

**Supporting Information**

**Gelation in Photoinduced ATRP with Tuned Dispersity of the  
Primary Chains**

Frances Dawson, Hugo Jafari, Vytenis Rimkevicius, Maciej Kopec\*

Department of Chemistry, University of Bath, Claverton Down, Bath BA2 7AY, UK

\*e-mail: [mk2297@bath.ac.uk](mailto:mk2297@bath.ac.uk)

## Flory-Stockmayer equation for ATRP systems

Derivation of the equation 2 after Gao and Matyjaszewski<sup>1,2</sup> is reproduced here for reader's convenience.

From the Flory-Stockmayer theory:

$$v_c = \rho p_c (DP_w - 1) = 1$$

where  $v_c$  is the weight-average number of crosslinks per primary chain (equal to 1 at incipient gelation),  $\rho$  is the fraction of vinyl bonds residing on the divinyl crosslinker,  $p_c$  is the conversion of double bonds at the gel point and  $DP_w$  is the weight-average degree of polymerisation of the primary chains in the absence of crosslinks.

Assuming  $DP_w \gg 1$  and since  $\mathcal{D} = DP_w/DP_n$  as well as  $\rho = \frac{2[X]_0}{[M]_0 + 2[X]_0}$

then,

$$1 = \frac{2[X]_0}{[M]_0 + 2[X]_0} p_c \mathcal{D} DP_n$$

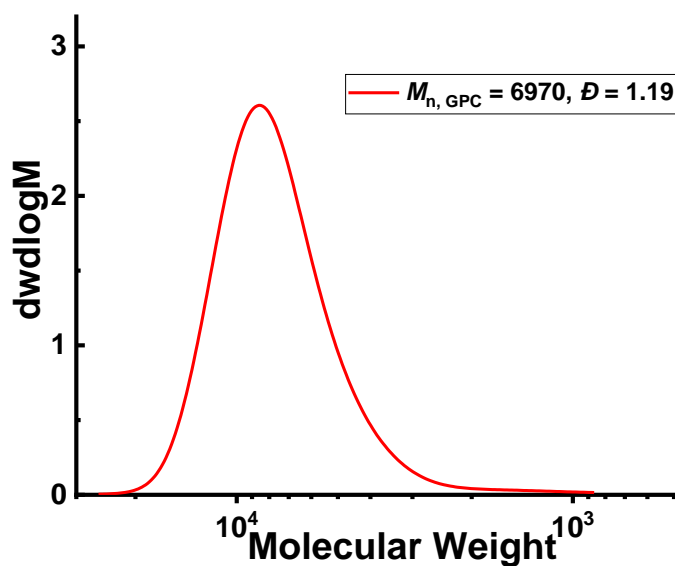
Further, in an ATRP of a monomer with initial concentration  $[M]_0$  and a divinyl crosslinker with initial concentration of vinyl bonds  $2[X]_0$ ,  $DP_n = \frac{[M]_0 + 2[X]_0}{[PC]_t} p_c$ , where  $[PC]_t$  is the instantaneous concentration of the primary chains.

Thus,

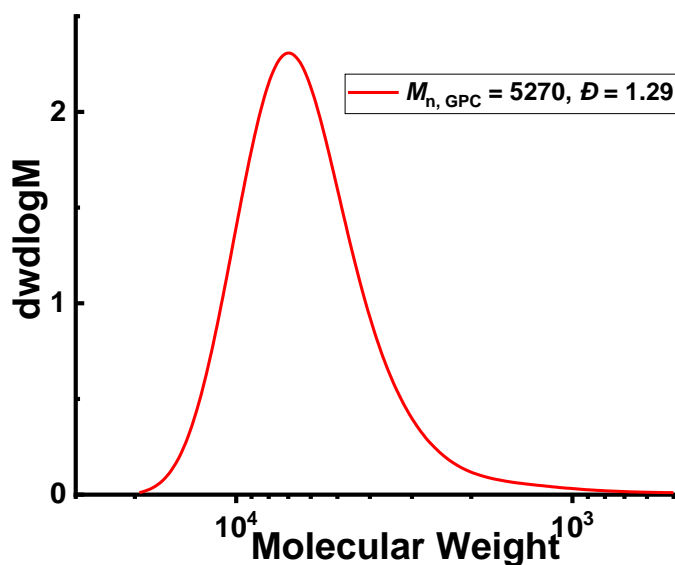
$$1 = \frac{2[X]_0}{[M]_0 + 2[X]_0} p_c \mathcal{D} \frac{[M]_0 + 2[X]_0}{[PC]_t} p_c = p_c^2 \mathcal{D} \frac{2[X]_0}{[PC]_t}$$

