

# Structural & Physical Characterization of Supramolecular Diblock Copolymers

Cheng-Yuk Lee, Chemical Engineering, University of Massachusetts Amherst  
NNIN REU Site: Nanotech, University of California at Santa Barbara

NNIN REU Principal Investigator: Dr. Edward J. Kramer, Chemical Engr, University of California Santa Barbara

NNIN REU Mentor: Kathleen E. Schaefer, Materials Dept, University of California Santa Barbara

Contact: ChengL@student.umass.edu, dkramer@mrl.ucsb.edu, schaefer@mrl.ucsb.edu

## Abstract:

Recent interest in diblock copolymers has grown because of their ability to form periodic structures on the size scale of 10-100 nm; hence, these materials can be used for advanced lithographic templating applications. However, supramolecular diblock copolymers, in which the bond between the two blocks can be reversibly broken at high temperature, have not yet been effectively characterized. In order to better understand their behavior, we are developing a model covalent diblock copolymer system. We were especially interested in measuring their order-disorder transition (ODT) temperatures ( $T_{ODT}$ ) by using small-angle X-ray scattering and rheology to determine the relationship between  $T_{ODT}$  and the degree of polymerization, providing a reference point for future studies of more complex systems.

## Introduction:

Block copolymers are very common in our daily life, for example in upholstery foam and adhesive tape [1]. Diblock copolymers consist of two thermodynamically incompatible homopolymers linked by a covalent bond. Due to thermodynamic incompatibility, they tend to phase separate from each other. The phase separation depends on three variables: temperature, chemical incompatibility, and chain length. At temperatures below the characteristic ODT, the two blocks microphase separate; however, above  $T_{ODT}$  they become miscible. The goal of this project is the measurement of  $T_{ODT}$  for symmetric diblock copolymers of different molecular weights of poly(benzyl methacrylate-block-tert butyl acrylate) (P(bnMA-b-tBA)).

## Materials and Procedure:

Living free radical polymerization by reversible addition-fragmentation (RAFT) was used to synthesize the symmetric diblock copolymers [2]. The synthesis of p(bnMA-b-tBA) involved two steps. First poly(benzyl methacrylate) was synthesized by dissolving benzyl methacrylate (3.3M), RAFT agent (0.066M), and 2,2'-Azobis(2-methylpropionitrile) (AIBN, 0.0132M) initiators in 10 mL of dioxane. The reaction mixture

was sealed in a glass ampule under vacuum and heated at 70°C for the desired reaction time, then cooled and precipitated into methanol to isolate the p(bnMA) macro-RAFT agent. The second block was added by mixing tert-butyl acrylate (4.5M) with p(bnMA) macro-RAFT agent (0.0155M) and AIBN (0.9M) into 10 mL of dioxane. The reaction mixture was again sealed under vacuum and heated at 70°C for their desired reaction time.

Polymers were characterized by nuclear magnetic resonance (NMR), gel permeation chromatography (GPC) and rheology. NMR was used to determine the conversion of the reaction and the estimated molar composition of the diblock copolymers. GPC was used to determine the average molecular weight ( $M_n$ ) of the polymer relative to polystyrene and the polydispersity index (PDI). Rheological measurements were performed to obtain the  $T_{ODT}$ .

## Results and Discussion:

In RAFT polymerizations, the molecular weight of the polymer can be controlled either by the reaction time or the molar ratio of monomer to RAFT agent in the reaction mixture. Polymerization kinetics were studied by keeping the reactant concentrations constant while running the reaction for different amounts of

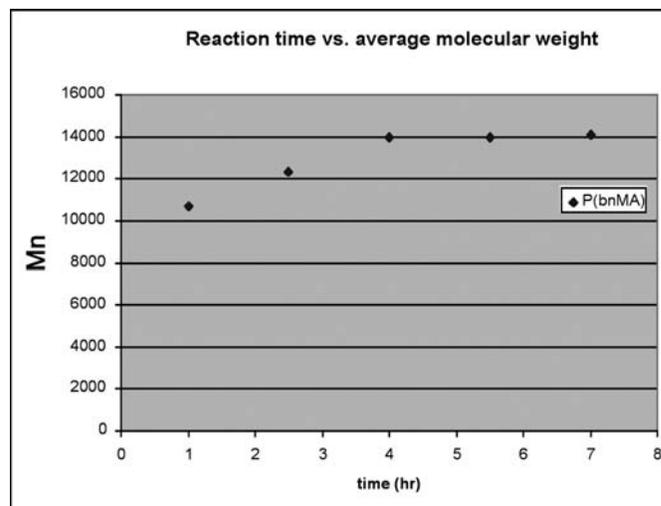


Figure 1: GPC data from poly(benzyl methacrylate) samples.

