# Supporting information

# Allylthioketone Mediated Free Radical Polymerization of Methacrylates

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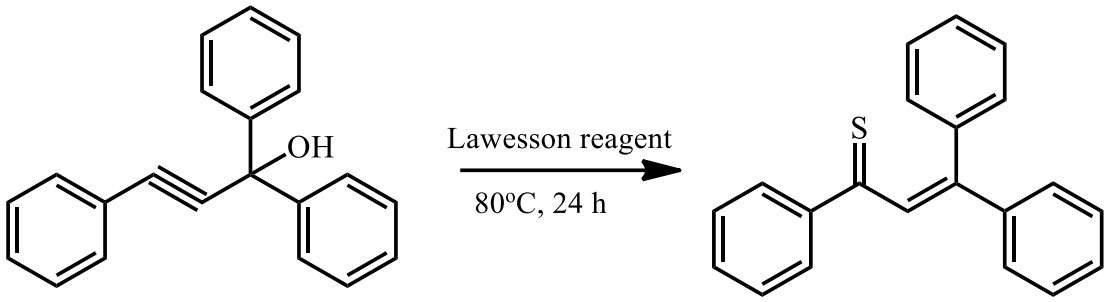


**Scheme S1**. Synthesis of 1,3,3-triphenylprop-2-ene-1-thione

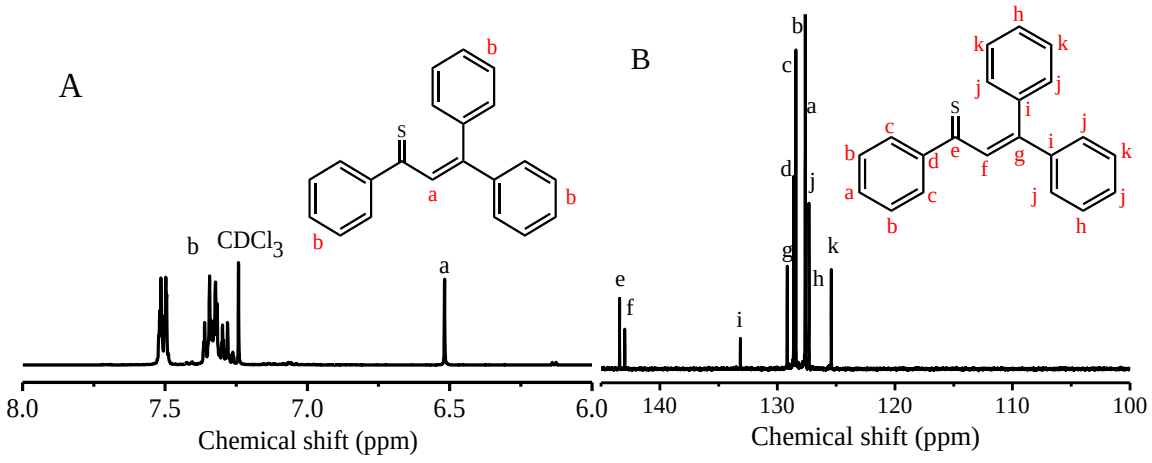