Finally, conversion at the gel point:

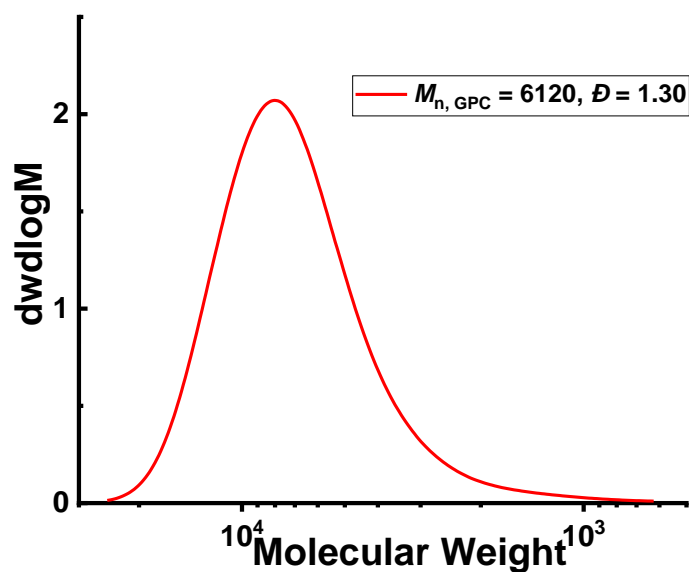
$$p_c = \sqrt{\frac{[PC]_t}{2[X]_0} \frac{1}{\mathcal{D}}}$$



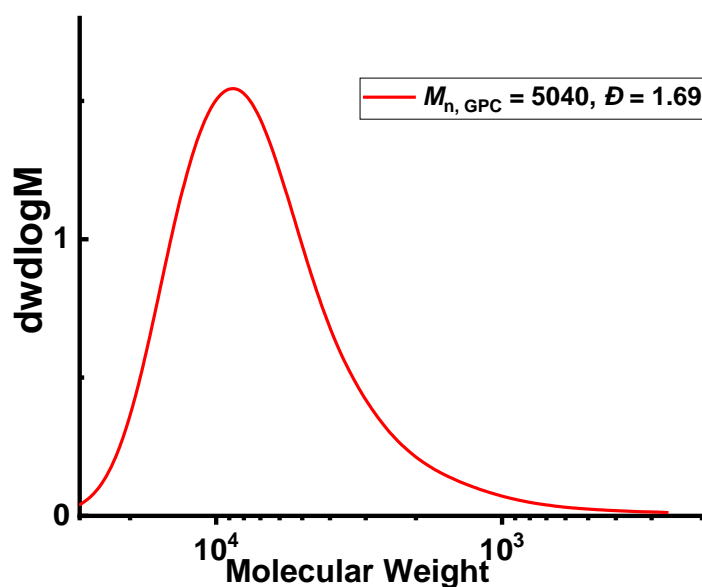
**Figure S1.** GPC trace of a reaction with conditions [MA]:[EBiB] = 100:1 and 200 ppm of the  $\text{CuBr}_2/\text{Me}_6\text{TREN}$  catalyst (Table 1, entry 1). The sample was taken after 23 min and the polymerization reached 66% conversion measured by  $^1\text{H}$  NMR. The parallel reaction with 3 equiv, of the HDDA crosslinker gelled in 25 min and the conversion at the gel point was estimated to be 62%.



