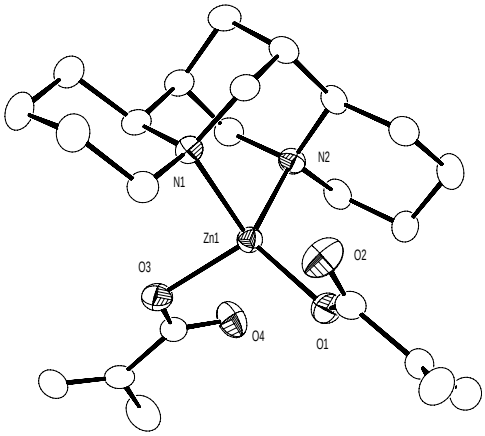
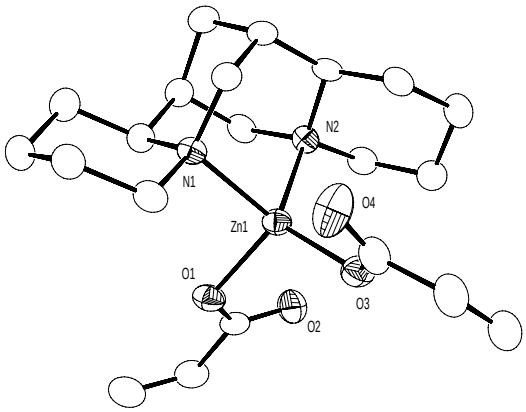
Supplementary Material (ESI) for Journal of Materials Chemistry


# Synthesis of main chain chiral (meth)acrylate copolymers via chirality transfer from polymerizable chiral metal complexes

Satyasankar Jana*, Peter A. G. Cormack, Alan R. Kennedy and David C. Sherrington*

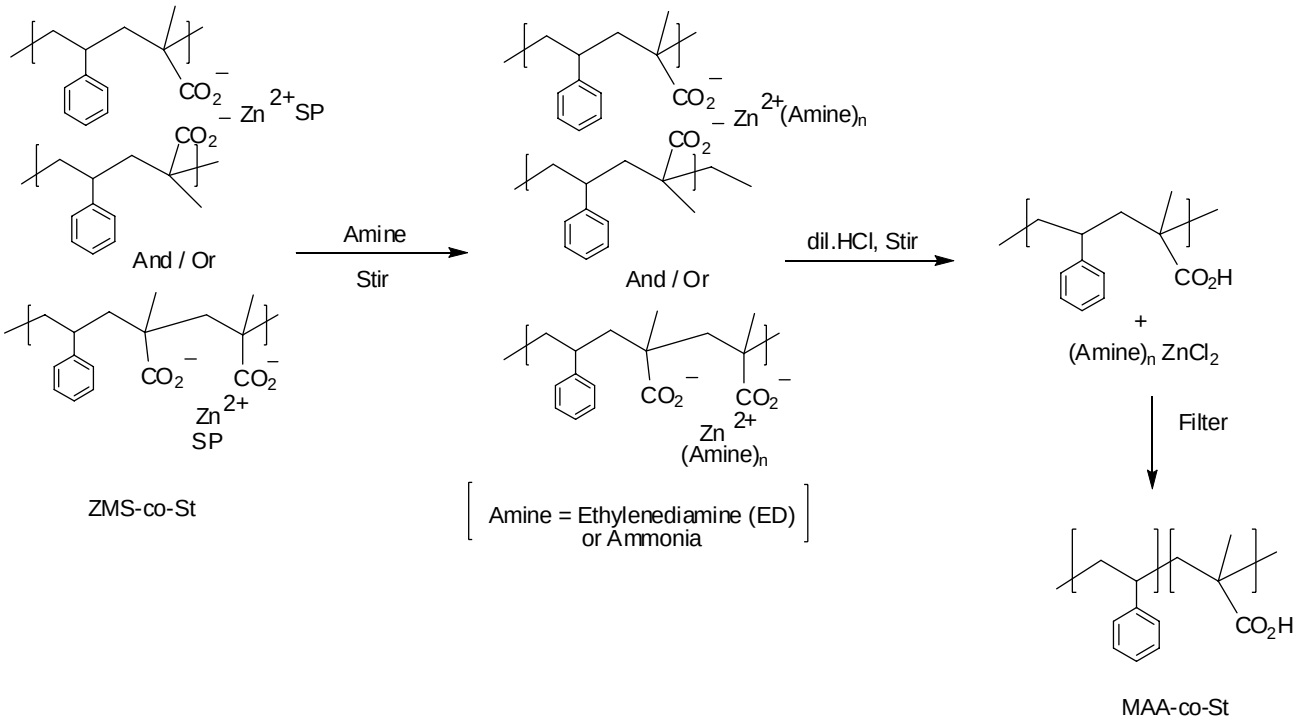



(a)




