

## Electronic Supplementary Information

# Accelerated Nitroxide-Mediated Polymerization of Styrene and Butyl Acrylate Initiated by BlocBuilder MA Using Flow Reactors

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## Materials

All reagents were used as received without any purification. BlocBuider MA (BBMA) was provided by Arkema. Styrene (St), acetol, malononitrile, acetylacetone, were purchased from WAKO. Butyl acrylate (BA), acetoin,  $\alpha$ -hydroxy- $\gamma$ -butyrolactone, ethyl acetoacetate and diethyl malonate were purchased from TCI. 2-Methoxypropyl-1-acetate (PMA) was purchased from Nippon Nyukazai.

## Analysis

### *Conversion determination for polymerization*

0.3-0.4 g of the obtained polymer solution after polymerization was put into an aluminum plate, and then diluted and spread with ethyl acetate on it. The diluted solution was heated at 150 °C for 30 min. After the drying process, the aluminum cup was weighed. The conversion for polymerization was calculated by the equation below.

$$\text{Conversion} = \frac{W_{\text{before}} - W_{\text{after}}}{W_{\text{sample}}} * \frac{m_{\text{monomer}} + m_{\text{alkoxyamine}} + m_{\text{solvent}} + m_{\text{additive}}}{m_{\text{monomer}} + m_{\text{alkoxyamine}}}$$

Equation 1

$W_{\text{before}}$ : the weight of the aluminum cup before the drying process

$W_{\text{after}}$ : the weight of the aluminum cup after the drying process

$W_{\text{sample}}$ : the weight of the sample on the aluminum cup before the drying process

$m_{\text{monomer, alkoxyamine, solvent}}$ : the weight of each component

$m_{\text{additive}}$ : the weight of the additive like acetol

### *Molecular weight determination*

The number-average molecular mass ( $M_n$ ) and polydispersity index (PDI) of the resulting polymer were determined by means of a gel permeation chromatography (GPC), which is equipped with a Waters Separation module e2695 and Waters Refractive index detector 2414. The combination of Straygel HR1, 2, 4 was used as the separation columns. Tetrahydrofuran (THF) was used as the mobile phase at a flow rate 1.0 mL/min at 40 °C.

## **Procedures for polymerization**

### *General procedure for NMP of St in batch reactors*

BB MA (0.600 g, 1.57 mmol) and St (8.1913 g, 78.6 mmol) are dissolved in PMA (5.850 g, 40 wt%) ([St]: [BBMA]=50: 1) in a 35 mL test-tube. The test tube was equipped with a magnetic stirrer, and sealed with a cap. The test tube was immersed in an oil bath at 120 °C with stirring for 2h. The obtained reaction mixture was analyzed for monomer conversion using Equation 1, and for  $M_n$ ,  $M_w$  and PDI by GPC without any work-up.

#### *General procedure for NMP of St in flow reactors*

BB MA (0.600 g, 1.57 mmol) and St (8.1913 g, 78.6 mmol) are dissolved in PMA (5.850 g, 40 wt%) ([St]: [BBMA]=50: 1). The solution was charged into a 10 mL syringe, and it was put to a syringe pump. The solution went through a 1.5 m stain-less tube with internal diameter (i.d.) of 1 mm, which was immersed in an oil bath at 120 °C. The tube reactor's volume was 1.178 mL, and the retention time was 2h with the flow rate 0.589 mL/h. The obtained reaction mixture was analyzed for monomer conversion using Equation 1, and for  $M_n$ ,  $M_w$  and PDI by GPC without any work-up.

#### *General procedure for NMP of BA in batch reactors*

BB MA (0.400 g, 1.05 mmol) and BA (6.7203 g, 52.4 mmol) are dissolved in PMA (5.480 g, 43.5 wt%) ([BA]: [BBMA]=50: 1). The test tube was equipped with a magnetic stirrer, and sealed with a cap. The test tube was immersed in an oil bath at 120 °C with stirring for 2h. The obtained reaction mixture was analyzed for monomer conversion using Equation 1, and for  $M_n$ ,  $M_w$  and PDI by GPC without any work-up.

#### *General procedure for NMP of BA in flow reactors*

BB MA (0.400 g, 1.05 mmol) and BA (6.7203 g, 52.4 mmol) are dissolved in PMA (5.480 g, 43.5 wt%) ([BA]: [BBMA]=50: 1). The solution was charged into a 10 mL syringe, and it was put to a syringe pump. The solution went through a 1.5 m stain-less tube with internal diameter (i.d.)

of 1 mm, which was immersed in an oil bath at 120 °C. The tube reactor's volume was 1.178 mL, and the retention time was 2h with the flow rate 0.589 mL/h. The obtained reaction mixture was analyzed for monomer conversion using Equation 1, and for  $M_n$ ,  $M_w$  and PDI by GPC without any work-up.

*General procedure for NMP with additives for accelerating reaction in flow reactors*

BB MA (0.400 g, 1.05 mmol), BA (6.7203 g, 52.4 mmol), additives like acetol or malononitrile are dissolved in PMA (5.480 g, 43.5 wt%) ([BA]: [BBMA]=50: 1). The solution was charged into a 10 mL syringe, and it was put to a syringe pump. The solution went through a 1.5 m stain-less tube with internal diameter (i.d.) of 1 mm, which was immersed in an oil bath at 120 °C. The tube reactor's volume was 1.178 mL, and the retention time was 2h with the flow rate 0.589 mL/h. The obtained reaction mixture was analyzed for monomer conversion using Equation 1, and for  $M_n$ ,  $M_w$  and PDI by GPC without any work-up.