Roberto Fernandez Alvarez, Ph.D.
LAM-X a.s.
Inovační 122, 252 41 Zlatniky-Hodkovice
Czech Republic

04st of September, 2024

Ing. Mariusz Marcin Uchman, Ph.D
Charles University
Hlavova 2030/8, 128 00 Prague 2
Czech Republic

Dear Dr. Uchman:

The bachelor thesis of Eliška Müllerová deals with the synthesis of stimuli responsive homopolymers and copolymers via ATRP. The synthesized polymers are able to respond to changes of temperature by changing their solubility. Extensive variables were explored during the polymer synthesis to obtain good control of the polymerization process and ensure low dispersity of the resulting polymer. The work performed for this thesis encompasses a great number of techniques in synthetic chemistry, and characterization techniques for polymer systems.

The introduction of the thesis is well structured, the ample coverage on how the individual components of the reaction affect the end-product mirror the careful work performed along the entire thesis. The results and discussion are extensive with most experimental results being justified in an articulate way which allow to easily understand the main point.

From Table 1. and its subsequent explanation it is not clear which of the variables is responsible for the changes observed. When comparing *EM1* vs *EM3* the component ratio was varied but also there is a vast difference in time of reaction. Same when comparing *EM7* vs *EM12*, the difference between entries are in component ratio, time of reaction and temperature. The data thus presented does not allow for a clear conclusion of which of the variables affect the observed molecular weight and molar mass distribution. The above discussed also applies to Table 3.

The entire thesis is relatively free of mistakes with the only exception of Figures 21 and 23 there is an incorrect structure of 3-APBAE group after polymerization. Namely, the relative position of the aromatic ring substituents changes from *meta*- to *para*- position. Furthermore, this mistake extends to the NMR signal analysis in Figure 23, once the correct position is considered. Additionally, there is no Figure 22.

There could be a deeper discussion on how each variable truly affects the end polymer. As previously mentioned, by changing one variable at a time and observing the result. This process, understandably, takes a long time and potentially escapes the scope of the current thesis. Nonetheless, establishing

such methodology and way of working will help the student perform even higher quality work than the one presented here.

Furthermore, the conclusions about copolymers and their T_{cp} would be strengthened considerably by preparing polymers with different fractions of each monomeric unit and observe if there is a trend of decreasing T_{cp} with increasing fraction of 3-APBAE.

Finally, as part of my review I would like to submit a series of questions for the author of the bachelor thesis:

1) Explain why more polar solvents increase the activation rates of ATRP reactions?
2) During the preparation of mDEGA, the NMR shows 4 triplet signals in the 4.3-3.5 ppm area. These correspond to the protons of the ethylene glycol units. Which of these protons do you expect to be the one at 4.3 ppm and why?
3) Why is EBiB a more efficient initiator than EBP?
4) Why does the high hygroscopicity of polymeric boronic acids affects the characterization via GPC method?
5) What is happening at a molecular level to p(mDEGA) at the T_{cp}?
6) Why does the cloud point decreases with increasing polymer concentration?

In conclusion, the work performed encompasses many experimentally complex tasks ranging from synthesis of monomers, polymer synthesis, synthesis under inert atmosphere, post polymerization modifications, purification and isolation and subsequent molecular characterization. All of which reflect a great amount of work and dedication not commonly seen at this level. Because of all these and the meticulous testing of experimental variables I grade this work as 1-Excellent.

Kind regards,

Roberto Fernandez Alvarez, Ph.D.
COO
LAM-X a.s.

Date