

Supporting Information

Polymerization Behaviors and Polymer Branching Structures in ATRP of Monovinyl and Divinyl Monomers

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Table S1. Optimized Polymerization Conditions

Branching Agent	Reactant Ratio (mole)	$m_{(\text{styrene+BMA})}/m_{\text{anisole}}$ (weight)	Tem. (°C)
BMIH ^a	[<i>t</i> -BBiB]/[BMIH]/[styrene]/[PMDETA]/[CuBr]=1.0/0.9/30/1.0/1.0	2/1	80
<i>tri</i> -EGDMA ^b	[<i>t</i> -BBiB]/[<i>tri</i> -EGDMA]/[styrene]/[Bpy]/[CuBr]=1.0/0.9/30/2.0/1.0	3/1	90
DVB ^c	[<i>t</i> -BBiB]/[DVB]/[styrene]/[BMA]/[Bpy]/[CuBr]=1.0/0.9/28.2/1.8/2.0/1.0	2/1	90

a: *t*-BBiB_{1.0}-BMIH_{0.9}-styrene₃₀-PMDETA_{1.0}-CuBr_{1.0}

b: *t*-BBiB_{1.0}-*tri*-EGDMA_{0.9}-styrene₃₀-Bpy_{2.0}-CuBr_{1.0}

c: *t*-BBiB_{1.0}-DVB_{0.9}-styrene_{28.2}-BMA_{1.8}-Bpy_{2.0}-CuBr_{1.0}

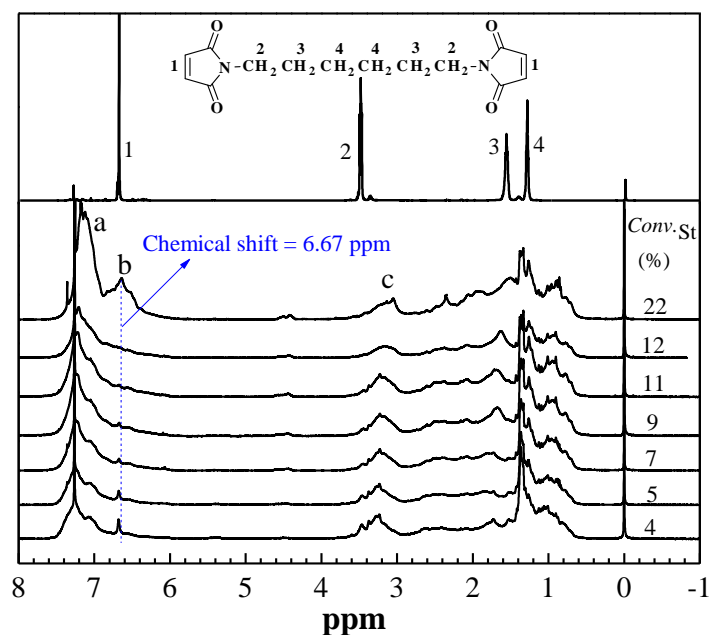


Fig. S1 ¹H-NMR spectra of branching agent BMIH and the copolymers obtained during the copolymerization of styrene and BMIH in anisole at 80 °C: *t*-BBiB_{1.0}-BMIH_{0.9}-styrene₃₀-PMDETA_{1.0}-CuBr_{1.0}, $m_{\text{styrene}}/m_{\text{anisole}} = 2/1$. ¹H-NMR conditions: 25 °C, CDCl₃ as the solvent.

Fig. S1 is $^1\text{H-NMR}$ spectra of BMIH and the branched polymer prepared using BMIH as the branching agent. The related peaks in Fig. S1 are marked in *a* (benzene ring from styrene monomer unit), *b* (the pendent vinyl group from BMIH), and *c* (the methylene next to nitrogen from BMIH), respectively. The integral values of these three signals are expressed as S_a , S_b , and S_c . The conversions of BMIH ($Conv_{\text{BMIH}}$) and pendent vinyl group (C_P) are calculated using the following equations:

$$Conv_{\text{BMIH}} = \frac{S_c/4}{S_a/5} \times \frac{[\text{St}]_0}{[\text{BMIH}]_0} \times Conv_{\text{St}} = \frac{S_c/4}{S_a/5} \times \frac{30}{0.9} \times Conv_{\text{St}}$$

