Electronic Supplementary Material (ESI) for Polymer Chemistry.

Application of an Addition-Fragmentation-Chain Transfer Monomer in Di(meth)acrylate Network Formation to Reduce Polymerization Shrinkage Stress

Supplementary Information

Table S1 – Comparison of maximum reaction rate ($R_p$max) during polymerization, double bond conversion at 30 s (after turning on the light) and 20 min for BisGMA/TEGDMA and BisGA/TEGDA series as a function of AFM amount. Incident irradiation intensity = 200 mW/cm^2

		BisGMA/TEGDMA series				BisGA/TEGDA series		
		R_pMax (%/s)	Conversion at 30 s	Conversion at 20 mins		R_pMax (%/s)	Conversion at 30 s	Conversion at 20 mins
	0	6.2	68.9(0.8)	70.1(0.7)		8.2	89.7(0.4)	89.9(0.4)
	2.5	5.6	63.8(1.8)	65.7(1.6)		7.8	86.7(2.4)	86.9(2.4)
AFM wt%								
	5	5.5	62.7(2.1)	64.1(2.4)		5.7	74.2(4.5)	75.4(3.6)
	10	4.5	55.3(2.5)	58.3(1.9)		1.8	34.7(1.2)	37.0(1.3)
	20	3.4	46.8(4.4)	50.9(3.7)		0.8	14.6(1.2)	17.4(3.9)

Table S2 – Crossover times and conversions for BisGMA/TEGDMA and BisGA/TEGDA series as a function of AFM amount. Irradiation intensity – 2 mW/cm^2 for 30 s. Light was started at 30 s after start of run. Sample dimensions – 20 mm diameter disc with 0.5 mm thickness

	BisGMA/TEGDMA series			BisGA/TEGDA series	
AFM wt%	**Crossover time (s)**	**Crossover conversion (%)**		**Crossover time (s)**	**Crossover conversion (%)**
0	35(1)	<1		33(1)	<1
2.5	49(1)	2.8(0.7)		85(4)	2.9(0.4)
5	54(2)	2.2(0.6)		103(6)	5.8(1.6)
10	64(1)	4.2(0.1)		145(9)	5.7(0.5)
20	79(6)	4.7(0.2)		208(13)	5.7(0.3)

Table S3 – Double bond conversion of samples before and after measurement in the DMA.

Series	AFM amount (wt%)	% Double bond conversion before DMA measurement	% Double bond conversion after DMA measurement
BisGMA/TEGDMA	0	74.6	90.7
	2.5	72.0	88.3
	5	70.8	85.8
	10	69.5	84.9
	20	64.4	80.8
BisGA/TEGDA	0	87.5	89.6
	2.5	81.5	87.7
	5	76.1	86.9
	10	69.1	85.5
	20	47.2	74.2