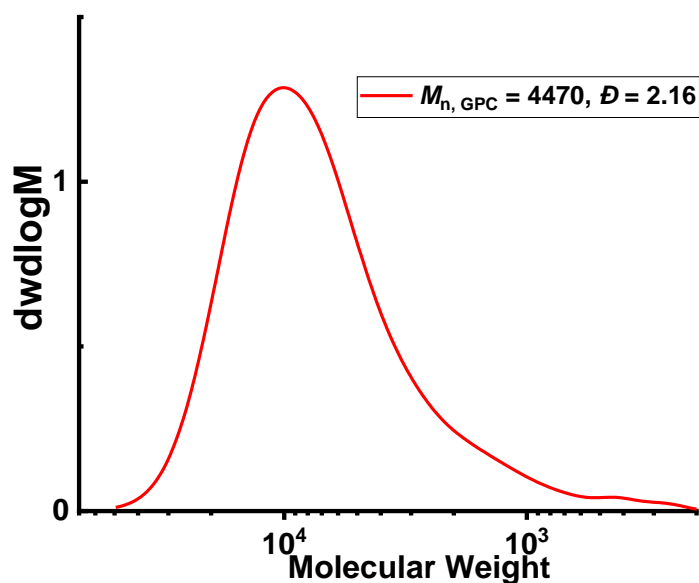
**Figure S2.** GPC trace of a reaction with conditions MA/EBiB 100:1 and 100 ppm of the  $\text{CuBr}_2/\text{Me}_6\text{TREN}$  catalyst (Table 1, entry 2). The sample was taken after 25 min and the polymerization reached 52% conversion measured by  $^1\text{H}$  NMR. The parallel reaction with 3 equiv, of the HDDA crosslinker gelled in 30 min and the conversion at the gel point was estimated to be 55%.



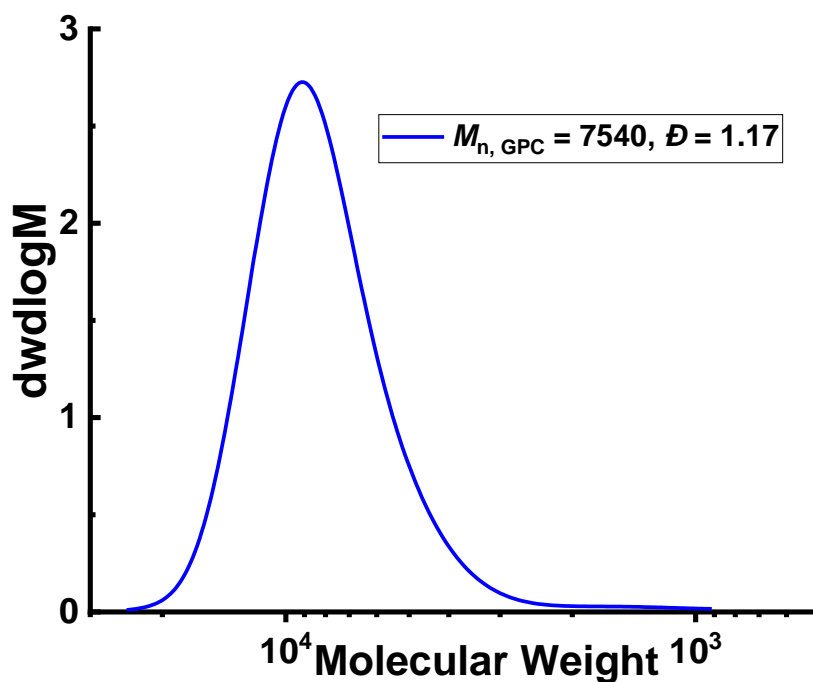
**Figure S3.** GPC trace of a reaction with conditions  $[MA]:[EBiB] = 100:1$  and 50 ppm of the  $CuBr_2/Me_6TREN$  catalyst (**Table 1, entry 3**). The sample was taken after 40 min and the polymerization reached 55% conversion measured by  $^1H$  NMR. The parallel reaction with 3 equiv, of the HDDA crosslinker gelled in 25 min and the conversion at the gel point was estimated to be 50%.