$$N_{\text{pendent vinylgroupconsumed}} = 0.9 \times Conv_{\text{BMIH}} \times \left(\frac{S_c}{4} - \frac{S_b}{2} \right) / \left(\frac{S_c}{4} \right)$$

$$C_P = N_{\text{pendent vinylgroupconsumed}} / 0.9$$

4, 5 and 2 in the above two equations mean that one BMIH unit has 4 methylene protons next to nitrogen at chemical shift 3.4 ppm, one styrene unit has 5 protons in the benzene ring, and one pendent vinyl group has 2 protons. $Conv_{\text{St}}$ is the styrene conversion determined using GC.

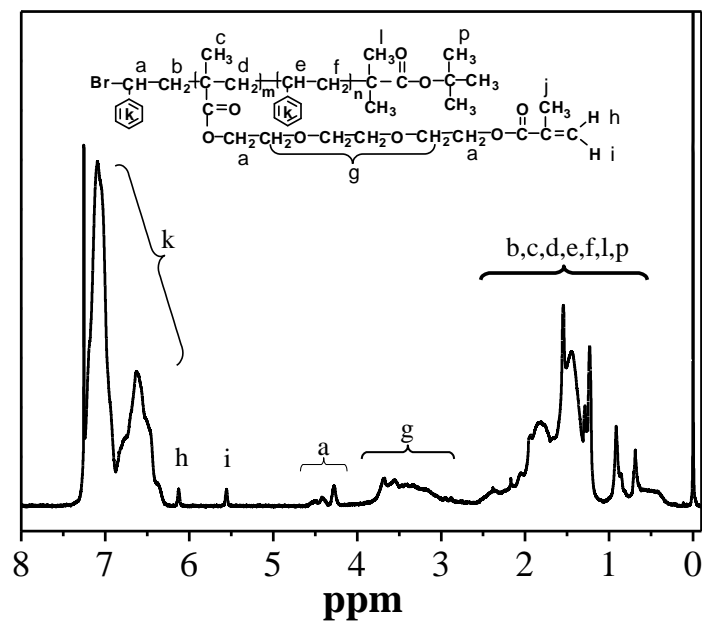


Fig. S2 Typical $^1\text{H-NMR}$ spectrum of the copolymers obtained during the copolymerization of styrene and *tri*-EGDMA in anisole at 90 °C: $t\text{-BBiB}_{1.0}\text{-tri-EGDMA}_{0.9}\text{-styrene}_{30}\text{-Bpy}_{2.0}\text{-CuBr}_{1.0}$, $m_{\text{styrene}}/m_{\text{anisole}} = 3/1$. $^1\text{H-NMR}$ conditions: 25 °C, CDCl_3 as the solvent.

Fig. S2 is a typical $^1\text{H-NMR}$ spectrum of the branched polymer prepared using *tri*-EGDMA as the branching agent. Conversion of the pendent vinyl group (C_P) from *tri*-EGDMA was calculated according to the following equation (*Macromolecules* **2009**, *42*, 5976-5982.):

$$C_P = \frac{N_{\text{tri-EGDMA}} - N_P}{N_{\text{tri-EGDMA}}} = 1 - \frac{(S_i + S_h)/2}{S_g/8}$$