NMR characterization

AFM - precursor

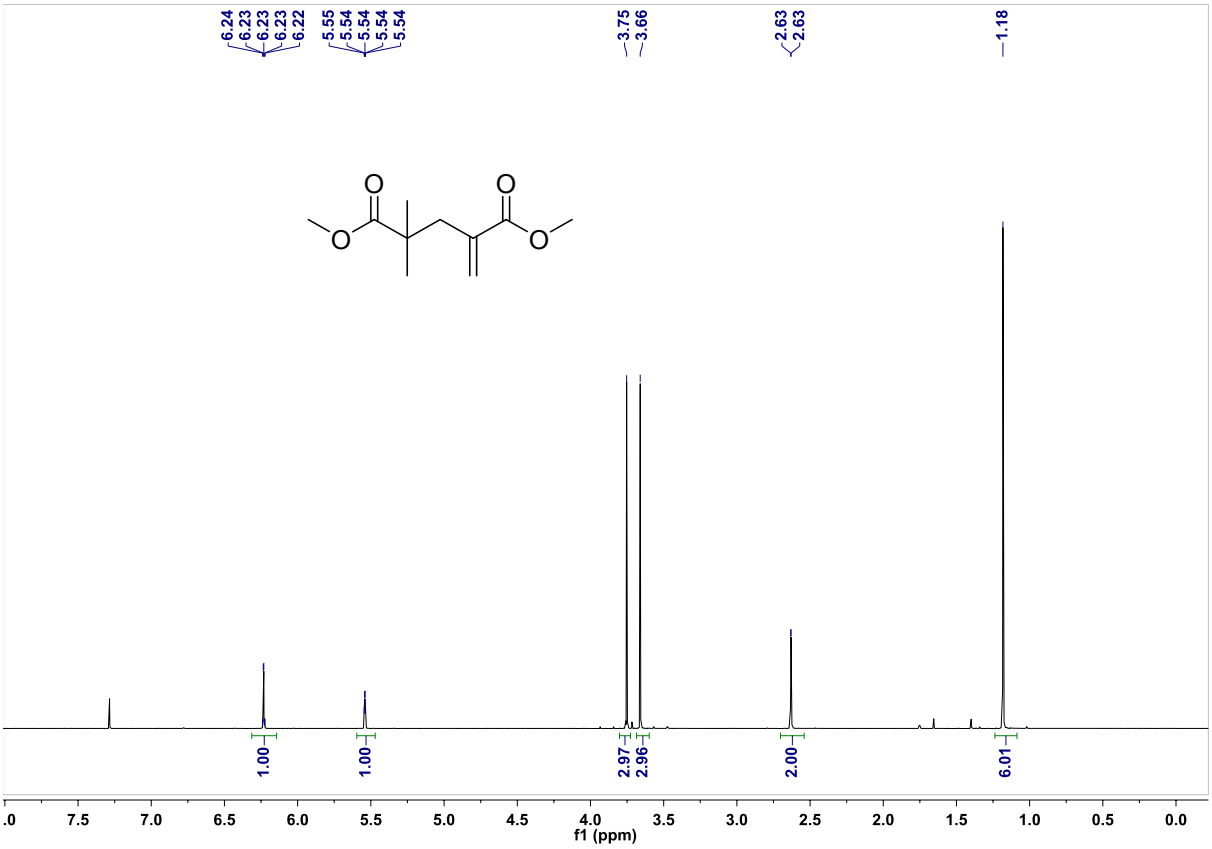


Figure S1 – Proton NMR for AFM precursor

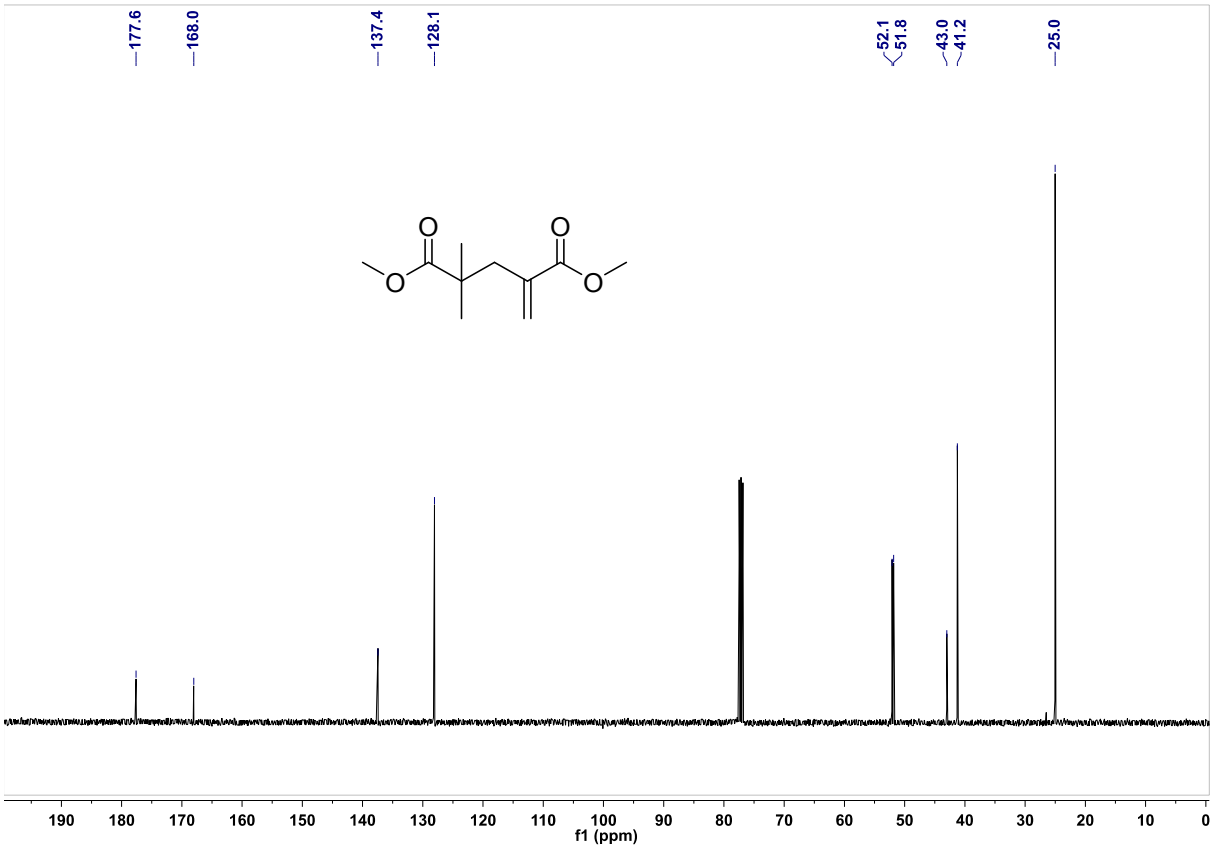


