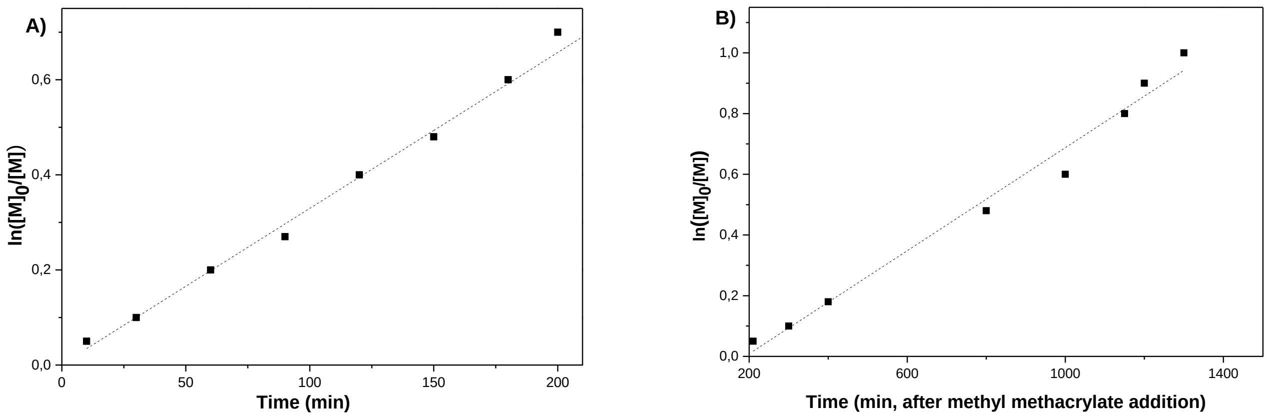
polymerization was controlled before and after MMA addition, as evidenced by the two-linear first-order kinetic plots (Fig. 2).



<u>Figure 2</u>: First-order kinetic plot for (A) AGET ATRP of AN and (B) for chain extension by adding MMA in situ at 200 min in an ab initio emulsion.

References

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