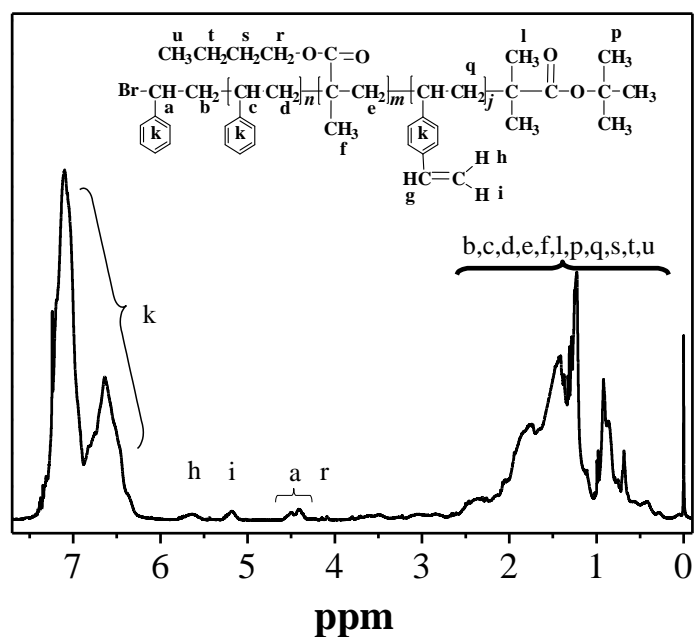


Fig. S3 Typical $^1\text{H-NMR}$ spectrum of the copolymers obtained during the copolymerization of styrene and BMA with DVB in anisole at $90\text{ }^\circ\text{C}$: $t\text{-BBiB}_{1.0}\text{-DVB}_{0.9}\text{-styrene}_{28.2}\text{-BMA}_{1.8}\text{-Bpy}_{2.0}\text{-CuBr}_{1.0}$, $m_{(\text{styrene+BMA})}/m_{\text{anisole}} = 2/1$. $^1\text{H-NMR}$ conditions: $25\text{ }^\circ\text{C}$, CDCl_3 as the solvent.

Fig. S3 is a typical $^1\text{H-NMR}$ spectrum of the branched polymer prepared using DVB as the branching agent. The related peaks are marked in k (chemical shift 6.25-7.5 ppm, phenyl ring from styrene or DVB), h and i (chemical shift 5.25 and 5.75 ppm, the pendent vinyl group from DVB). The integral values of these signals are expressed as S_k , S_h and S_i . It is noted that the signal relating to the third proton of the pendent vinyl group from DVB overlapped with that of the phenyl ring. The conversions of the pendent vinyl group (C_p) from DVB were calculated according to the following equations:

$$N_{\text{H-benzenering}} = 5 \times [\text{St}]_0 \times \text{Conv}_{\text{St}} + 4 \times [\text{DVB}]_0 \times \text{Conv}_{\text{DVB}}$$

$$S_{\text{unitproton}} = [S_k - (S_h + S_i)/2] / N_{\text{H-benzenering}}$$

$$N_{\text{pendent vinylgroup assuming no consumption}} = [\text{DVB}]_0 \times \text{Conv.}_{\text{DVB}}$$

$$N_{\text{pendent vinylgroup from NMR}} = [(S_h + S_i)/2] / S_{\text{unitproton}}$$

$$N_{\text{pendent vinylgroup consumed}} = [\text{DVB}]_0 \times \text{Conv.}_{\text{DVB}} - [(S_h + S_i)/2] / S_{\text{unitproton}}$$

$$C_P = N_{\text{pendent vinylgroup consumed}} / 0.9$$

In above equations, 2 means that one pendent vinyl group has 2 protons as marked with *h* and *i*. 5 and 4 mean that the benzene ring of styrene and DVB have 5 and 4 protons, respectively.

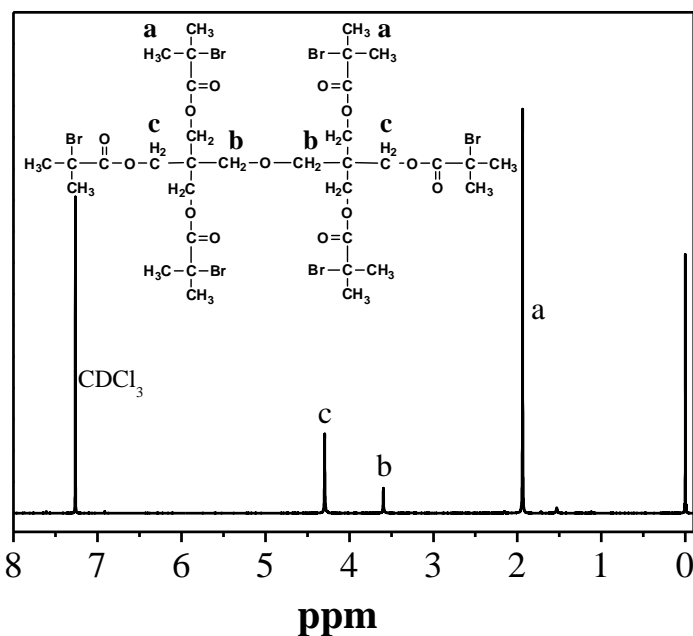


Fig. S4 ¹H-NMR spectrum of dipentaerythritol ester-2-bromoisobutyrate (6BrBu).