**Figure S1**. $^{1}$H NMR (A) and $^{13}$C NMR (B) spectra of 1,3,3-triphenylprop-2-ene-1-thione (TPPT)

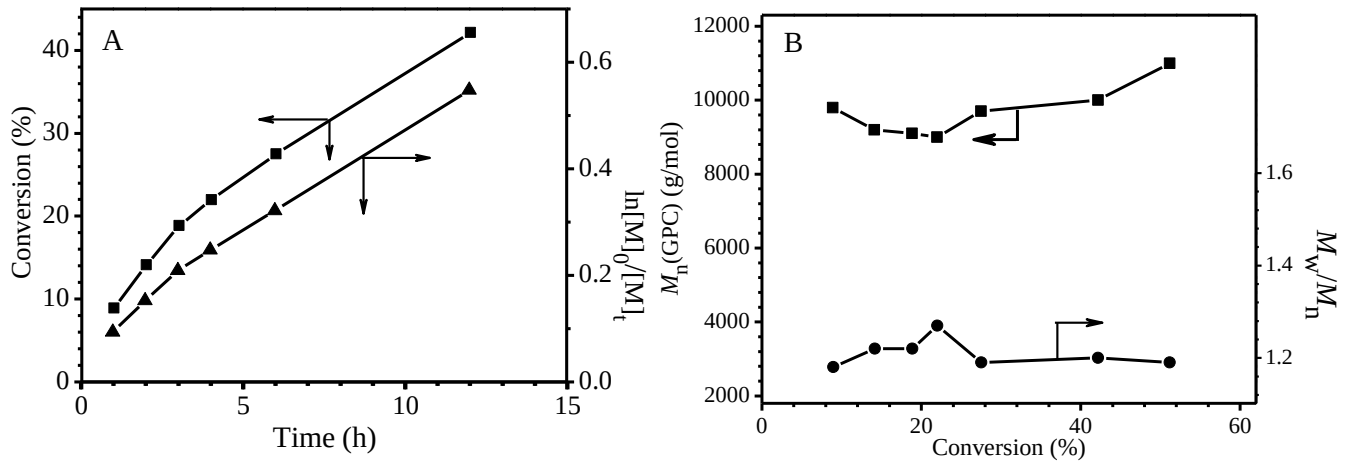


**Figure S2**. Polymerization kinetics (A) and relationship of $M_n$ (GPC) and $M_w/M_n$ with the conversion (B) for the polymerization in anisole (50 wt%) with feed molar ratio of MMA/TPPT/AIBME = 100/2/1 at 70°C.

