# **Supplementary Information: The Structure of Randomly Branched Polymers Synthesised by Living Radical Methods**

# Experimental

## Materials

All materials were purchased from the Aldrich Chemical Company and used as received unless otherwise stated. Carbon disulphide (99.9+%, HPLC grade), bromobenzene (99.9%). magnesium turnings (AnalaR), Methyl-abromophenylacetate (97%), 1,4-dioxane (99%). Methyl methacrylate (MMA, 99%), styrene (Sty, 99%+), ethylene glycoldimethacrylate (EGDMA, 98%) and divinylbenzene (DVB, 80%) were all purified by filtering through aluminium oxide (activated basic Brockmann I). Azobisisobutyrolnitrile (AIBN, Fisher) was recrystalised twice from methanol and dried overnight in vacuo. Maleic anhydride (MAN, Fisher, 99%) was recrystalised twice from ethanol and dried overnight in *vacuo*. Flash column chromatography was performed on silica gel (60Å, Aldrich).

## Instrumentation

## Gel Permeation Chromatography

For the MMA-20-EGDMA and MMA-20-DVB.; molecular weight distributions were recorded using gel permeation chromatography (GPC) at ambient temperature using a system equipped with a guard column and two mixed C columns (Polymer Laboratories) with a differential refractive index detector. Tetrahydrofuran was used as an eluent at a flow rate of 1 mL min<sup>-1</sup> and toluene was used as a flow rate marker. Poly-(methyl methacrylate) standards in the range of 1,944,000 to 1,020 g mol<sup>-1</sup> were used as calibrants. This is because the low molecular weight samples produced at low conversion were outside the light scattering detectors range of accuracy. For the ,MMA-200-EGDMA molecular weight distributions and all branching data were recorded using gel permeation chromatography (GPC) on a Polymer Laboratories

GPC 50 and a Wyatt Technology Dawn 8+, with THF as eluent. ASTRA<sup>™</sup> software was used to analyse the data obtained from light scattering experiments to determine the size mass scaling.

# NMR spectroscopy

Both <sup>1</sup>H (400MHz) and <sup>13</sup>C (100MHz) NMR spectra were recorded on a Bruker 400 UltraShield spectrometer at  $25^{\circ}$ C and chloroform-*d* with 0.3% TMS was used as solvent for all compounds except alternating polymers where acetone-*d* with 0.03% TMS was used as solvent.

## Synthesis of CTA

The CTA used in this study has been previously reported in our group.<sup>1</sup>

# Synthesis of S-methoxycarbonylphenylmethyl dithiobenzoate (MCPDB)

Phenyl magnesium bromide was synthesised from bromobenzene (3.14 g, 20.0 mmol), magnesium turnings (0.50 g, 21.0 mmol) and several crystals of iodine in dry THF. The solution was heated to 40 °C and carbon disulphide (1.53 g, 20.0 mmol) was added dropwise over 15 min, to produce a dark brown solution. Methyl- $\alpha$ -bromophenylacetate (5.00 g, 21.8 mmol) was then added to the solution. The reaction temperature was raised to 80 °C and maintained for 24 h. Ice water was then added to the solution. The organic products were extracted three times with diethylether. The combined organic extracts were rinsed with water and dried over anhydrous magnesium sulphate. After solvent removal, column chromatography was undertaken (diethylether:n-hexane (1:9)) affording an orange-red oil (52.4%).

<sup>1</sup>H-NMR; (400 MHz , CDCl<sub>3</sub>),  $\delta$  (ppm from TMS); 3.70 (3H, s, O-C<u>H</u><sub>3</sub>), 5.65 (1H, s, -S(Ph)C<u>H</u>-CO<sub>2</sub>Me), 7.20–7.48 (8H, m, Ar-<u>H</u>), 7.91 (2H, dd, J = 7.26, 1.31 Hz, SC(Ar-<u>H</u>)S).

## **Polymerizations of MMA**

# Low degree of polymerization (DP=20) polymer synthesis

Two stock solutions consisting of, MMA (48.0 mmols, 5g), MCPDB (2.42 mmols, 0.58g), AIBN (2.42 mmols, 0.041g) and toluene (5.3 mols, 20g) were prepared. To the stock solutions either EGDMA or DVB was added to the stock in the amounts detailed in Table S.1 entries 1 and 2 respectively. 10mL of each stock solution were

transferred into Schlenk tubes then sealed and subsequently purged with nitrogen to remove dissolved oxygen. The Schlenk tubes were then placed in a preheated oil bath equipped with a thermo couple to ensure the temperature remained at 60°C. Samples were removed periodically to follow the kinetics of each polymerization. Conversions were calculated from <sup>1</sup>HNMR data. Following precipitation into hexane, molecular weight and branching data was determined using GPC. The highest conversion samples were analyzed using the ASTRA software to determine the size mass scaling. For the series MMA<sup>EGDMA</sup><sub>20</sub> the highest conversion was 95%.