Figure S2 – Carbon NMR for AFM-precursor

AFM

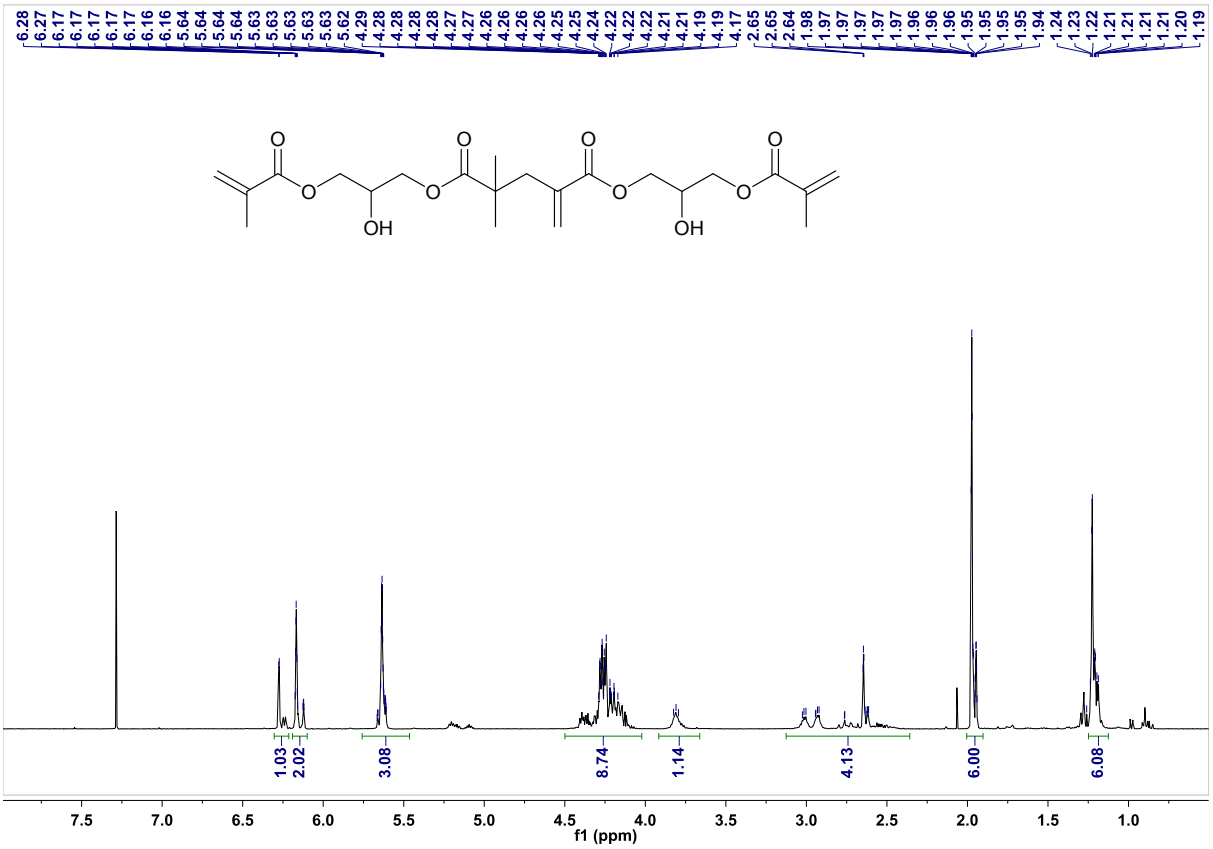


Figure S3 – Proton NMR for AFM

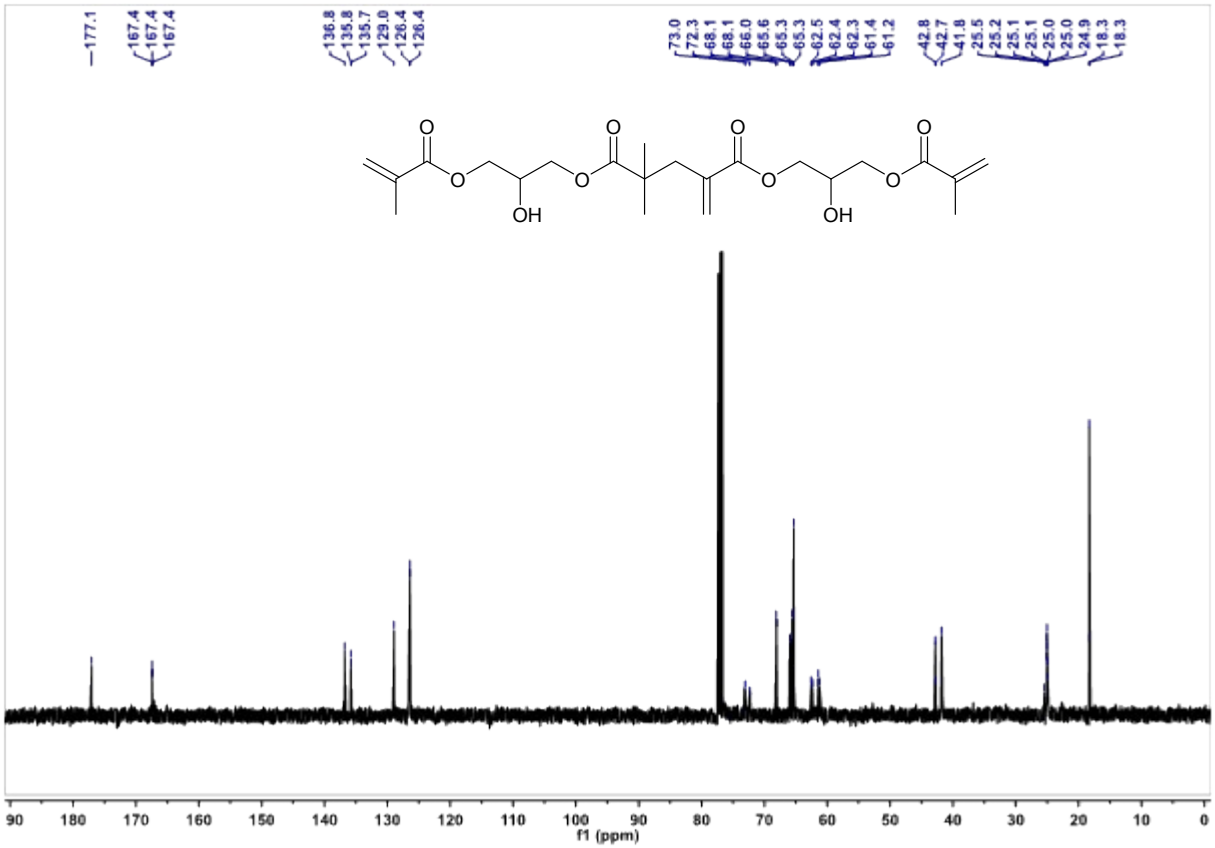