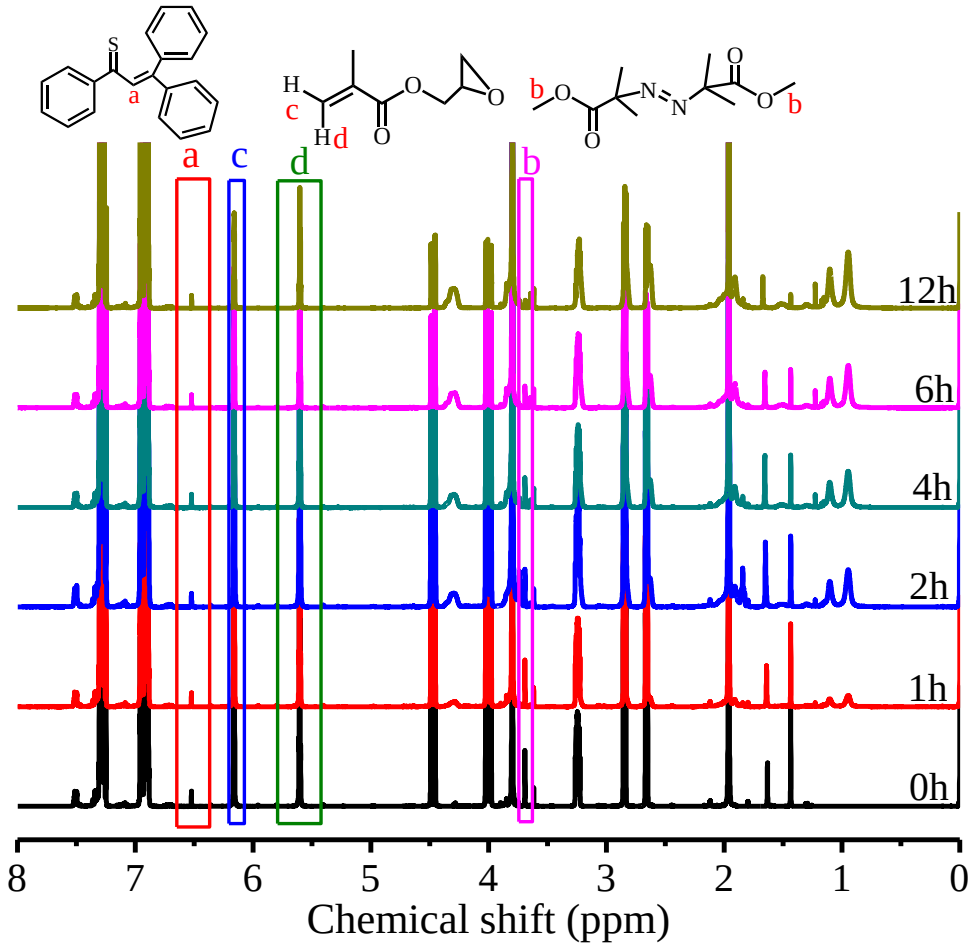


**Figure S3.** $^{1}$H NMR spectra of the polymerization solutions for the polymerization of GMA with feed molar ratio of GMA/TPPT/AIBN=100/2/1 at 70$^{o}$C in anisole (50 wt%) for different reaction time.

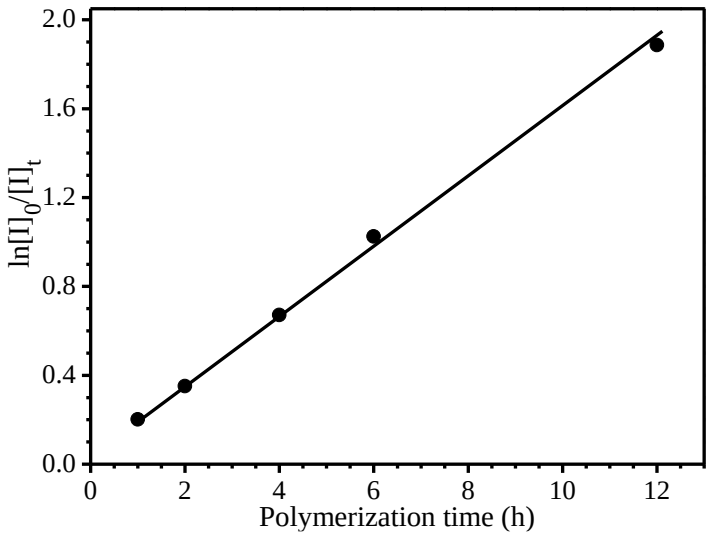


**Figure S4**. Kinetics of AIBME decomposition in the polymerization of GMA with the feed molar ratio of GMA/TPPT/AIBME=100/2/1 in anisole (50 wt%) at 70ºC.