|                | Polymer                    | Molar ratio of stock    | Brancher |      |
|----------------|----------------------------|-------------------------|----------|------|
|                |                            | MMA:Brancher:MCPDB:AIBN | mmol     | g    |
| 1 <sup>a</sup> | ,MMA <sup>EGDMA</sup> 20.  | 20:1.2:1:0.1            | 2.92     | 0.58 |
| 2 <sup>b</sup> | ,MMA <sup>DVB</sup> 20.    | 20:1.2:1:0.1            | 2.92     | 0.38 |
| 3 <sup>a</sup> | ,MMA <sup>EGDMA</sup> 200. | 200:0.9:1:0.1           | 0.45     | 0.09 |

Table S.1 Stock solution details used in chapter 2. <sup>a</sup>EGDMA used as brancher. <sup>b</sup>DVB used as brancher

#### High degree of polymerization (DP=200) polymer synthesis

A stock solution consisting of, MMA (96.0 mmols, 10g), MCPDB (0.49 mmols, 0.15g), AIBN (0.05 mmols, 82.0 mg) and toluene (10.6 mols, 40g) was prepared. To the stock solutions EGDMA was added to the stock in the amounts detailed in Table S.1 entry 3. 10mL of each stock solution were transferred into Schlenk tubes then sealed and subsequently purged with nitrogen to remove dissolved oxygen. The Schlenk tubes were then placed in a preheated oil bath equipped with a thermo couple to ensure the temperature remained at 60°C. Samples were removed periodically to follow the kinetics of each polymerization. Conversions were calculated from <sup>1</sup>HNMR data. Following precipitation into hexane, molecular weight and branching data was determined using GPC. The highest conversion sample was analyzed using the ASTRA software to determine the size mass scaling. For the series MMA<sup>EGDMA</sup><sub>200</sub> the highest conversion was 87%.

#### Polymerizations of Alternating Styrene-Maleic Anhydride.

Two stock solutions consisting of, Sty (96.0 mmols, 10g), MAN (96.0 mmols, 9.4g), MCPDB (0.49 mmols, 0.15g), AIBN (0.05 mmols, 82 mg) and dioxane (10.6 mols, 40g) were prepared. To the stock solutions DVB was added in the amounts detailed in Table S.2 10mL of each stock solution were transferred into Schlenk tubes then sealed and subsequently purged with nitrogen to remove dissolved oxygen. The Schlenk tubes were then placed in a preheated oil bath equipped with a thermo couple to ensure the temperature remained at 60°C. Samples were removed periodically to follow the kinetics of each polymerization. Conversions were calculated from <sup>1</sup>HNMR data. Following precipitation into hexane, molecular weight and branching data was determined using GPC. The highest conversion samples were analyzed using the ASTRA software to determine the size mass scaling. For the series ,Sty-MAN<sup>DVB=0.8</sup> the highest conversion was 94%, for the series ,Sty-MAN<sup>DVB=1</sup> the highest conversion was 93%.

|   | Polymer                       | Molar ratio of stock | Brancher |      |
|---|-------------------------------|----------------------|----------|------|
|   |                               | Sty:MAN:DVB:MCPDB    | mmol     | g    |
| 1 | ,Sty-MAN <sup>DVB=0.8</sup> . | 25:25:0.8:1:0.1      | 0.96     | 0.12 |
| 2 | , Sty-MAN <sup>DVB=1</sup> .  | 25:25:1.0:1:0.1      | 1.2      | 0.16 |

Table S.2 Stock solution details used in chapter 4

#### **Polymerizations of Divinyl Benzene only Polymers**

Conversion data for DVB only polymers could not be obtained from NMR using the vinyl protons of the monomer as pendant vinyl protons interfere with such measurement. Therefore polymers of the DVB<sub>20</sub> and DVB<sub>1</sub> series were precipitated in hexane and polymers for the DVB-MAN<sub>1</sub> series were precipitated in methanol. Following separation by filtration; the precipitated polymers were dried under vacuum at 30°C and subsequently weighed to obtain conversion data. Obtaining conversion data in this manner also removed the possibility of further polymerization or branching reactions whilst the samples were dissolved in solvent during drying.

# DVB<sub>20</sub> polymerizations

A stock solution consisting of, DVB (76.8 mmols, 10g), MCPDB (3.8 mmols, 1.16g), AIBN (0.04 mmols, 62.8mg) and toluene (10.6 mols, 40g) was prepared. 10mL of the stock solution was transferred into Schlenk tubes then sealed and subsequently purged with nitrogen to remove dissolved oxygen. The Schlenk tubes were then placed in a preheated oil bath equipped with a thermo couple to ensure the temperature remained at  $60^{\circ}$ C. Samples were removed periodically to follow the kinetics of each polymerization. Following precipitation into hexane, molecular weight and branching data was determined using GPC. The highest conversion sample was analyzed using the ASTRA software to determine the size mass scaling. For the series DVB<sub>20</sub> the highest conversion was 32%.