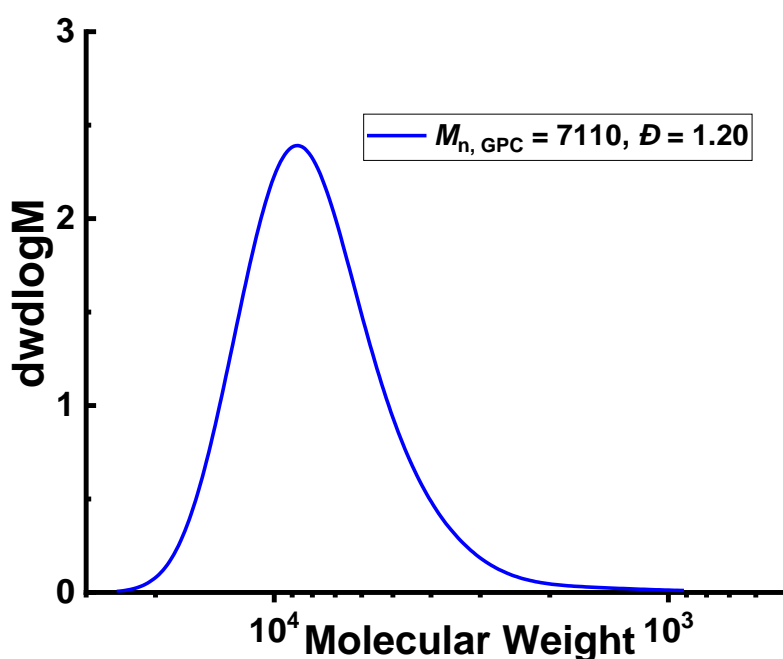
**Figure S4.** GPC trace of a reaction with conditions  $[MA]:[EBiB] = 100:1$  and 20 ppm of the  $CuBr_2/Me_6TREN$  catalyst (**Table 1, entry 4**). The sample was taken after 60 min and the polymerization reached 50% conversion measured by  $^1H$  NMR. The parallel reaction with 3 equiv, of the HDDA crosslinker gelled in 70 min and the conversion at the gel point was estimated to be 50%.



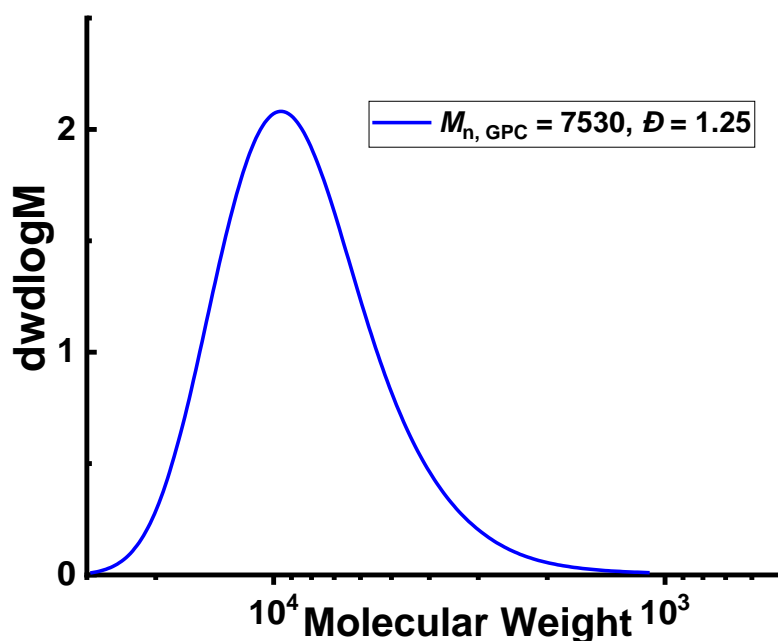
**Figure S5.** GPC trace of a reaction with conditions [MA]:[EBiB] = 100:1 and 10 ppm of the  $\text{CuBr}_2/\text{Me}_6\text{TREN}$  catalyst (**Table 1, entry 5**). The sample was taken after 105 min and the polymerization reached 48% conversion measured by  $^1\text{H}$  NMR. The parallel reaction with 3 equiv, of the HDDA crosslinker gelled in 105 min and the conversion at the gel point was estimated to be 48%.