(b)

**Figure S1.** Single crystal X-ray crystal structures of (a) **ZMS** and (b) **ZAS****.




**Scheme S1**. Purification of crude ZMS-St copolymers to yield MAA-St copolymers by method B/C.

**Data S1.** Microanalytical data, FT-IR and $^1$H NMR spectra of copolymer derived from ZMS and St before and after purification and also following methylation

*Before purification*

Found (Polymer code **2a**): C, 68.98; H, 7.40; N, 3.17%.

$\nu_{max}$/cm$^{-1}$(KBr): 2935, 1600, 1493, 1451, 758, 699.

$^1$H NMR – not recorded as the sample was insoluble.

*After purification and before methylation*

Found (Polymer code **2b**): C, 79.28; H, 7.22; N, trace / nil%.

Found (Polymer code **2c**): C, 78.35; H, 7.40; N, 0.47%.

FTIR (both **2b** and **2c**): $\nu_{max}/cm^{-1}$(KBr): 1698 (acid C=O), 1600, 1493, 1451, 758, 699.

$\delta_H$(400 MHz; DMSO) (both **2b** and **2c**): 0.41, 1.60 (backbone C*H*$_2$ and C*H* and sidechain C*H*$_3$), 6.81-7.11 (aromatic C*H*), 11.86 (acidic CO$_2$*H*).

*After methylation*

Found (Polymer code **2bm**): C, 78.79; H, 7.95; N, trace / nil%.

Found (Polymer code **2cm**): C, 78.18; H, 7.61; N, 0.45%.

FTIR (both **2bm** and **2cm**): $\nu_{max}/cm^{-1}$(KBr): 1728 (ester C=O), 1600, 1493, 1452, 758, 699.

$\delta_H$(400 MHz; $CDCl_3$): 0.05, 0.56, 1.27 (backbone C*H*$_2$ and C*H* and sidechain C*H*$_3$), 2.89-3.7 (sidechain OC*H*$_3$), 6.85-7.32 (aromatic C*H*)

