Summary of Stew's Star Project 6-7-99 to 7-7-99

So far the highest percent yield of star material I have obtained is 37%. I have taken the following variables into consideration.

(1) Polymer concentration: My studies seem to indicate that there is an optimum concentration for achieving higher yields. Dilute polymer solutions (ie. 5mL of solvent to 1g polymer or less) give yields under 20% irrespective of the solvent's identity or reaction temperature. But neat reactions don't give the highest yields either.

(2) Nature of the solvent: Changing to a more hydrophobic solvent appears to reduce the yield of star material obtained at a specific polymer concentration.

(3) Reaction temperature: Increasing the reaction temperature appears to increase the number of arms in the stars. However, increasing the reaction temperature does not increase the overall yield of star material and in several cases actually induces decomposition.

(4) Catalyst pH and concentration: Decreasing the catalyst pH seems to do little. Furthermore, increasing the amount of catalyst present also seems to have little effect on the outcome of the reaction.

All reactions carried out for 24 hours

6 armed stars

1.0g PIB / 250mL THF / 10 drops 0.15N HCl (OR) 10 drops 0.5 N HCl / 70°C

18% yield

Star $\overline{M_n}$ ~54,300 g/mol ; $\overline{M_w}$ ~58,100 g/mol ; PDI ~ 1.07

Arm $\overline{M_n}$ ~ 9,500 g/mol ; $\overline{M_w}$ ~ 10,000 g/mol ; PDI ~ 1.06

Note: if this material containing 18% stars is dissolved in o-dichlorobenzene and refluxed at about 145°C there is no change.

3 armed stars

1.0g PIB / 20mL THF / 10 drops 1.0N HCl / 70°C

36% yield

Star $\overline{M_n}$ ~32,900 g/mol ; $\overline{M_w}$ ~ 35,500 g/mol ; PDI ~ 1.08

Arm $\overline{M_n}$ ~ 9,600 g/mol ; $\overline{M_w}$ ~ 10,100 g/mol ; PDI ~ 1.05

Starred stars (see PDI)

Note: if this material is heated to 180°C the material starts to decompose – $\overline{M_n}$ ~ 530 g/mol, $\overline{M_w}$ ~ 1900 g/mol

1.0g PIB / 1.0mL THF / 10 drops 1.0N HCl / 70°C

37% yield

star $\overline{M_n}$ ~ 47,100 g/mol ; $\overline{M_w}$ 53,400 g/mol ; PDI ~ 1.13

arm $\overline{M_n}$ ~ 9,800 g/mol ; $\overline{M_w}$ 10,200 g/mol ; PDI ~ 1.04

Note: heating this material to 120°C increased the number of arms to (8) That is Star $\overline{M_n}$ ~ 84,000 g/mol ; $\overline{M_w}$ ~ 88,800 g/mol ; PDI ~ 1.06. Heating it to about 160°C caused decomposition.

All reactions carried out for 24 hours

1.0g PIB / 0.5mL THF / 20 drops 5N HCl / 70°C

5 armed stars

37% yield

star $\overline{M_n}$ ~ 52,700 g/mol; $\overline{M_w}$ ~ 58,600 g/mol; PDI ~ 1.11

arm $\overline{M_n}$ ~ 10,300 g/mol; $\overline{M_w}$ ~ 10,600 g/mol; PDI ~ 1.04

most concentrated

1.0g PIB / 10.0mL 1.0N HCl / 85-90°C

29% yield

star $\overline{M_n}$ ~ 47,300 g/mol; $\overline{M_w}$ ~ 73,400 g/mol; PDI ~ 1.55

arm $\overline{M_n}$ ~ 9,700 g/mol; $\overline{M_w}$ ~ 10,400 g/mol; PDI ~ 1.07

All reactions carried out for 24 hours

5 armed stars { 1.0g PIB / 25.0mL o-dichlorobenzene / 10 drops 0.5 N HCl / 147°C

8% yield

star $\overline{M_n}$ ~ 45,600 g/mol ; $\overline{M_w}$ ~ 48,800 g/mol ; PDI ~ 1.07

arm $\overline{M_n}$ ~ 4,500 g/mol ; $\overline{M_w}$ ~ 9,700 g/mol ; PDI ~ 2.16

decomposition?

5 armed stars { 1.0g PIB / 5.0mL o-dichlorobenzene / 10 drops 0.5 N HCl / 147°C

14% yield

star $\overline{M_n}$ ~ 45,600 g/mol ; $\overline{M_w}$ ~ 48,200 g/mol ; PDI ~ 1.06

arm $\overline{M_n}$ ~ 2,600 g/mol ; $\overline{M_w}$ ~ 8,500 g/mol ; PDI ~ 3.28

decomposition?