Supplementary Material

Radical Copolymerization Kinetics of Bio-Renewable Butyrolactone Monomer in Aqueous Solution

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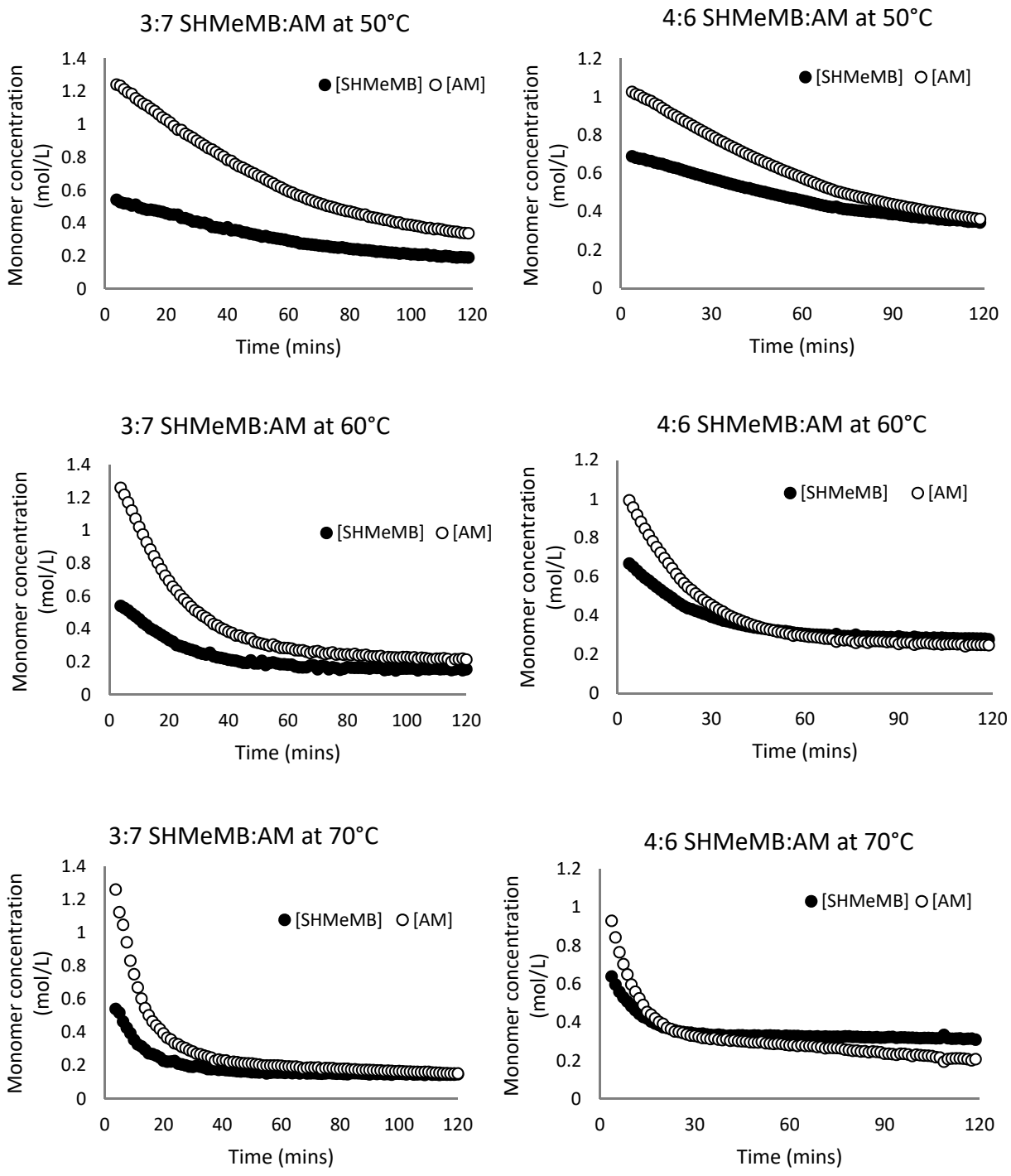

Figure S1: SHMeMB and AM concentrations as a function of reaction time for aqueous solutions with 15 wt% monomer, 0.5 wt% V-50, and 3:7 (left) and 4:6 (right) SHMeMB:AM molar ratios polymerized at 50 (top), 60 (middle) and 70 (bottom) °C.