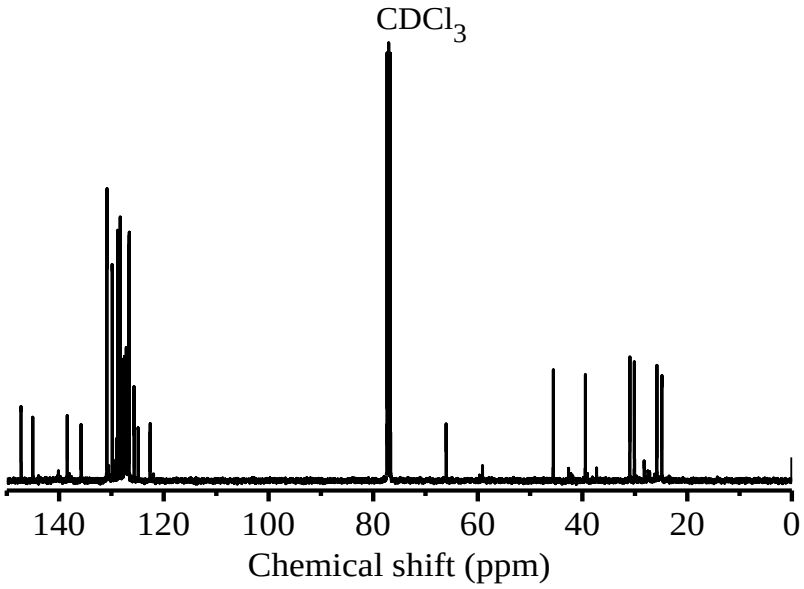


**Figure S5**. $^{13}C$ NMR spectrum of 1,3,3-triphenyl-1-isobutylnitilesulfo-3- isobutylnitrileprop-2-ene.

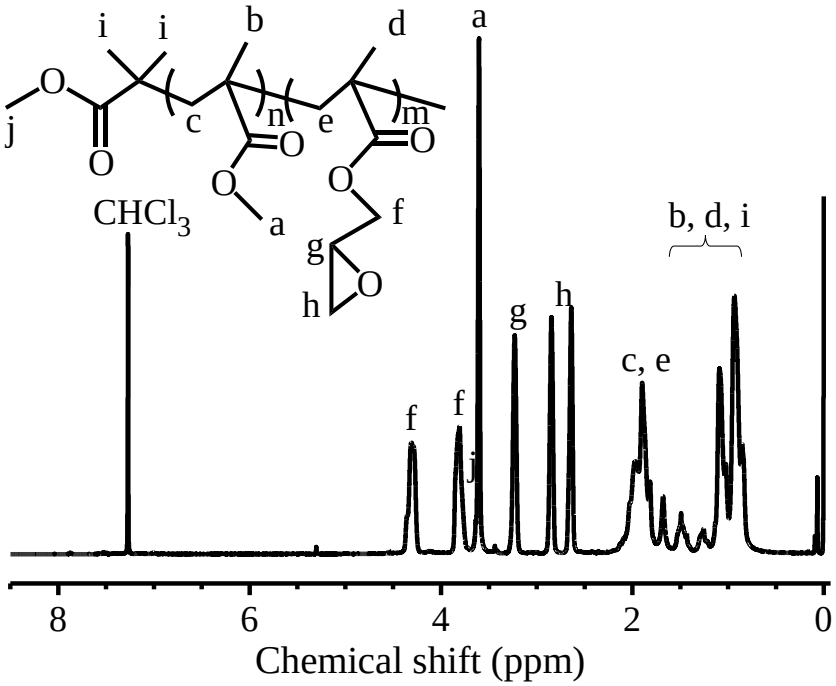


**Figure S6**. $^{1}$H NMR spectrum of the block copolymer, PMMA-*b*-PGMA obtained from the extension polymerization of PMMA ($M_n$=6400 and $M_w/M_n$=1.23) by directly adding the GMA (double moles of MMA) into the PMMA solution, which was obtained by the polymerization of MMA with feed molar ratio of MMA/TPPT/AIBME=50/2/1 in anisole (50 wt%) at 70$^{o}$C for 24 h, and then continuous polymerization in anisole (30 wt%) at 70$^{o}$C for 12 h.