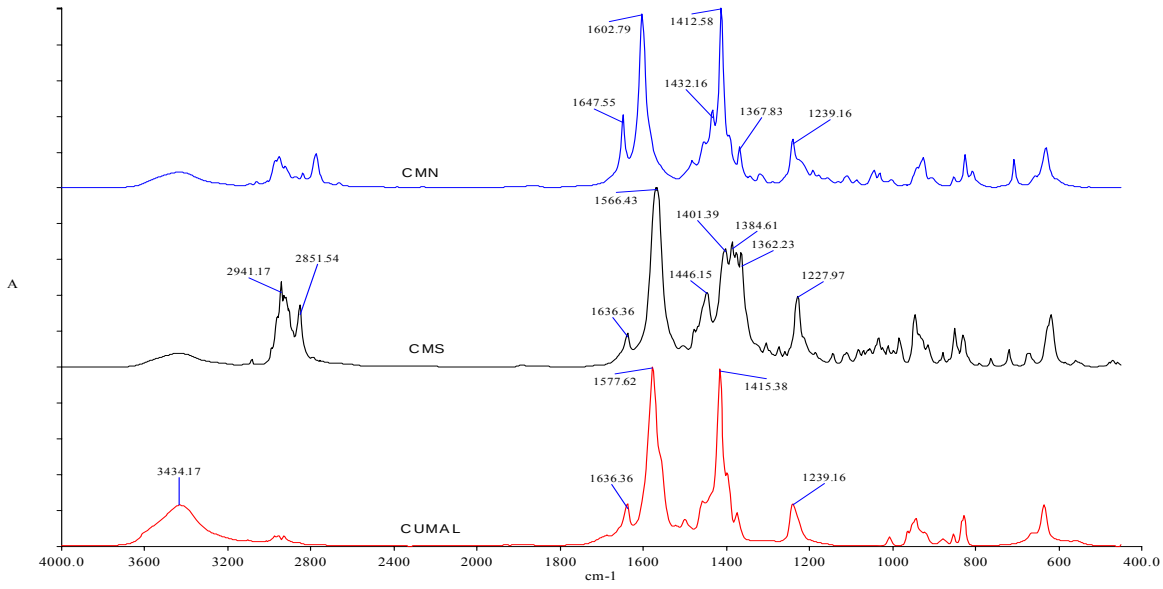



**Figure S2.** FT-IR spectra of copper(II) (meth)acrylate complexes, **CUMAL**, **CMS** and **CMN**

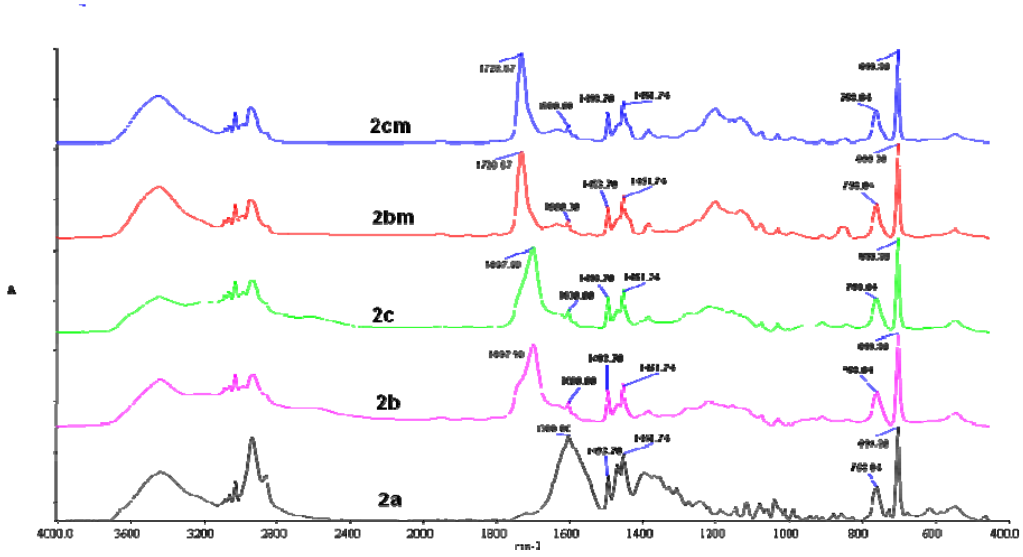



**Figure S3.** FT-IR spectra of unpurified (**2a**), purified (**2b, 2c**) and methylated copolymers (**2bm, 2cm**) synthesized from **ZMS** and styrene.