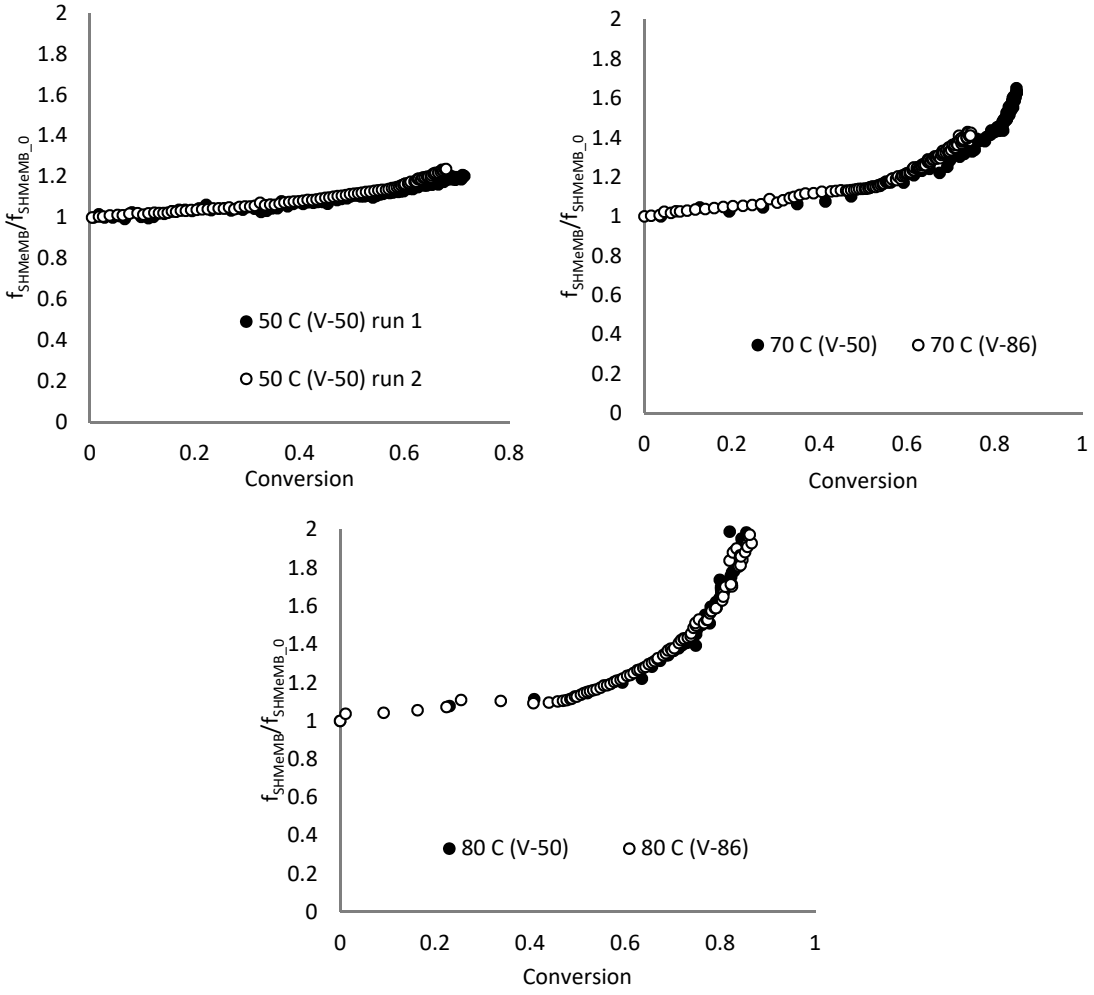

Figure S2: A comparison of monomer composition drift measured using two different initiators (V-50 and V-86) for copolymerization of 3:7 molar ratio of SHMeMB:AM with 15 wt% monomer at various temperatures.