Figure S4 – Carbon NMR for AFM

Development of EPR spectra during polymerization

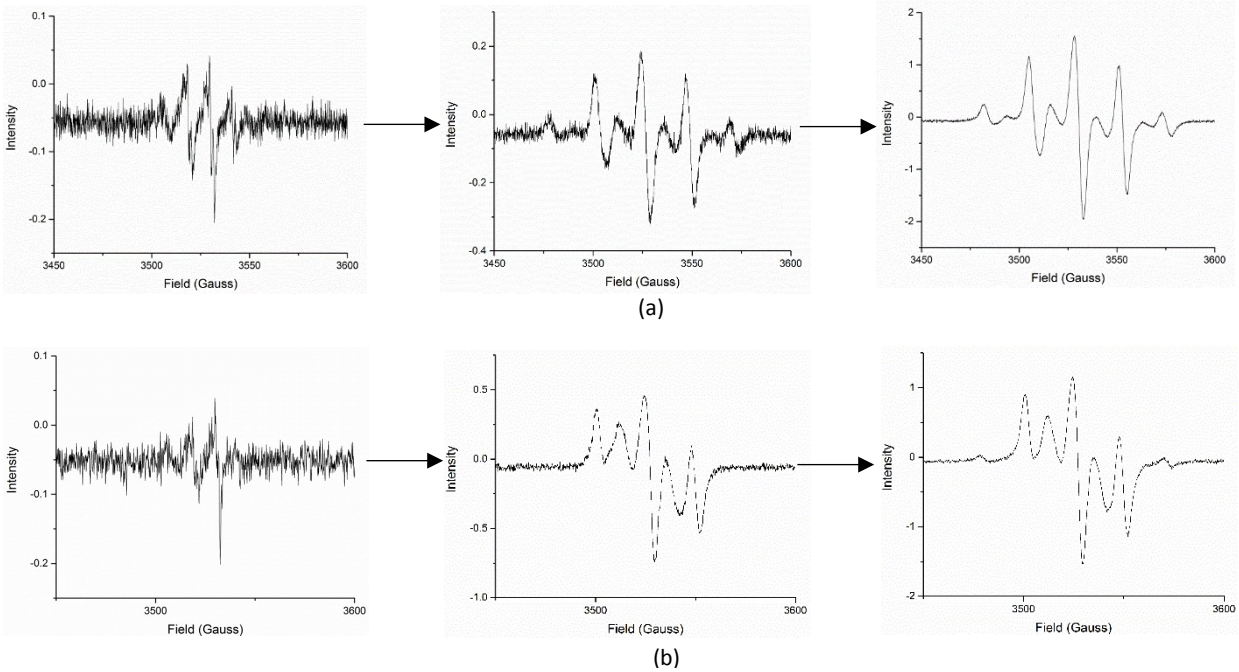


Figure S5 - Progressive EPR spectra of polymerization of (a) BisGMA/TEGDMA and (b) BisGMA/TEGDMA with 20 wt% AFM. Spectra are representative of the initial, midway and final stages of polymerization.