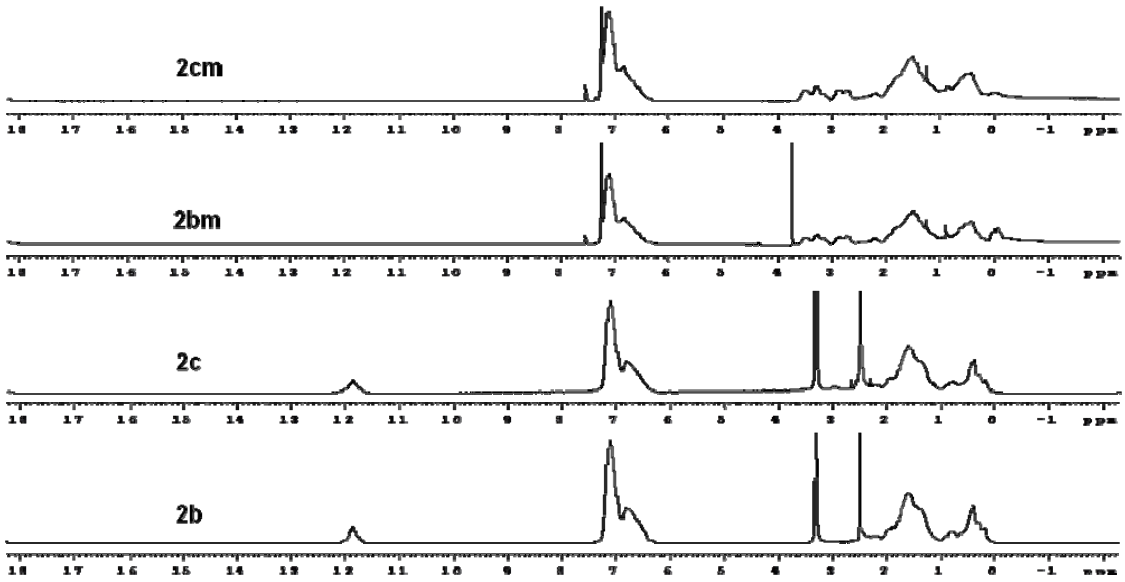



**Figure S4.** [1]HNMR spectra of purified (**2b, 2c**) and methylated (**2bm, 2cm**) copolymers.

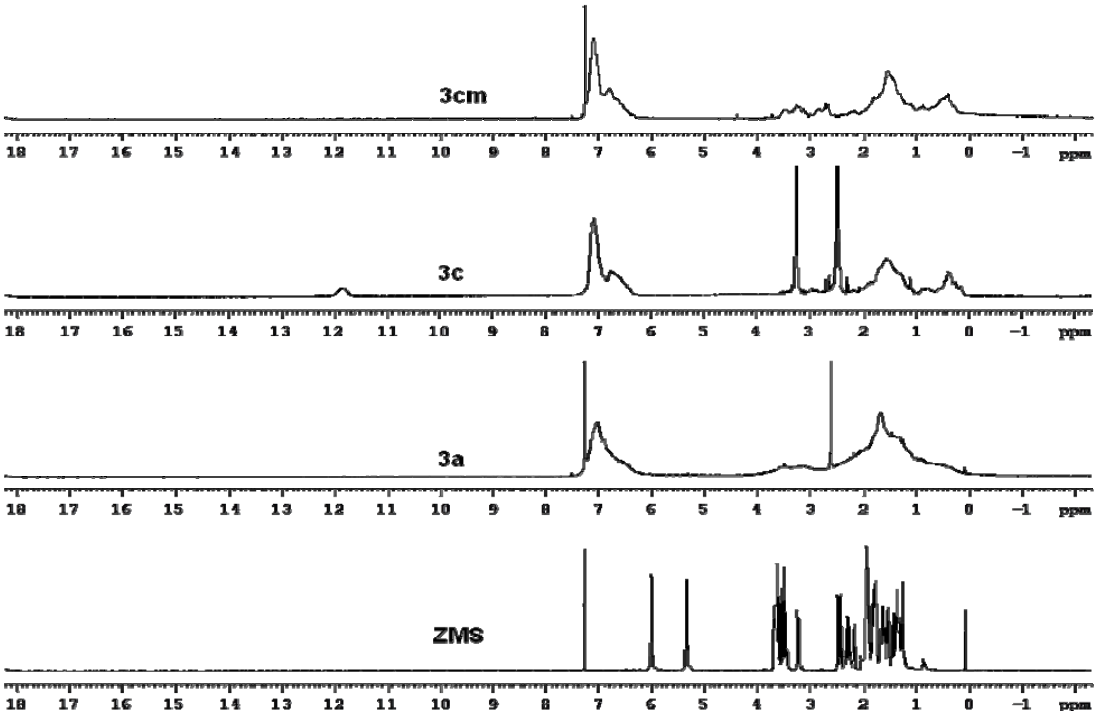



**Figure S5.** $^{1}$H NMR spectra of **ZMS**, unpurified (**3a**), purified (**3c**) and methylated copolymers (**3cm**).