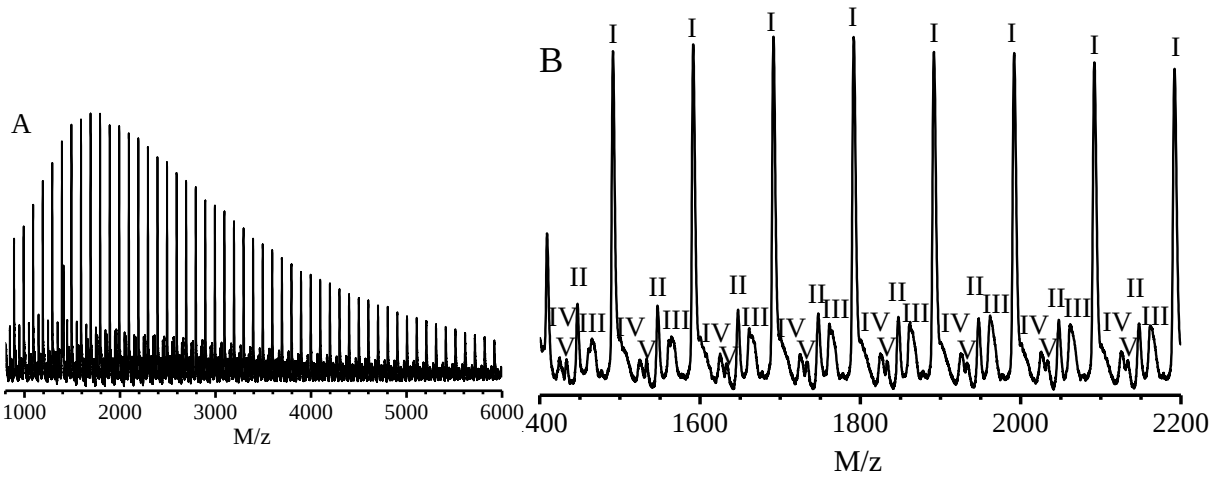


**Figure S7**. MALDI-TOF spectrum (A) and enlarged spectrum (B) of the poly(methyl methacrylate) obtained by radical polymerization with feed molar ratio of MMA/TPPT/AIBN=20/2/1 in anisole (concentration = 20%) at 70°C for 24h.

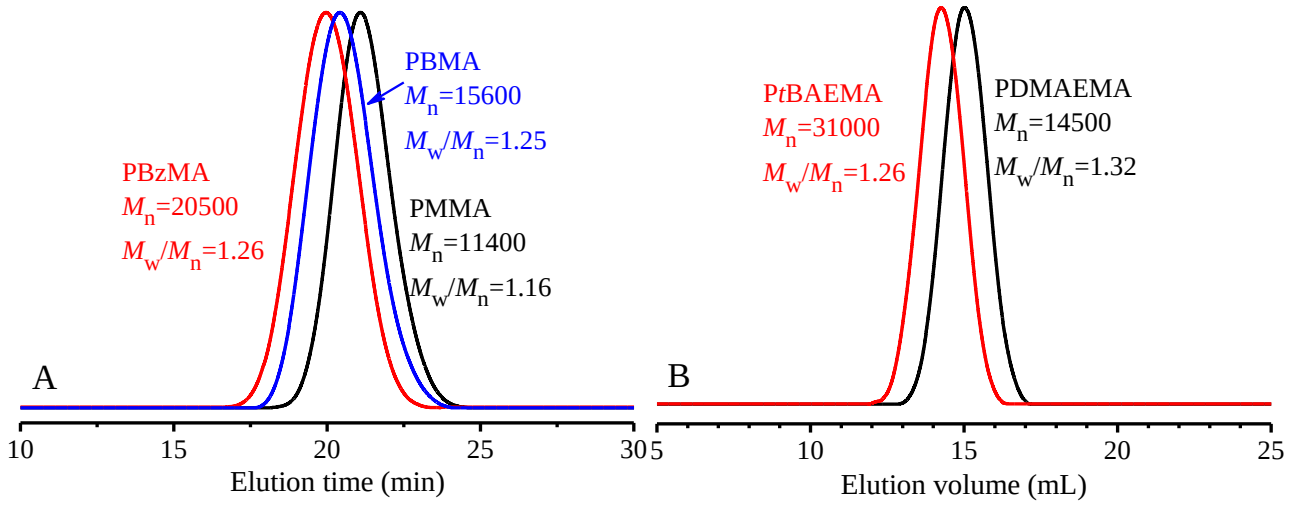


**Figure S8.** GPC traces of the PMMA, PBMA, PBzMA, PDMAEMA and P*t*BAEMA prepared by the polymerization with feed molar ratio of M/TPPT/AIBME=100/2/1 in anisole (50 wt%) at 70°C for 12 h. For PMMA, PBMA and PBzMA, THF was used as eluent, for PDMAEMA and P*t*BAEMA, DMF was used as eluent.