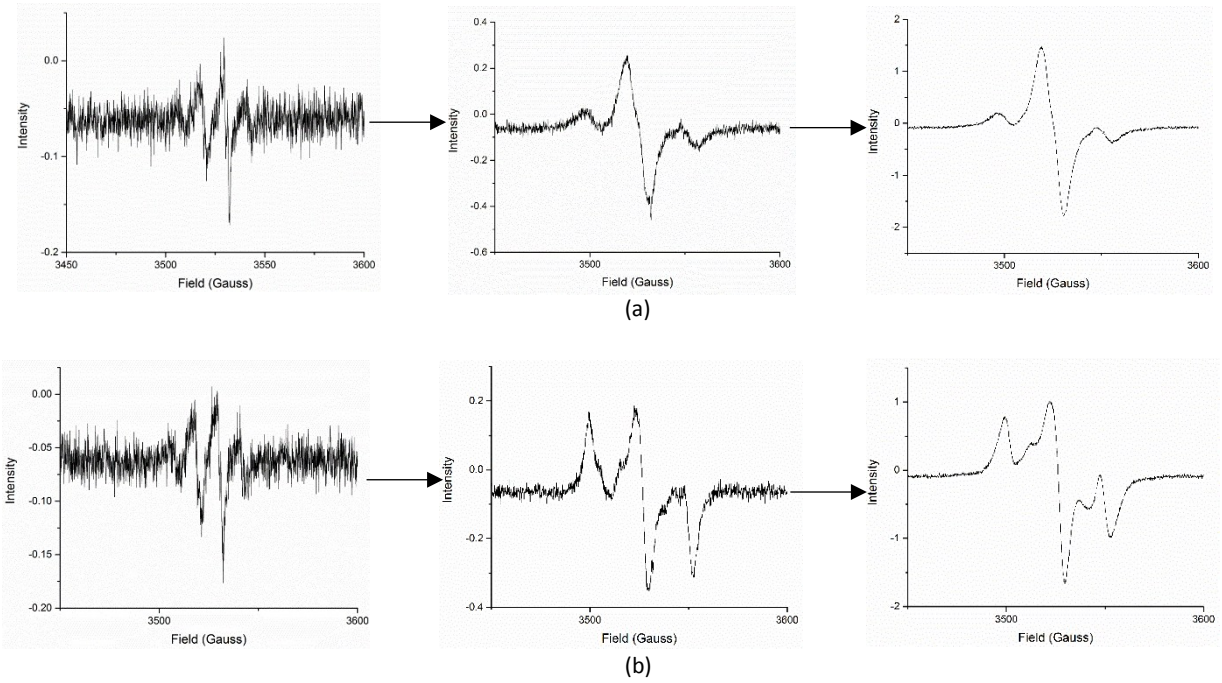
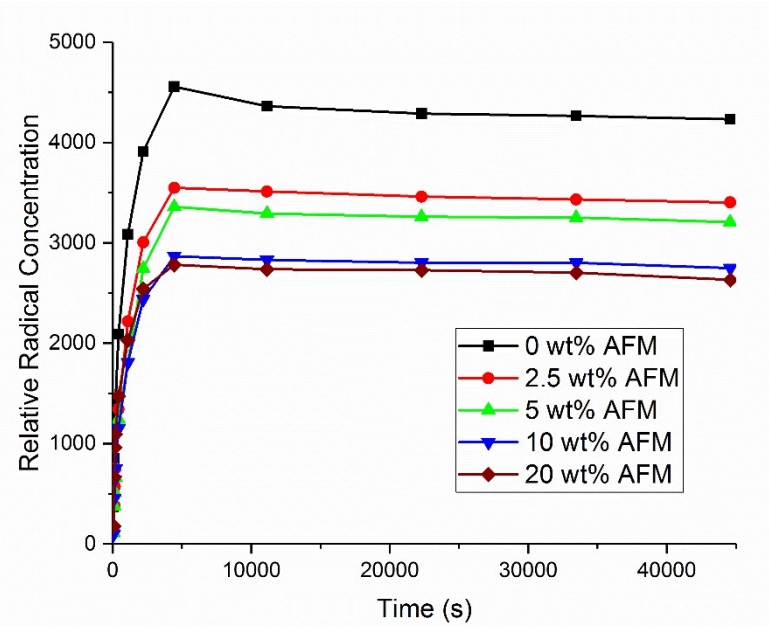


Figure S6 - Progressive EPR spectra of polymerization of (a) BisGA/TEGDA and (b) BisGA/TEGDA with 20 wt% AFM. Spectra are representative of the initial, midway and final stages of polymerization.