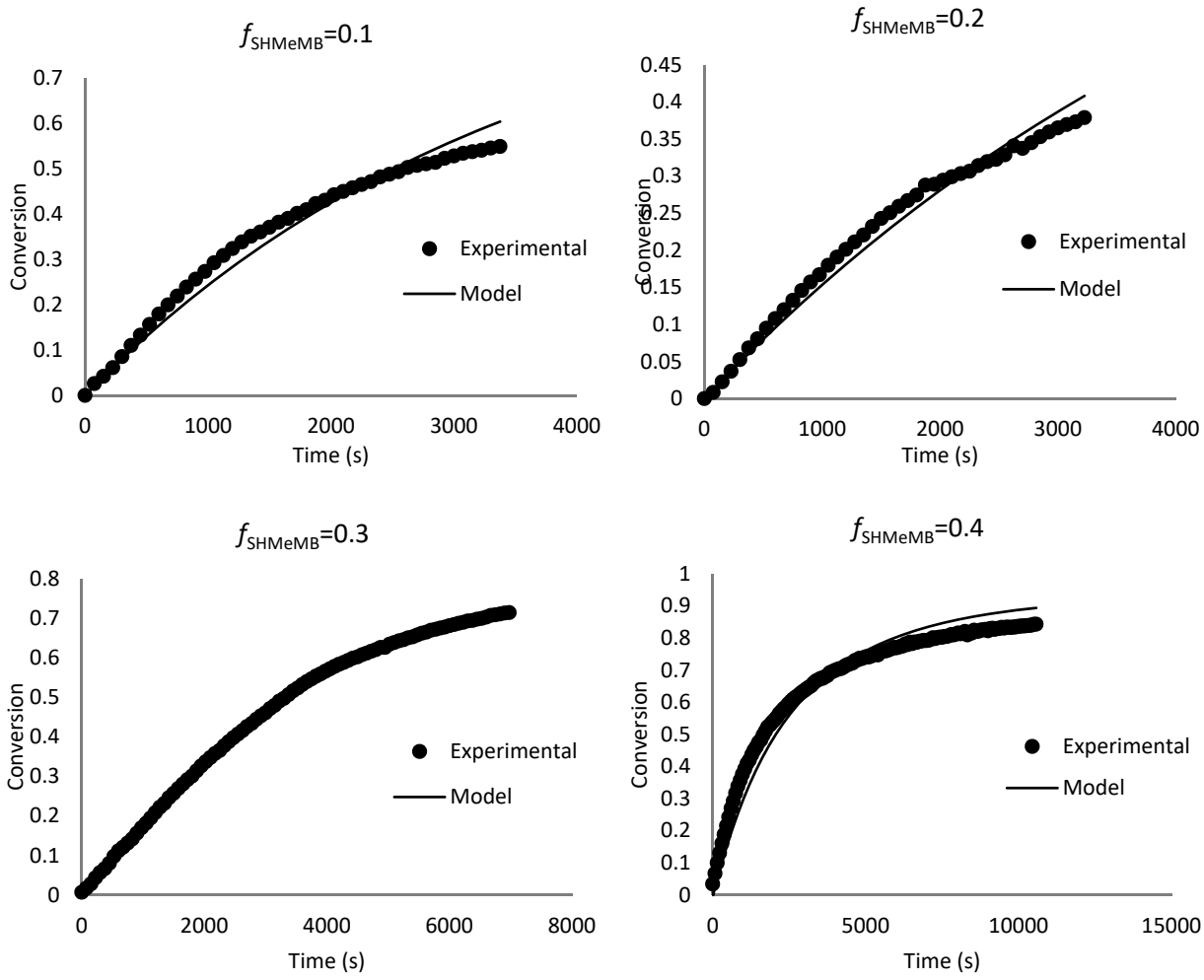

Figure S3 (with figure caption) continued on next page.