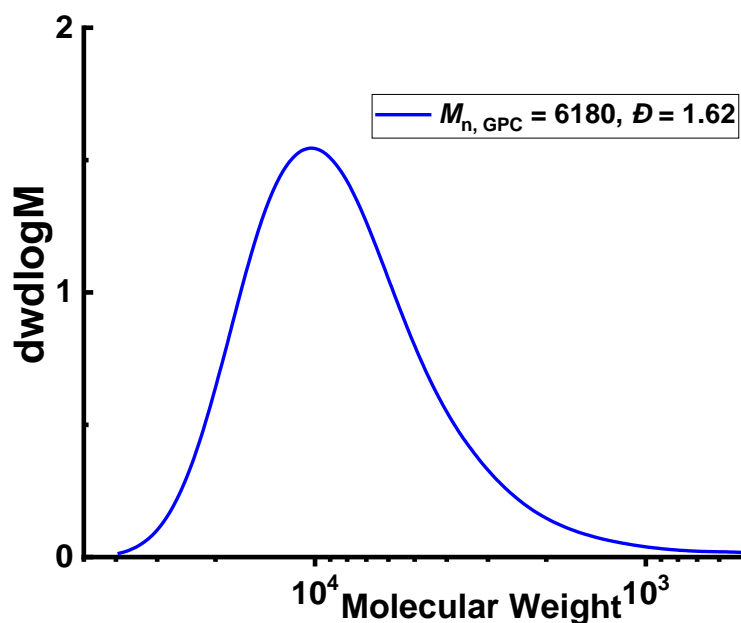
**Figure S6.** GPC trace of a reaction with conditions [MA]:[EBiB] = 100:1 and 200 ppm of the  $\text{CuBr}_2/\text{Me}_6\text{TREN}$  catalyst (**Table 1, entry 6**). The sample was taken after 26 min and the polymerization reached 77% conversion measured by  $^1\text{H}$  NMR. The parallel reaction with 1.5 equiv, of the HDDA crosslinker gelled in 35 min and the conversion at the gel point was estimated to be 77%.