Radical decay profiles for the BisGMA/TEGDMA and BisGA/TEGDA series as a function of double bond conversion level.

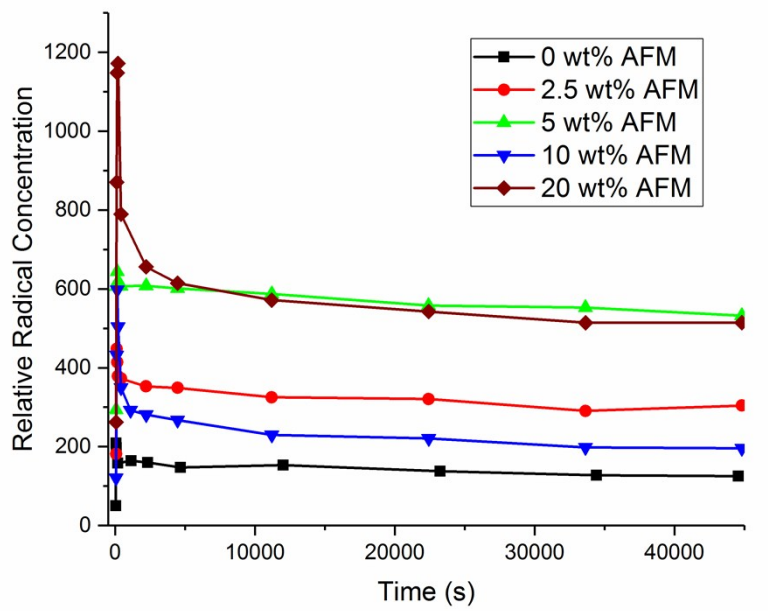
EPR measurements were performed simultaneously with polymerization. Samples were irradiated for different times to achieve high, moderate and low levels of double bond conversion



and then the light turned off and radical profiles monitored in dark.