¹H-NMR conditions: 25 °C, CDCl₃ as the solvent.

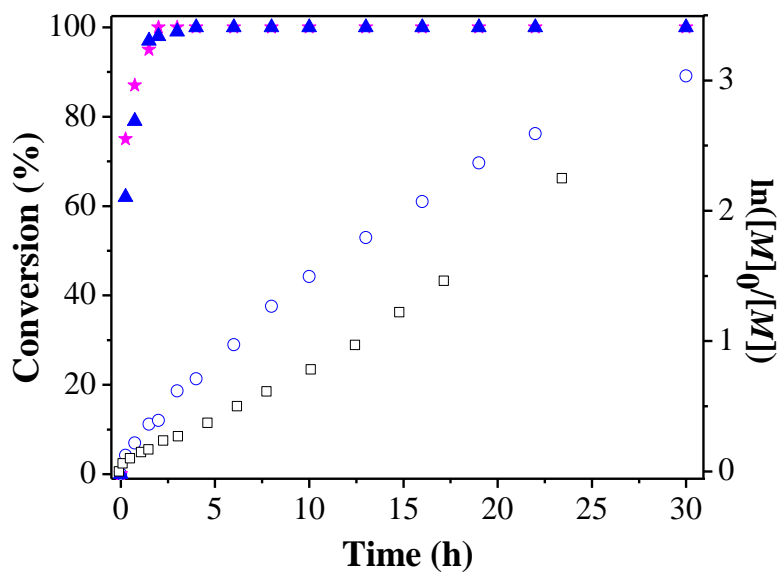


Fig. S5 Kinetics for the copolymerization of styrene and BMIH initiated by *t*-BBiB in anisole at 80 °C. *t*-BBiB_{1.0}-BMIH_{0.9}-styrene₃₀-PMDETA_{1.0}-CuBr_{1.0}, $m_{\text{styrene}}/m_{\text{anisole}} = 2/1$. (★): *t*-BBiB, (▲): BMIH, (○): styrene, (□): $\ln([M]_0/[M])$.

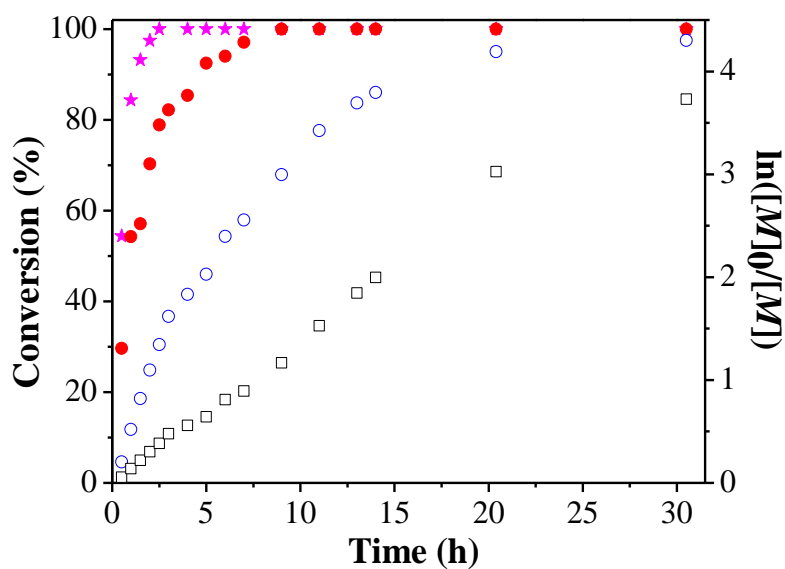


Fig. S6 Kinetics for the copolymerization of styrene and *tri*-EGDMA initiated by *t*-BBiB in anisole at 90 °C. *t*-BBiB_{1.0}-*tri*-EGDMA_{0.9}-styrene₃₀-Bpy_{2.0}-CuBr_{1.0}, $m_{\text{styrene}}/m_{\text{anisole}} = 3/1$. (★): *t*-BBiB, (●): *tri*-EGDMA, (○): styrene, (□): $\ln([M]_0/[M])$.