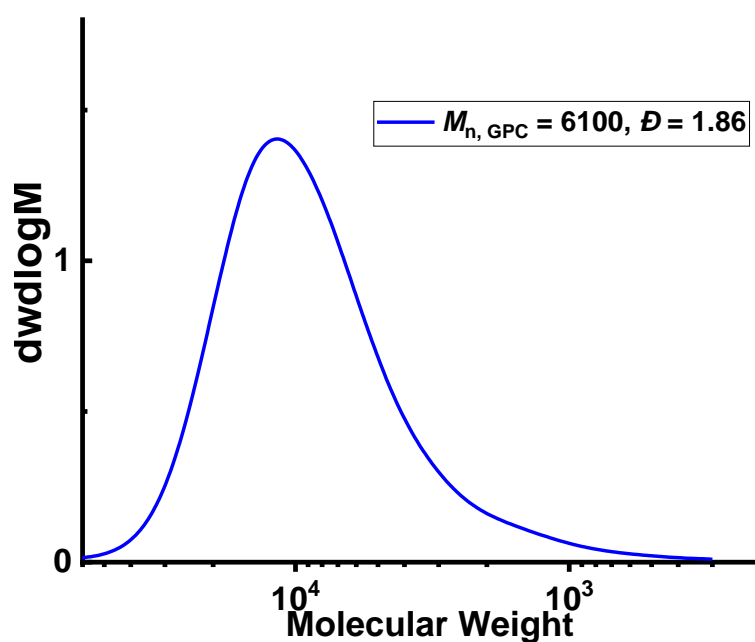
**Figure S7.** GPC trace of a reaction with conditions [MA]:[EBiB] = 100:1 and 100 ppm of the  $\text{CuBr}_2/\text{Me}_6\text{TREN}$  catalyst (**Table 1, entry 7**). The sample was taken after 27 min and the polymerization reached 74% conversion measured by  $^1\text{H}$  NMR. The parallel reaction with 1.5 equiv, of the HDDA crosslinker gelled in 31 min and the conversion at the gel point was estimated to be 72%.



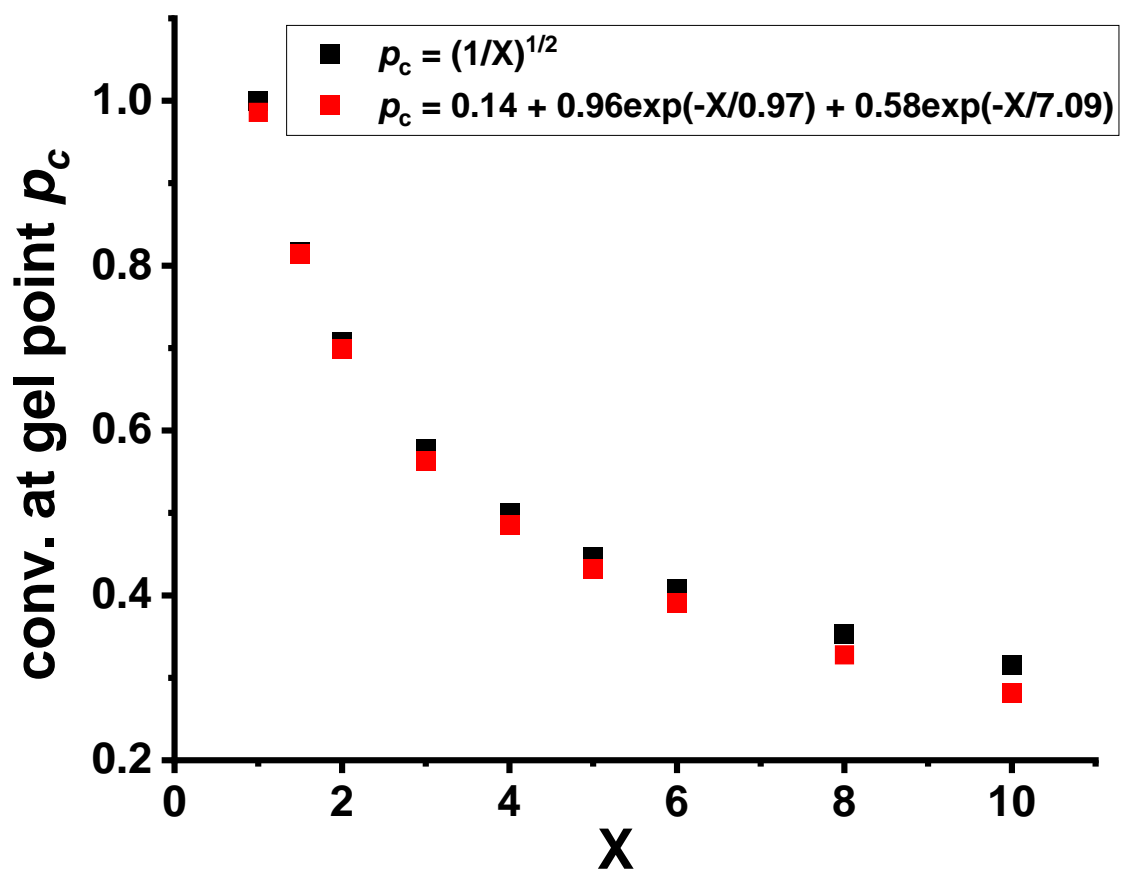
**Figure S8.** GPC trace of a reaction with conditions [MA]:[EBiB] = 100:1 and 50 ppm of the  $\text{CuBr}_2/\text{Me}_6\text{TREN}$  catalyst (**Table 1, entry 8**). The sample was taken after 30 min and the polymerization reached 69% conversion measured by  $^1\text{H}$  NMR. The parallel reaction with 1.5 equiv, of the HDDA crosslinker gelled in 35 min and the conversion at the gel point was estimated to be 70%.