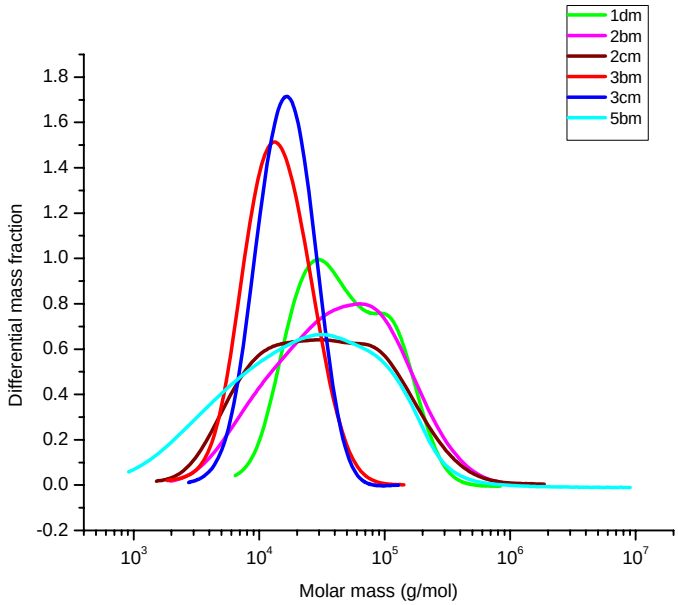
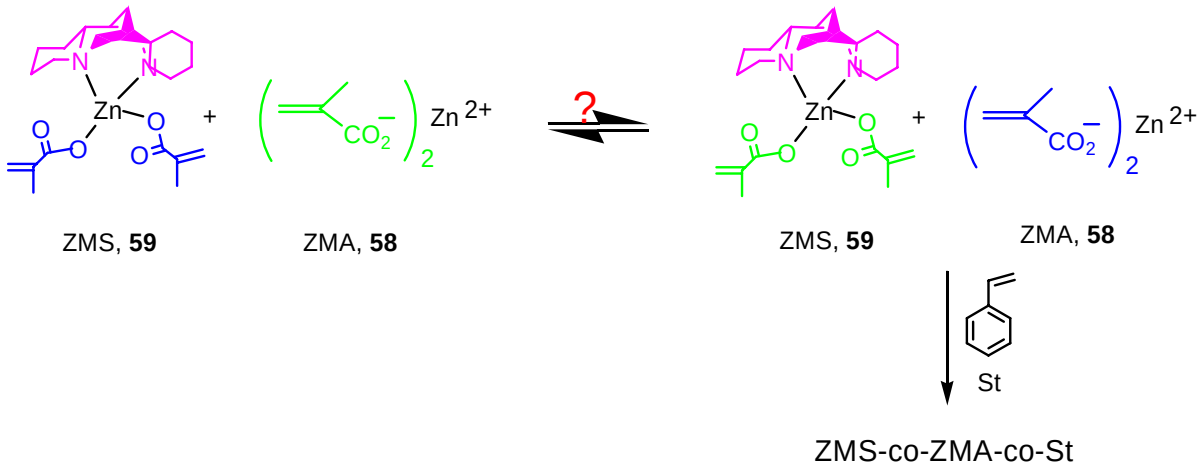



**Figure S6.** SEC derived molar mass distribution plots of chiral St-MMA copolymers synthesized from **ZMS** and St.




**Scheme S2.** Possible equilibrium between **ZMS** and **ZMA** involving exchange of methacrylate anion or (-)-sparteine ligand during copolymerization with styrene.

**Data S2.** Microanalytical data, FT-IR and $^{1}$H NMR spectra of copolymer derived from ZAS and St before and after purification and also following methylation.

*Before purification (**15a**)*

Found: C, 66.80; H, 6.74; N, 2.20%.

$\nu_{max}$/cm$^{-1}$(KBr): 1600, 1491, 1451, 1409, 761, 699.

$\delta_H$(400 MHz; $CDCl_3$): 0.8-3.7 (polymer backbone C*H*$_2$ and CH and sparteine C*H*$_2$ and C*H*), 7.05 (aromatic C*H*).

*After purification and before methylation (**15b**)*

Found: C, 77.02; H, 7.05; N, trace/nil%.

$\nu_{max}/cm^{-1}$(KBr): 1703, 1600, 1493, 760, 699.

$\delta_H$(400 MHz; DMSO): 1.0-2.3 (polymer backbone C*H*$_2$ and C*H*), 6.68-7.12 (aromatic C*H*) 11.9 (COO*H*).

*After methylation (**15bm**)*

Found: C, 77.79; H, 7.04; N, 0.82%.

$\nu_{max}/cm^{-1}$(KBr): 1731, 1600, 1493, 1163, 760, 699.

$\delta_H$(400 MHz; $CDCl_3$): 0.9-2.5 (polymer backbone C*H*$_2$ and C*H*), 3.0-3.7 (sidechain OC*H*$_3$) 6.7-7.1 (aromatic C*H*).