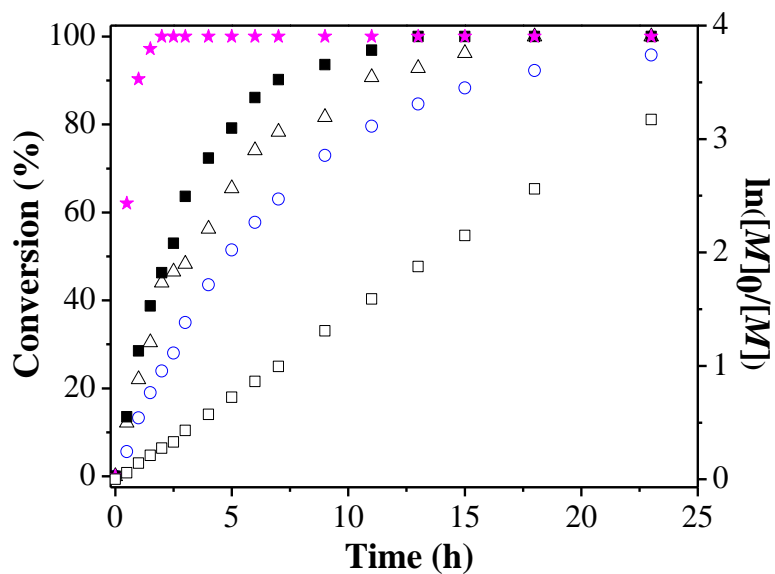


Fig. S7 Kinetics for the copolymerization of styrene and BMA with DVB initiated by *t*-BBiB in anisole at 90 °C. *t*-BBiB_{1.0}-DVB_{0.9}-styrene_{28.2}-BMA_{1.8}-Bpy_{2.0}-CuBr_{1.0}, $m_{(\text{styrene+BMA})}/m_{\text{anisole}} = 2/1$. *t*-BBiB: (★), DVB: (■), BMA: (Δ), styrene: (○), $\ln([M]_0/[M])$: (□)

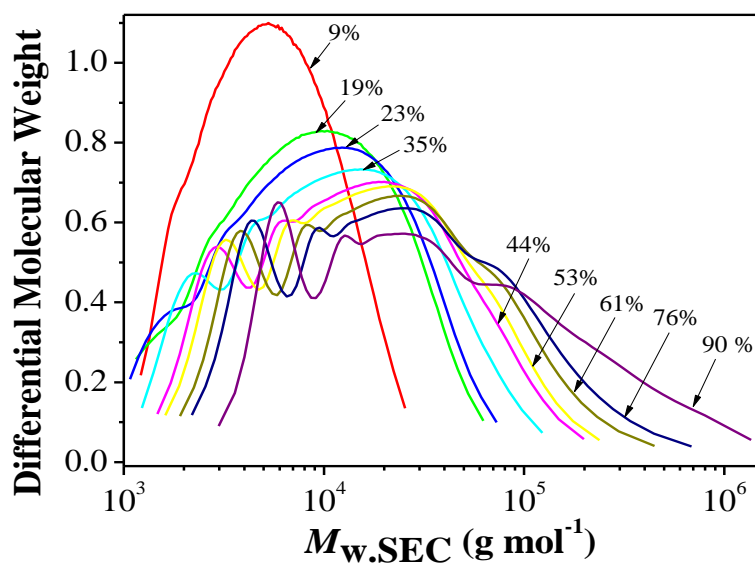


Fig. S8 Evolution of the differential molecular weight distribution with conversion for

the copolymerization of styrene and BMIH initiated by *t*-BBIb in anisole at 80 °C.

t-BBIb_{1.0}-BMIH_{0.9}-styrene₃₀-PMDETA_{1.0}-CuBr_{1.0}, $m_{\text{styrene}}/m_{\text{anisole}} = 2/1$.