**Figure S9.** GPC trace of a reaction with conditions [MA]:[EBiB] = 100:1 and 20 ppm of the  $\text{CuBr}_2/\text{Me}_6\text{TREN}$  catalyst (**Table 1, entry 9**). The sample was taken after 55 min and the polymerization reached 60% conversion measured by  $^1\text{H}$  NMR. The parallel reaction with 1.5 equiv, of the HDDA crosslinker gelled in 70 min and the conversion at the gel point was estimated to be 63%.

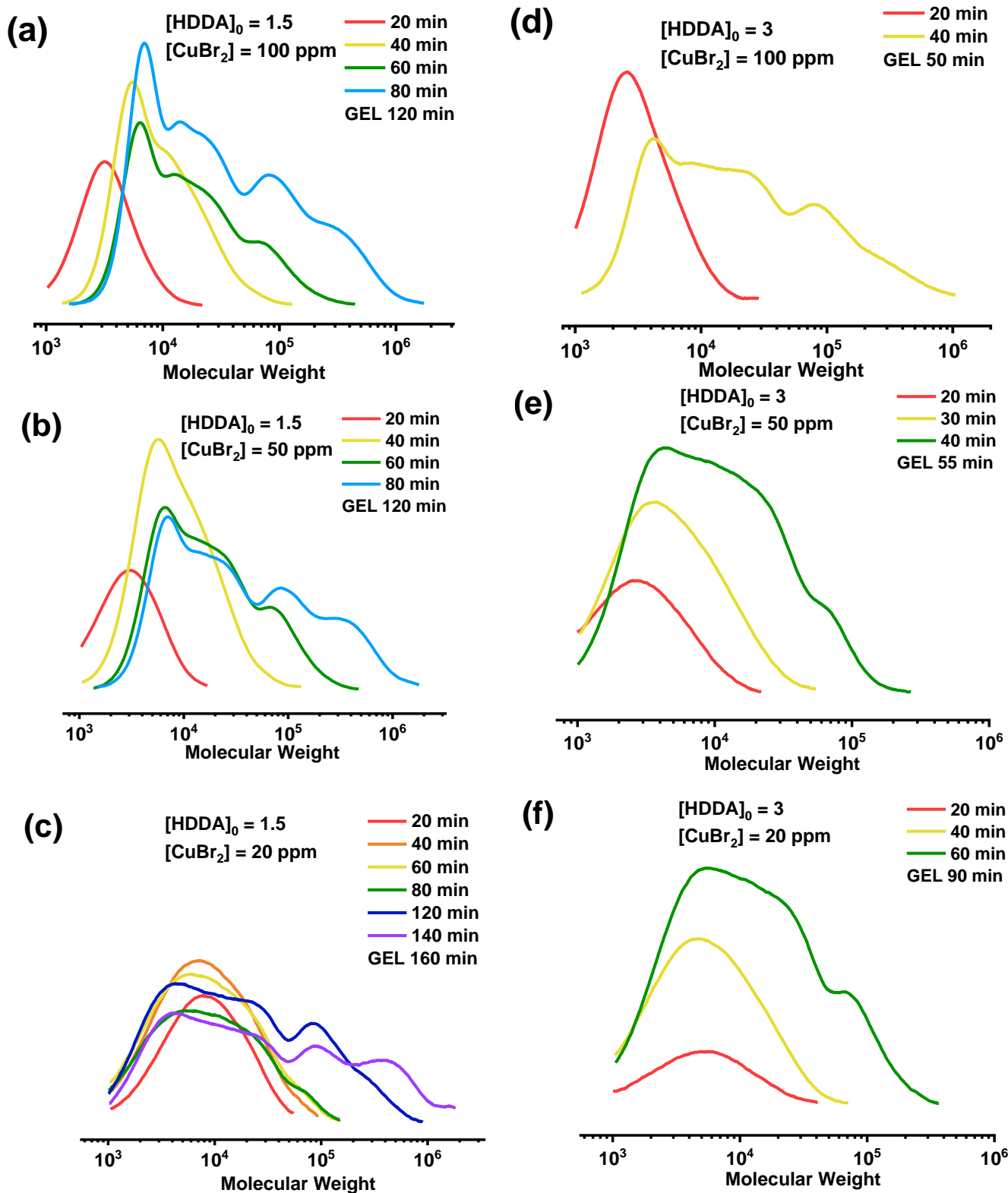


**Figure S10.** GPC trace of a reaction with conditions [MA]:[EBiB] = 100:1 and 10 ppm of the  $\text{CuBr}_2/\text{Me}_6\text{TREN}$  catalyst (**Table 1, entry 10**). The sample was taken after 110 min and the polymerization reached 66% conversion measured by  $^1\text{H}$  NMR. The parallel reaction with 1.5 equiv, of the HDDA crosslinker gelled in 110 min and the conversion at the gel point was estimated to be 63%.



**Figure S11.** Comparison of two formulas to calculate  $p_c$  as a function of the initial crosslinker concentration  $X = [X]_0/[I]_0$ . The second order exponential decay function (red squares) was obtained in ref. 3 using Predici simulation software.





**Figure S12.