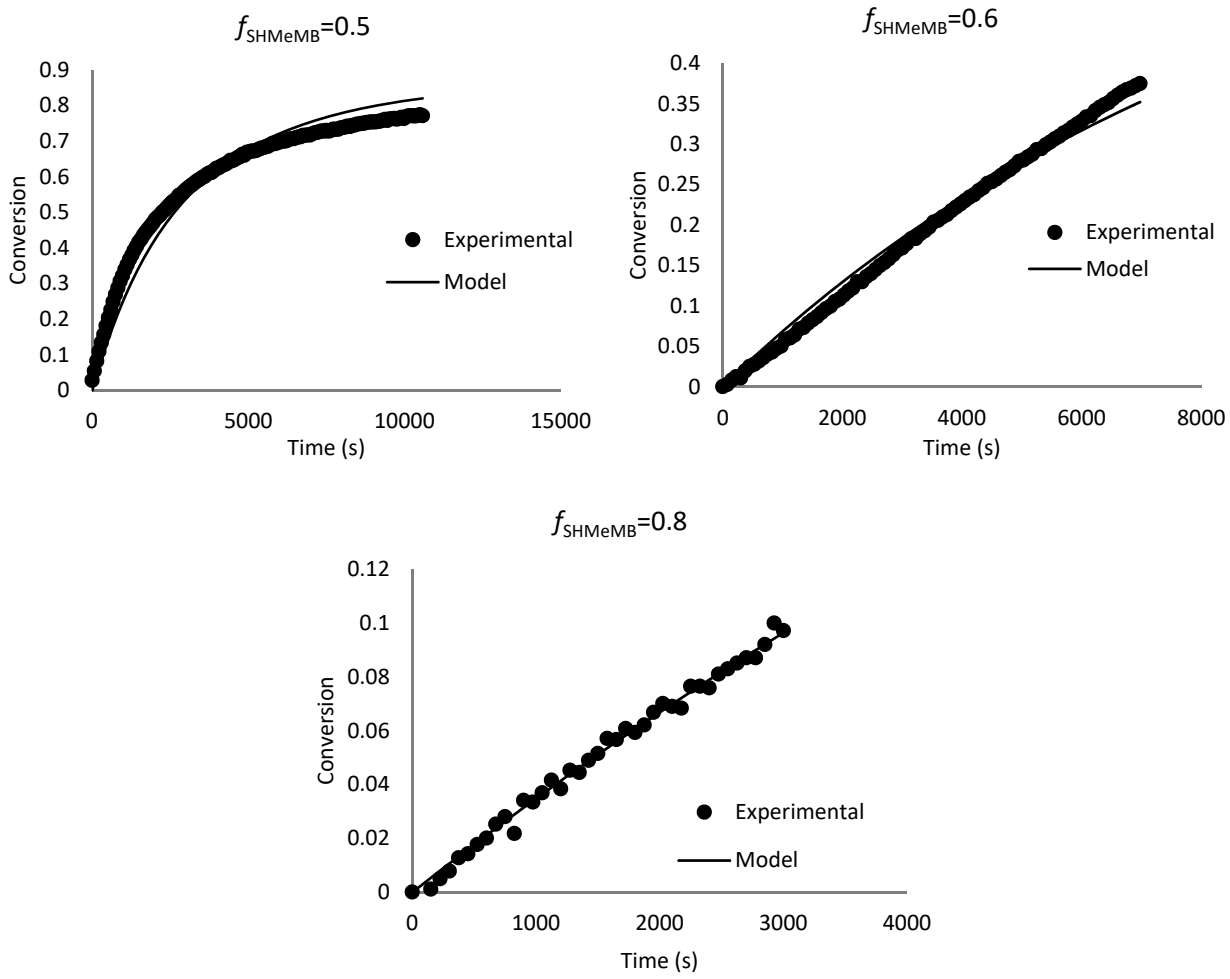

Figure S3: Monomer conversion (points) measured from SHMeMB:AM copolymerizations at 50 °C with 0.5 wt% V-50 and 15 wt% monomer conducted at various initial mole fractions of SHMeMB, as indicated. The lines are simulation output calculated using the best-fit k_t values estimated from the data (see Figure 11 of the paper), with the remaining kinetic coefficients taken from Table 2.

For all of the copolymerization simulations shown in Figure S3, a $k_{p,AM}$ value of 86037 L/mol·s (calculated at 15 wt% AM) was used. The impact of this assumption needs to be checked, as the PLP-SEC study (reference 18 of paper) demonstrated a slight variation in $k_{p,AM}$ with AM concentration. Actual AM concentrations in the various SHMeMB:AM mixtures are summarized in Table S1, along with the corresponding $k_{p,AM}$ values calculated using the correlations from [18]. However, since k_p^{cop} is dominated by the low value of $k_{p,SHMeMB}$ and not sensitive to small changes in $k_{p,AM}$, these small differences do not impact the k_t estimation. For example, SHMeMB:AM copolymerization with f_{SHMeMB}=0.8 at 50°C and 15 wt% monomer was also simulated using a $k_{p,AM}$ value of 104911 L/mol·s, The value of k_t estimated from the conversion profile was found to be 6.94 ± 0.26×10^5 L·mol^{-1}·s^{-1}, as opposed to 6.96 ± 0.26×10^5 L·mol^{-1}·s^{-1} when using a $k_{p,AM}$ value of 86037 L·mol^{-1}·s^{-1}, a negligible difference.

Table S1: Propagation rate coefficients of acrylamide calculated as a function of AM concentration for SHMeMB:AM copolymerization at 15 wt% and 50°C.

f_{SHMeMB}	AM wt%	$k_{p,AM}$ (L·mol^{-1}·s^{-1})
0.1	12.8	89040
0.2	10.8	91810
0.3	8.9	94393
0.4	7.3	96791
0.5	5.8	99028
0.6	4.5	101118
0.8	2.1	104911