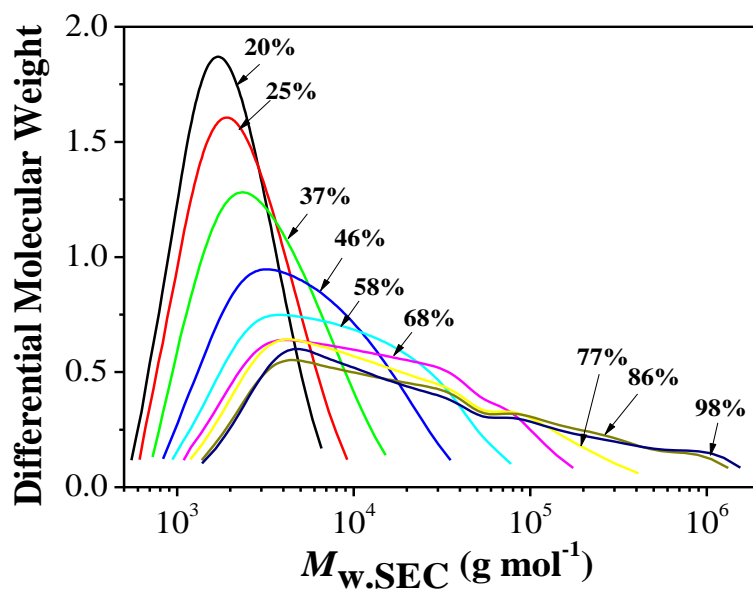


Fig. S9 Evolution of the differential molecular weight distribution with conversion for the copolymerization of styrene and *tri*-EGDMA initiated by *t*-BBIb in anisole at 90

°C. *t*-BBIb_{1.0}-*tri*-EGDMA_{0.9}-styrene₃₀-Bpy_{2.0}-CuBr_{1.0}, $m_{\text{styrene}}/m_{\text{anisole}} = 3/1$.

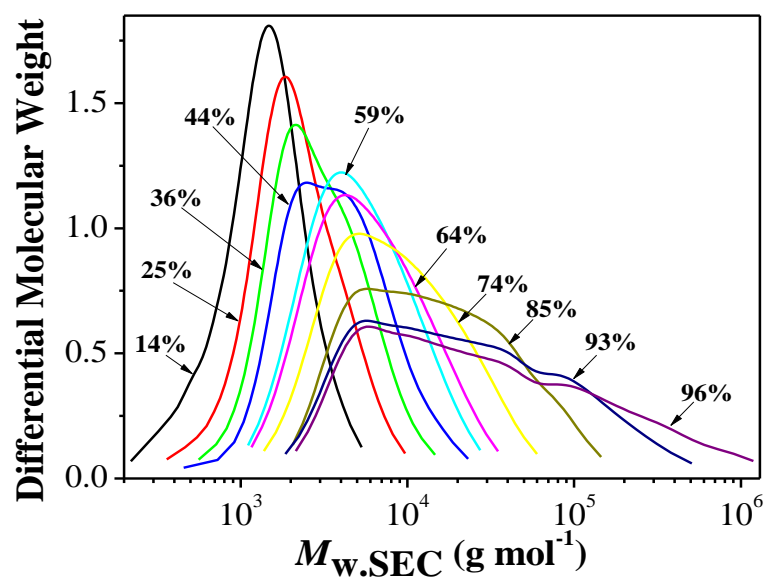


Fig. S10 Evolution of the differential molecular weight distribution with conversion for the copolymerization of styrene and BMA with DVB initiated by *t*-BBiB in anisole at 90 °C. $\text{DVB}_{1.0}\text{-tri-EGDMA}_{0.9}\text{-styrene}_{28.2}\text{-BMA}_{1.8}\text{-Bpy}_{2.0}\text{-CuBr}_{1.0}$, $m_{(\text{styrene+BMA})}/m_{\text{anisole}} = 2/1$.