** GPC traces recorded pre-gelation for reactions with 20-100 ppm of the catalyst used to synthesize fully developed networks for structural characterization. (a-c)  $[\text{HDDA}]_0 = 1.5$ ; (e-g)  $[\text{HDDA}]_0 = 3$ . Reaction conditions:  $[\text{MA}]:[\text{EBiB}]:[\text{HDDA}] = 100:1:1.5$  or  $3$ ;  $[\text{CuBr}_2] = 20\text{-}100$  ppm vs monomer;  $[\text{CuBr}_2]:[\text{Me6TREN}] = 1:6$ , MA/DMSO = 1:1 (v/v), rt,  $\lambda_{\text{max}} = 390$  nm, 10 h. Note that for 10-hour reactions, the LED lamp (Kessil PR106L-390) was set to 50% intensity, hence longer reaction/gelation times.

## References

1. Gao, H.; Matyjaszewski, K., Synthesis of functional polymers with controlled architecture by CRP of monomers in the presence of cross-linkers: From stars to gels. *Prog. Polym. Sci.* **2009**, *34* (4), 317-350.
2. Gao, H.; Li, W.; Min, K.; Matyjaszewski, K., Gelation in Atom Transfer Radical Copolymerization with a Divinyl Cross-linker. In *Controlled/Living Radical Polymerization: Progress in ATRP*, American Chemical Society: 2009; Vol. 1023, pp 203-213.
3. Gao, H.; Min, K.; Matyjaszewski, K., Determination of Gel Point during Atom Transfer Radical Copolymerization with Cross-Linker. *Macromolecules* **2007**, *40* (22), 7763-7770.