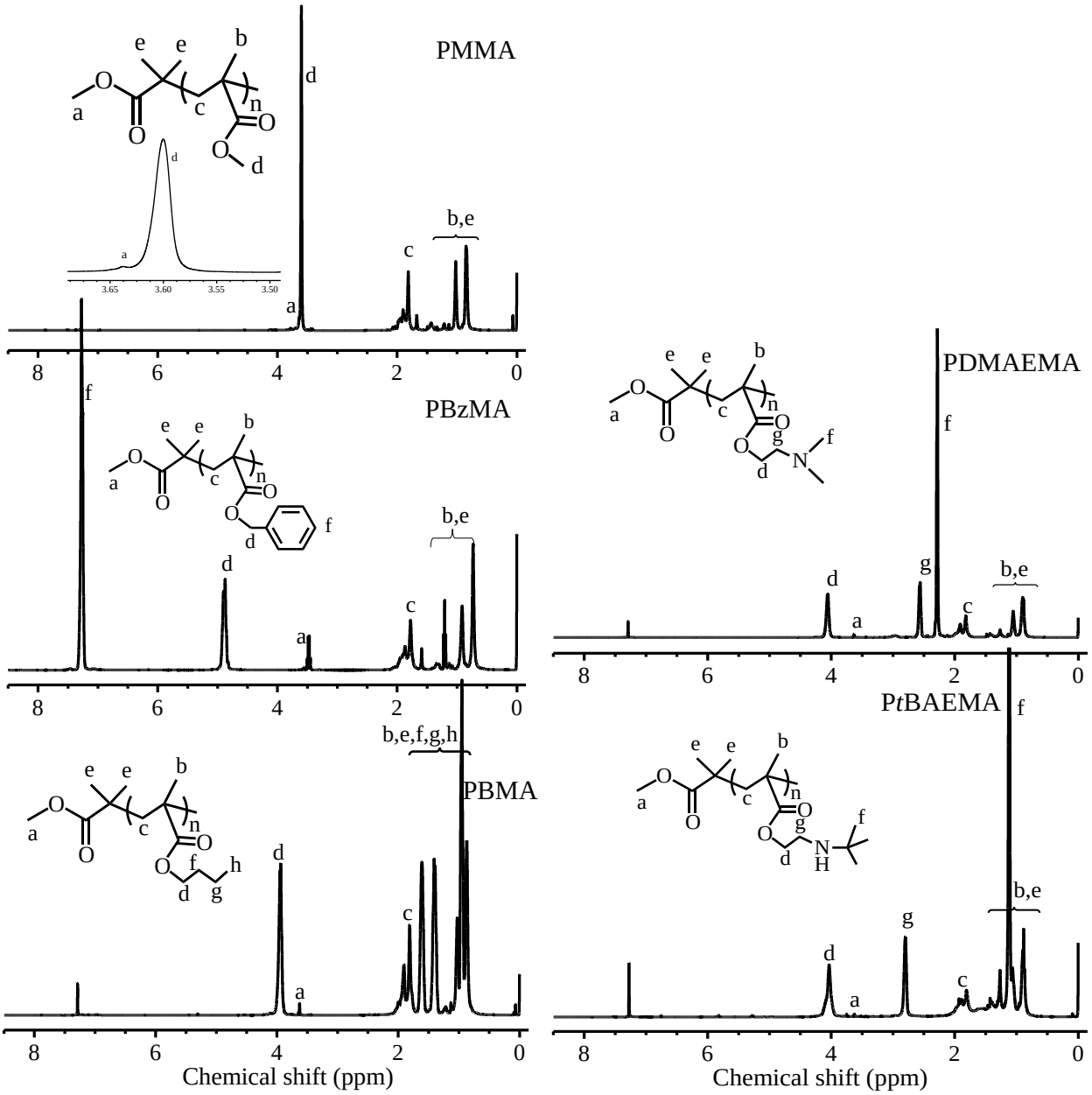


**Figure S9**. $^{1}$H NMR spectra of PMMA, PBzMA, PBMA, PDMAEMA and P*t*BAEMA prepared by the polymerizations with feed molar ratio of M/TPPT/AIBME = 100/2/1 in anisole (50 wt%) at 70$^{o}$C for 12 h.