## **Supplementary Information.**

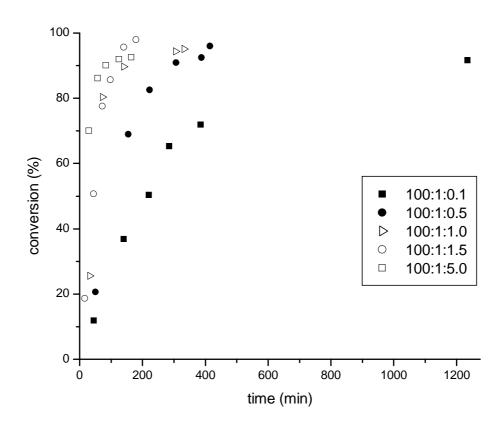
Investigation of the experimental factors affecting the trithiocarbonate-mediated RAFT polymerization of methyl acrylate.

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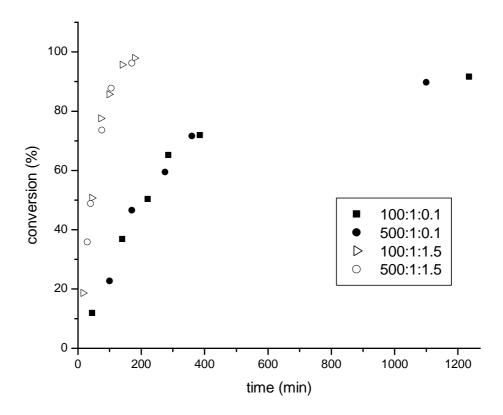
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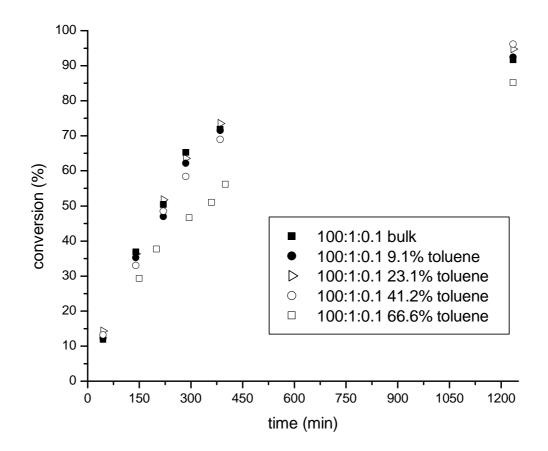
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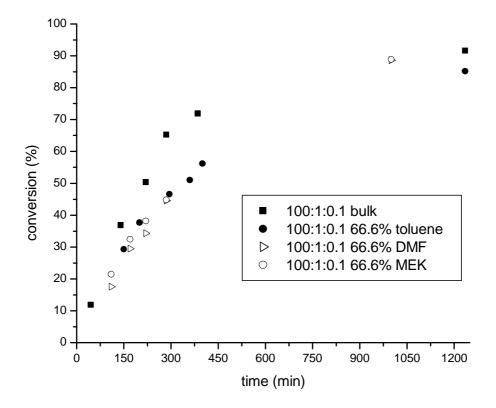
**Figure S1.** Comparison of conversion against time for the bulk polymerization of methyl acrylate (MA), at 50°C, mediated by 2-ethylsulfanylthiocarbonylsulfanylpropionic acid ethyl ester (ETSPE), in a ratio of 100:1, respectively. The concentration of initiator, 2,2'-azobisisobutyronitrile (AIBN), is varied according to the graph legend, which corresponds to MA: ETSPE: AIBN, respectively.



**Figure S2.** Comparison of conversion against time for the bulk polymerization of MA, at 50°C, mediated by ETSPE, and initiated by 2,2'-azobisisobutyronitrile (AIBN). The ratios of components in the systems are varied according to the graph legend, which corresponds to MA: ETSPE: AIBN, respectively.



**Figure S3.** Comparison of conversion against time for a bulk polymerization and four solution polymerizations of MA, at 50°C, mediated by ETSPE, and initiated by 2,2'- azobisisobutyronitrile (AIBN). The composition ratios of the pre polymerization solutions are indicated in the graph legend and correspond to MA: ETSPE: AIBN, respectively. The solution polymerizations were performed in toluene.



**Figure S4** Comparison of conversion against time for one bulk polymerization and three solution polymerizations of MA, at 50°C, mediated by ETSPE, and initiated by 2,2'-azobisisobutyronitrile (AIBN). The solution polymerizations were performed in toluene, *N*,*N*'-dimethylformamide (DMF) and methyl ethyl ketone (MEK) each with 66.6% (w/w) of the respective solvents. The composition ratios of the pre polymerization solutions are indicated in the graph legend and correspond to MA: ETSPE: AIBN, respectively.