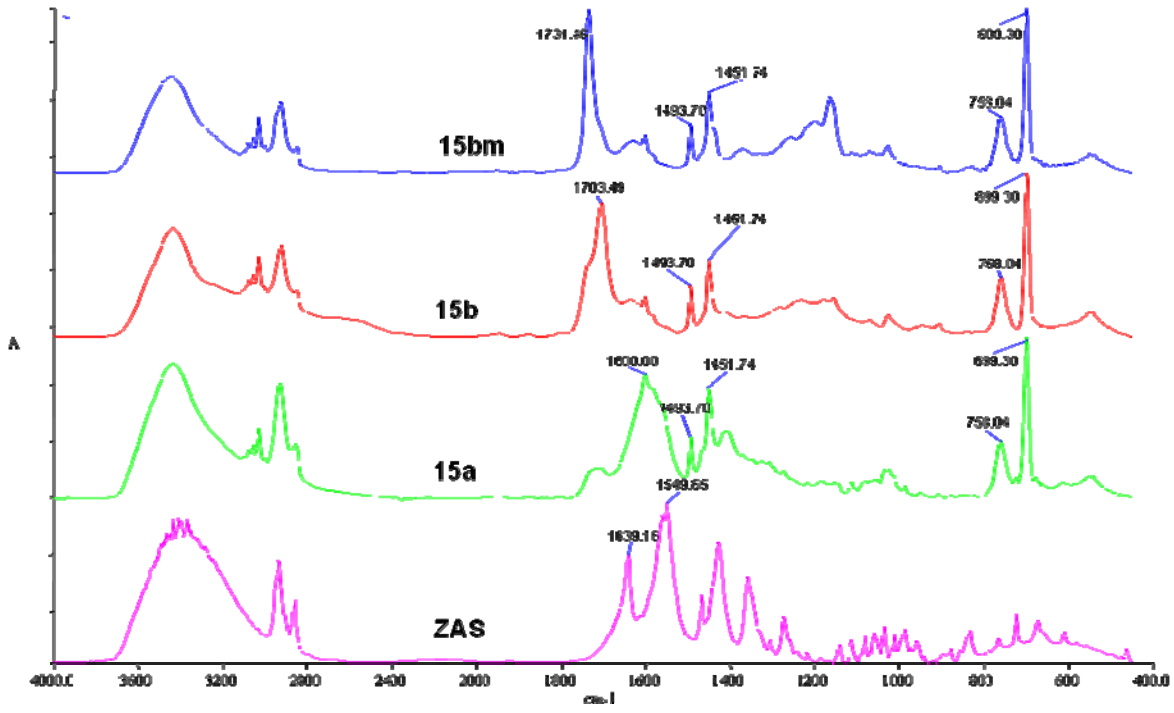



**Figure S7.** FT-IR Spectra of **ZAS**, unpurified copolymer (**15a**), purified copolymer (**15b**) and methylated copolymer (**15bm**).