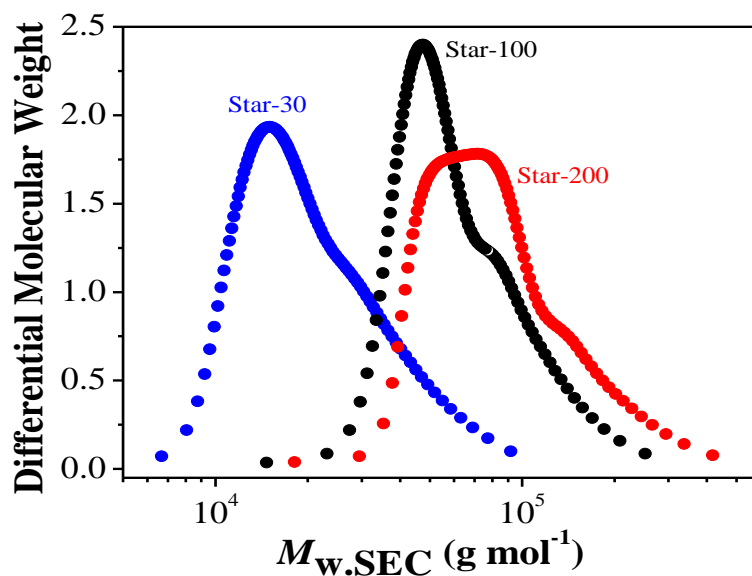


Fig. S11 Differential molecular weight distribution of the modal star polystyrene.

$6\text{BrBu}_{1.0}\text{-styrene}_x\text{-Bpy}_{12}\text{-CuBr}_{6.0}$, $m_{\text{styrene}}/m_{\text{anisole}} = 2/1$, 90 °C, $x = 180, 600$ and 1200 for Star-30, Star-100, and Star-200, 30, 100 and 200 represent the arm length at 100% styrene conversion, respectively.

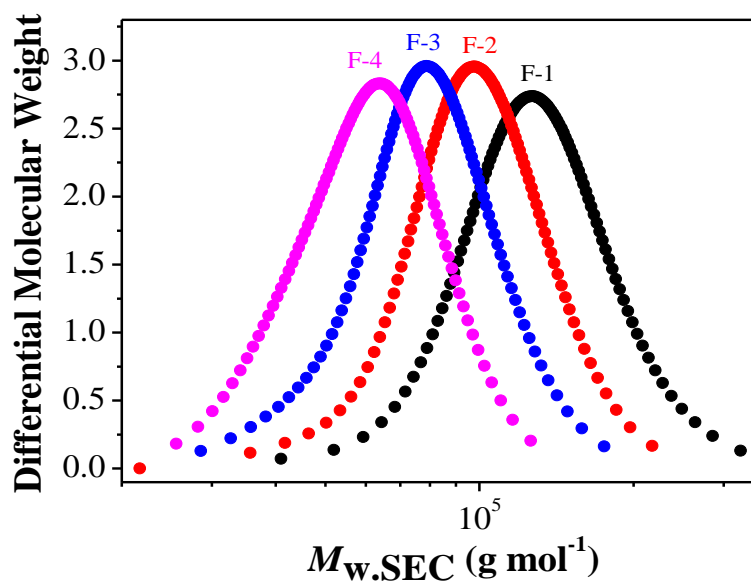


Fig. S12 Differential molecular weight distribution of the fractionations at 98 % monomer conversion.

t -BBiB_{1.0}-*tri*-EGDMA_{0.9}-styrene₃₀-Bpy_{2.0}-CuBr_{1.0}, $m_{styrene}/m_{anisole} = 3/1$, 90 °C.

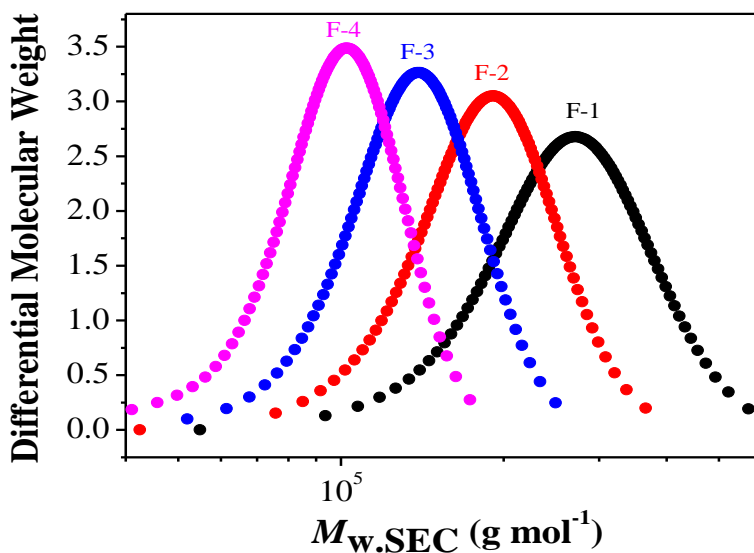


Fig. S13 Differential molecular weight distribution of the fractionations at 96 % monomer conversion. t -BBiB_{1.0}-DVB_{0.9}-styrene_{28.2}-BMA_{1.8}-Bpy_{2.0}-CuBr_{1.0},

$m_{(styrene+BMA)}/m_{anisole} = 2/1$, 90 °C.

