

## Template polymerization of multi-vinyl monomer with poly(2-hydroxyethyl methacrylate) backbone

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### Introduction

Template polymerization has been well investigated since mid-80s because it was highly expected to be a convenient and useful method to control the molecular weight and molecular weight distribution<sup>1,2</sup>. However, the strict control has not been succeeded due to the difficulty of control of radical concentration. It is possible to control the radical for polymerization by so-called "controlled/living radical polymerization"<sup>3,4</sup>. The introduction of the concept of controlled/living radical polymerization into the template polymerization provides novel approach to strictly control the architecture of macromolecules.

Based on this concept, authors have been synthesized the multi-vinyl monomers with  $\alpha$ - and  $\beta$ -cyclodextrins for templates, then copper-mediated atom transfer radical polymerization was carried out. When the polymerization conditions were optimized, the polymerization was limited in the molecules of multi-vinyl monomer, as a result, well-defined methacrylic acid oligomers with 6, 7, and 14 of with degrees of polymerization were selectively synthesized<sup>5,6</sup>. Additionally, cyclic oligomers were obtained by connect the initiated and propagating sides of the sequences<sup>6</sup>.

In case of multi-vinyl monomer with linear polymer for the template, if the template polymerization propagates along the backbone of the multi-vinyl monomer, ladder-like polymer will be

obtained. However, it is unclear that whether it is possible to propagate the polymerization along the backbone or not. In this work, multi-vinyl monomer was synthesized by esterification of hydroxyl group of poly(2-hydroxyethyl methacrylate), which was prepared by copper-mediated atom transfer radical polymerization, with methacryloyl chloride, and copper-mediated ATRP was carried out. The propagation of polymerization in the multi-vinyl monomer was investigated by kinetic analysis.

### Experimental, Results and discussion

Poly(2-hydroxyethyl methacrylate) was prepared with  $\alpha, \alpha'$ -dibromo-*p*-xylene and dipyriddy as an initiator and a ligand, respectively, by copper-mediated atom transfer radical polymerization at room temperature. Then, to prepare multi-vinyl monomer, hydroxyl groups were esterified with methacryloyl chloride by Shotten-Baumann method based on the literature<sup>7</sup>. The maximum conversion of esterification was 90.0%.

Multi-vinyl monomer was polymerized with and without  $\alpha, \alpha'$ -dibromo-*p*-xylene in water/1,4-dioxane mixtures and water/THF mixtures at different temperature in a range from 25 to 40 °C. The conversion of methacryloyl group was measured by FT-IR. When the initiator was not added to the multi-vinyl monomer, the GPC profile became bimodal, indicating that it was impossible to hinder the inter-molecular polymerization. It would be due to the fact the initiating sites existing on the chain ends were covered with ester groups of branches. When the initiator was newly added for the template polymerization, no gelation was observed, the maximum conversion of vinyl group reached 75.9% without inter-molecular polymerization.

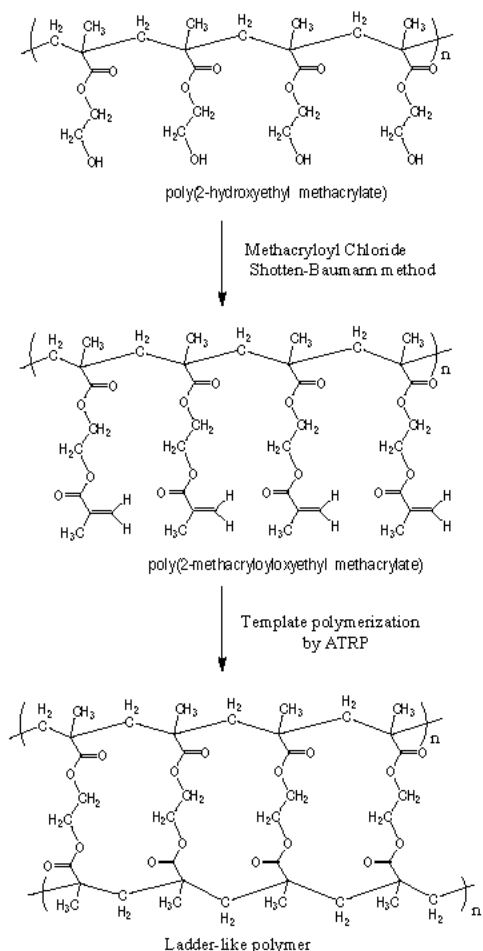
The kinetic plot was obtained in case of the addition of initiator. In case of 25 °C, the copper-mediated ATRP of multi-vinyl monomer proceeded in a living manner with the appeared polymerization rate,  $5.0 \times 10^{-5} \text{ s}^{-1}$ . It was very close to that of the copper-mediated ATRP in bulk. This indicates that the vinyl groups were highly concentrated in the molecule of multi-vinyl monomer.

### Conclusions

When ATRP was combined with template polymerization, it was possible to prevent the gelation of the solution. The polymerization of ATRP was limited in the molecule of multi-vinyl monomer and proceeded in a living manner. From kinetic analysis, the polymerization in the multi-vinyl monomer proceeded in a living manner.

### References

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**Scheme 1.** Synthesis of ladder-like polymer by combination of template polymerization and copper-mediated ATRP