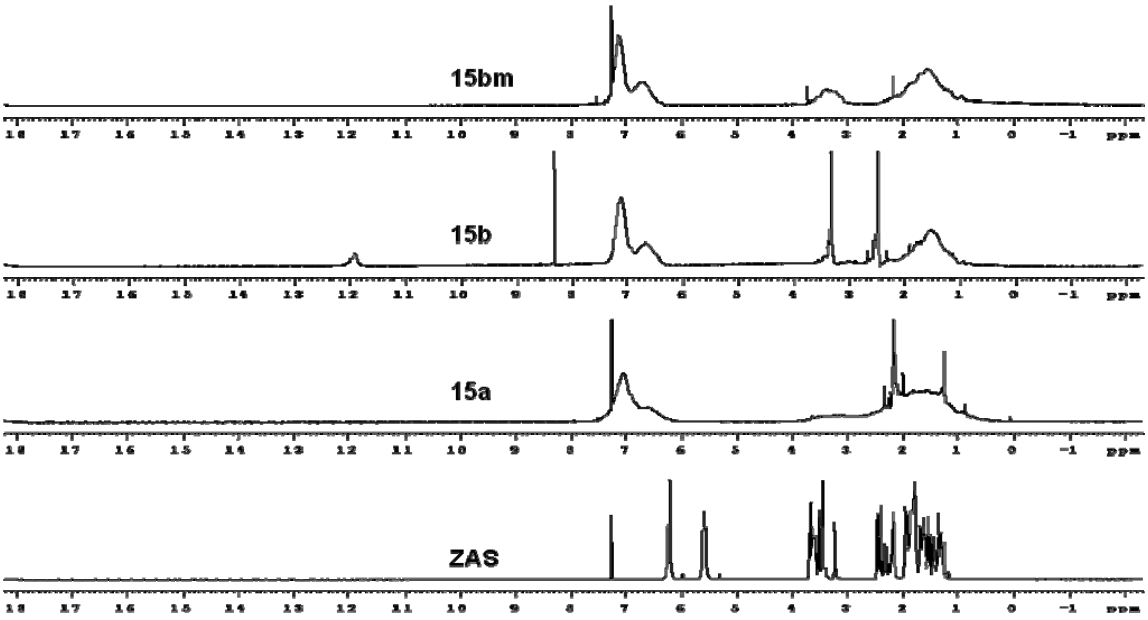



**Figure S8.** $^{1}$H NMR spectra of **ZAS**, unpurified (**15a**), purified (**15b**) and methylated copolymers (**15bm**) synthesized therefrom.

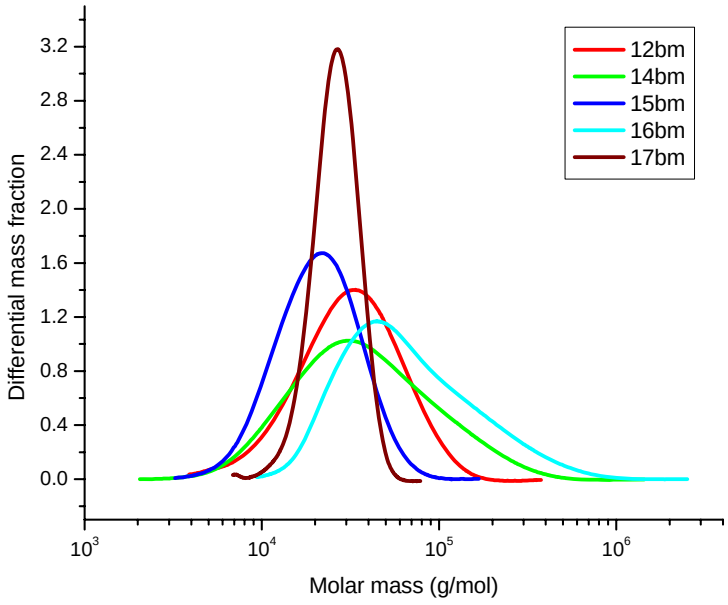
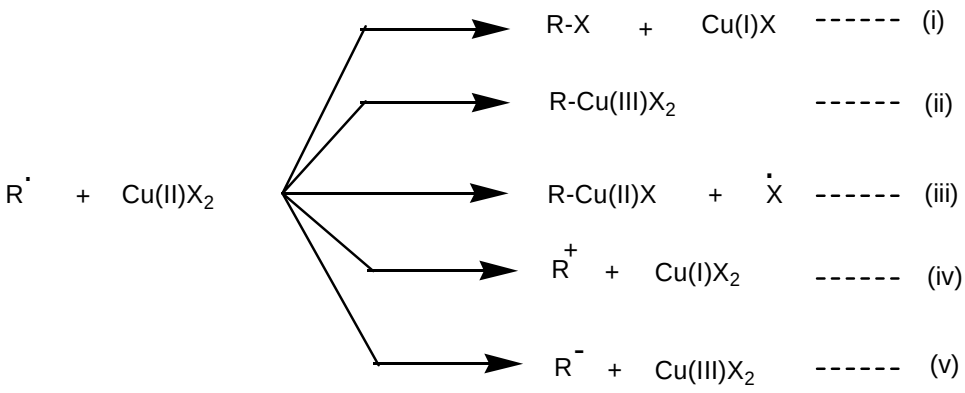



**Figure S9.** SEC derived molar mass distribution of chiral St-MA (**12bm-17bm**) copolymers synthesized using **ZAS** and St.

.




**Scheme S3.** Interaction of copper(II) compounds with propagating radicals.