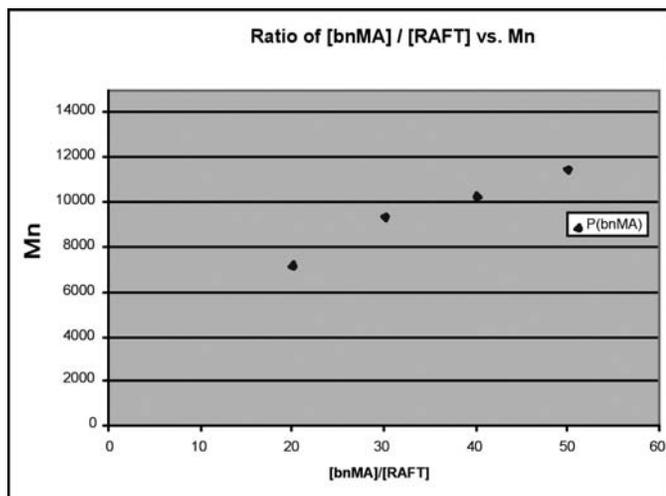


Figure 2: The relationship between  $M_n$  and concentration ratio of reactants.

time, ranging from 1 to 7 hours; Figure 1 is a plot of  $M_n$  as a function of reaction time, which indicated that the  $p(\text{bnMA})$  reached a maximum molecular weight at a reaction time of 4 hours. Four different molecular weights were also synthesized by running reactions at ratios of 20, 30, 40, and 50 moles of monomer per mole of RAFT agent.

GPC data are plotted in Figure 2, which displays that the molecular weight is directly proportional to the molar ratio of monomer to RAFT agent.  $^1\text{H}$  NMR and GPC were run to determine the molecular weight as well as the diblock copolymer composition. In order for  $p(\text{bnMA}-b-\text{tBA})$  to be symmetric (each block occupying the same volume), the number of monomers in the  $p(\text{bnMA})$  block  $N_{\text{bnMA}}$  and  $p(\text{tBA})$  block  $N_{\text{tBA}}$  must have the following relationship [3]:

$$N_{\text{tBA}} = 1.28N_{\text{bnMA}}$$

The estimated compositions were obtained by integrating the area of the corresponding peaks from  $^1\text{H}$  NMR data of  $p(\text{bnMA}-b-\text{tBA})$ , and are shown in Figure 3. It was observed that reaction time for the three lowest molecular weight  $p(\text{bnMA})$  samples should be shorter than 0.5 hr.  $^{13}\text{C}$  NMR was also used to measure the composition of the highest molecular weight diblock copolymer, and the estimated  $p(\text{tBA})$  block length was roughly 1.32 times that of  $p(\text{bnMA})$ , suggesting that the high molecular weight polymer was symmetric. This sample was then measured with the rheometer to determine  $T_{\text{ODT}}$ .

Due to instrumental limitations it was not possible to measure a clear transition, but it was certain that  $T_{\text{ODT}}$  was below  $80^\circ\text{C}$ .

## Conclusion & Future Work:

It was found that both reaction time and the concentration ratio of monomer to RAFT agent had major effects on the degree of polymerization. To compare the behavior of these diblocks against a related system in which the link between the two blocks can be broken at higher temperatures, it is necessary to study higher molecular weights with  $T_{\text{ODT}}$  around  $100^\circ\text{C}$  to  $150^\circ\text{C}$ . In the future, the covalent bonded diblock copolymers model system will be tested with small angle X-ray scattering (SAXS) and UV absorption. SAXS is an alternative method for determining the  $T_{\text{ODT}}$  as well as the morphology of the diblock copolymers, and UV absorption can be used to measure the absolute molecular weight of the diblock copolymers.

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## References:

- [1] F.S. Bates and G.H. Fredrickson, Block Copolymers-Designer Soft Materials, *Physics Today*, Feb 1999, 32-38.
- [2] S. Perrier, P. Takolpuckdee, and C.A. Mars, Reversible Addition-Fragmentation Chain Transfer Polymerization: End Group Modification for Functionalized Polymers and Chain Transfer Agent Recovery, *Macromolecules*, 2005, 38, 2033-2036.
- [3] This equation was obtained by Katie Schaefer, Materials Dept, University of California, Santa Barbara.

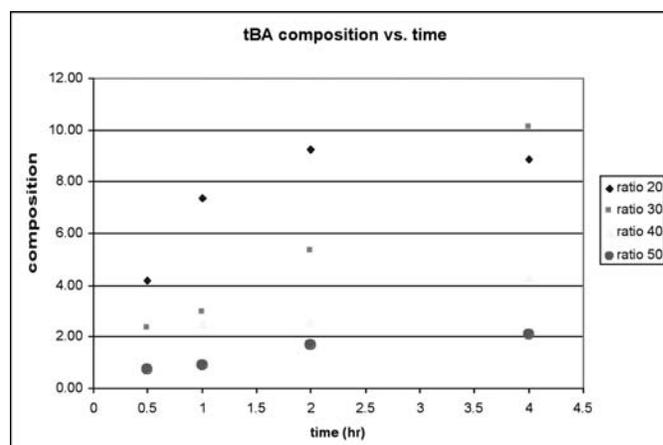


Figure 3:  $t\text{BA}$  block composition verse time.