## **DVB**<sub>1</sub> polymerizations

A stock solution consisting of, DVB (23.0 mmols, 3g), MCPDB (23.0 mmols, 6.96g), AIBN (2.3mmols, 0.38g) and toluene (3.18 mols, 12g) was prepared. 5mL of the stock solution was transferred into Schlenk tubes then sealed and subsequently purged with nitrogen to remove dissolved oxygen. The Schlenk tubes were then placed in a preheated oil bath equipped with a thermo couple to ensure the temperature remained at  $60^{\circ}$ C. Samples were removed periodically to follow the kinetics of each polymerization. Following precipitation into hexane, molecular weight and branching data was determined using GPC. The highest conversion sample was analyzed using the ASTRA software to determine the size mass scaling. For the series DVB<sub>1</sub> the highest conversion was 45%.

## **DVB-MAN**<sub>1</sub> polymerizations

A stock solution consisting of, DVB (11.5 mmols, 1.5g), MAN (11.5 mmols, 1.1g) MCPDB (23.0 mmols, 6.96g), AIBN (2.3mmols, 0.38g) and toluene (3.18 mols, 12g) was prepared. 5mL of the stock solution was transferred into Schlenk tubes then sealed and subsequently purged with nitrogen to remove dissolved oxygen. The Schlenk tubes were then placed in a preheated oil bath equipped with a thermo couple to ensure the temperature remained at 60°C. Samples were removed periodically to follow the kinetics of each polymerization. Following precipitation into hexane, molecular weight and branching data was determined using GPC. The highest

conversion sample was analyzed using the ASTRA software to determine the size mass scaling. For the series DVB-MAN<sub>1</sub> the highest conversion was 38%.

# Comparison Between Logarithmic and Power-law scaling.

In this section we compare the predicted logarithmic scaling for several data series to the power law of 0.5. As discussed in the main text in this paper we use the simplifying assumption that the physical size of a given simple unit is proportional to the square-root of its mass. Since the simple units are themselves branched polymers, ideally we would use a logarithmic relationship, such as the size of the simple unit is related to the logarithm of its mass. However, this leads to additional parameters that require estimation for every fit. Additionally, since we assume that the masses of the simple unit are exponentially distributed, the likelihood of finding a simple unit whose mass is much larger than the average is unlikely. Therefore, we only require approximate agreement for N < 5 to justify this assumption.

In Figure S.1 we compare the  $\sigma$  vs N scaling for the logarithmically growing units with the square root power law. These comparisons are for the fit to the experimental data MMA<sup>DVB</sup><sub>20</sub> and MMA<sup>EGDMA</sup><sub>200</sub>. To convert the fitted r<sub>g</sub> to sigma, we simply divide the fitted r<sub>g</sub> by  $\sqrt{3}$ . The power law agrees very well with the MMA<sup>DVB</sup><sub>20</sub> for a very wide range of *N*, and the agreement with MMA<sup>EGDMA</sup><sub>200</sub> is also acceptable.



Figure S.1: Comparison between fitted (logarithmic)  $\sigma$  and the square-root law approximation for the series MMA<sup>EGDMA</sup><sub>200</sub> and MMA<sup>DVB</sup><sub>20</sub>.

Similarly if we compare the fitted  $\sigma$  to the square-root law approximation for the Styrene-Maleic Anhydride (Sty-MAN) series we also obtain reasonably good agreement. In Figure S.2 we compare the fitted logarithmic  $\sigma$  to the square-root law approximation for the series Sty-MAN<sup>DVB=1</sup>. If we used Sty-MAN<sup>DVB=0.8</sup> the results are almost identical. In this case we also have good agreement for *N*<10, and excellent agreement for *N*<5. This justifies the approximation used in these cases.



Figure S.2: Comparison between fitted (logarithmic)  $\sigma$  and the square-root law approximation for the series STY-MAN<sup>DVB=1</sup>.

Finally we perform the same comparison for the brancher only experiments. In Figure S.3 we compare the fitted logarithmic law for  $DVB_1$  and  $DVB_{20}$  to the square-root law approximation. The comparison for the series  $DVB-MAN_1$  is almost the same as for  $DVB_1$ . The comparison suggests that for these series the square-root law is also acceptable.



Figure S.3: Comparison between fitted (logarithmic)  $\sigma$  and the square-root law approximation for the series STY-MAN<sup>DVB=1</sup>.

These comparisons in Figures S.1, S.2 and S.3 span quite a wide range of the parameters  $\kappa$  and  $\gamma$ . Therefore, the acceptable fit of each of these square-root law approximations to the fitted, logarithmic, series suggests that using the square root approximation is acceptable. This allows us to simplify each fit by removing one fitting parameter in each fit, and removes ambiguity over whether to use  $\sigma^2 \sim \log N$  or  $\sigma \sim \log N$ .

#### References

1. Perrier, S.; Takolpuckdee, P.; Westwood, J.; Lewis, D. M. *Macromolecules* **2004**, 37, 2709.