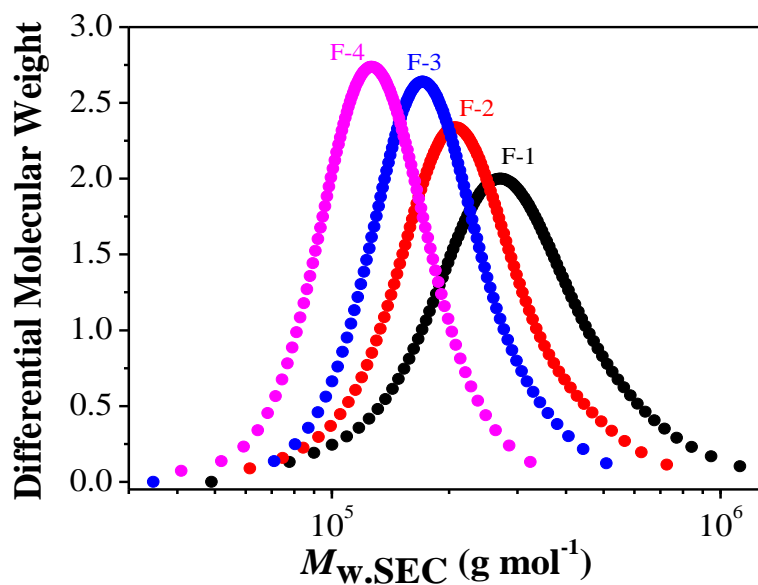


Fig. S14 Differential molecular weight distribution of the fractionations at 53 % monomer conversion.

t -BBiB_{1.0}-BMIH_{0.9}-styrene₃₀-PMDETA_{1.0}-CuBr_{1.0}, $m_{styrene}/m_{anisole} = 2/1$, 80 °C.

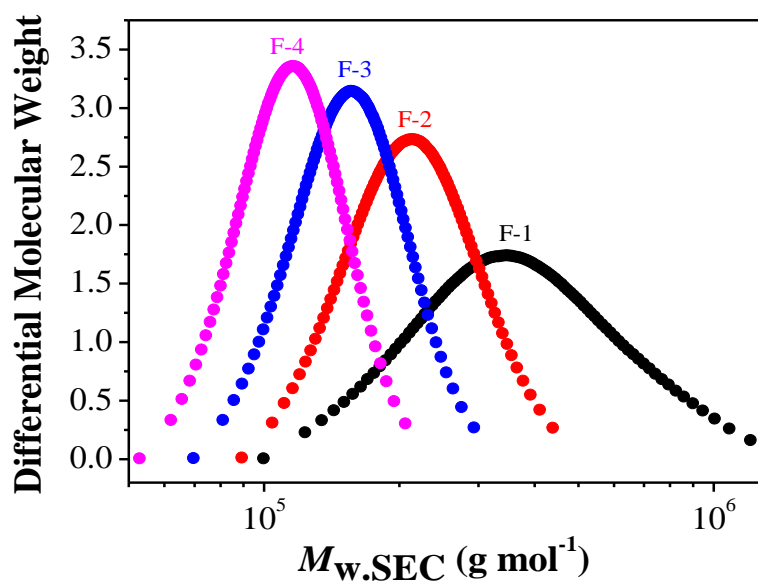


Fig. S15 Differential molecular weight distribution of the fractionations at 90 % monomer conversion.

t -BBiB_{1.0}-BMIH_{0.9}-styrene₃₀-PMDETA_{1.0}-CuBr_{1.0}, $m_{styrene}/m_{anisole} = 2/1$, 80 °C.