Figure S7 – BisGMA/TEGDMA series – High conversion

Figure S8 – BisGMA/TEGDMA series – Moderate conversion



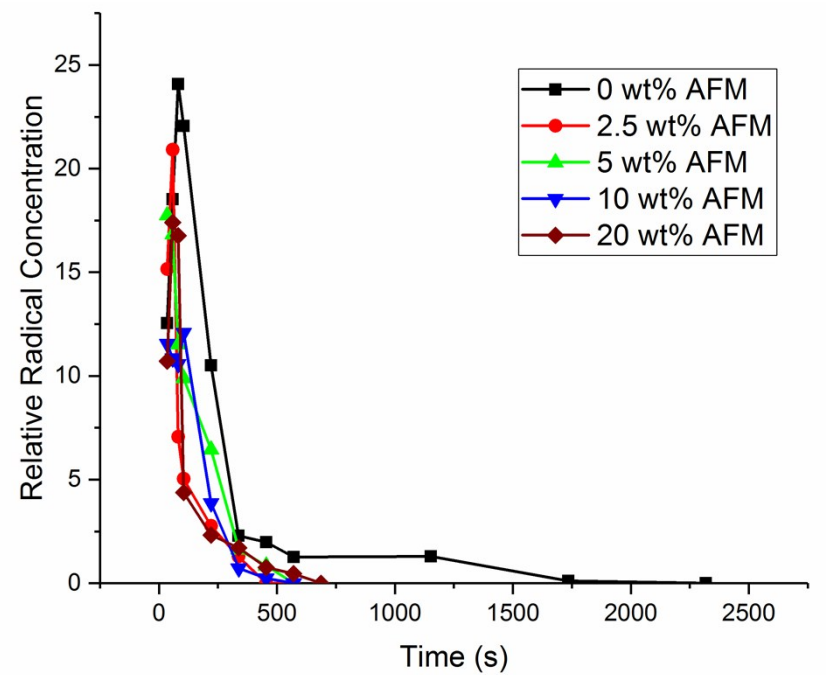


Figure S9 – BisGMA/TEGDMA series – Low conversion

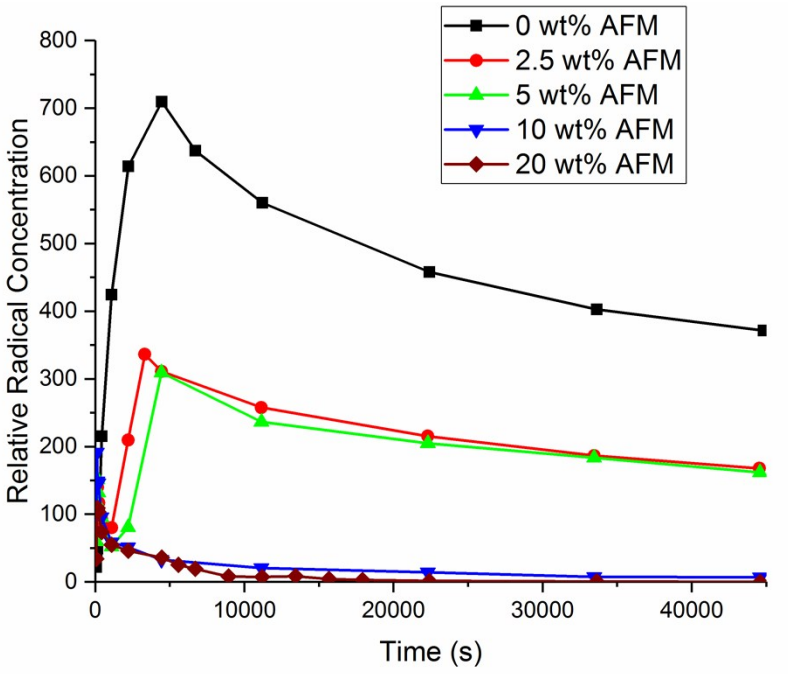


Figure S10 – BisGA/TEGDA series – High conversion

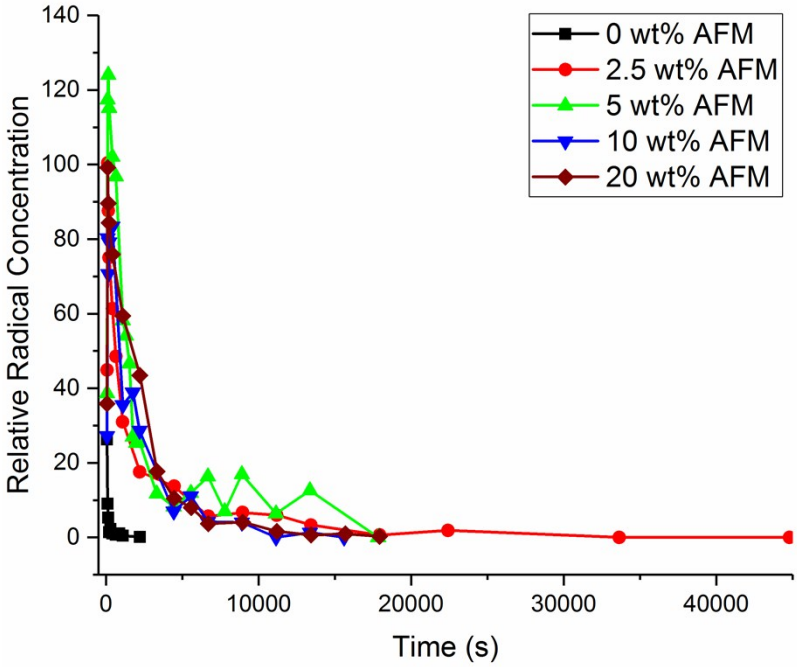


Figure S11 – BisGA/TEGDA series – Moderate conversion

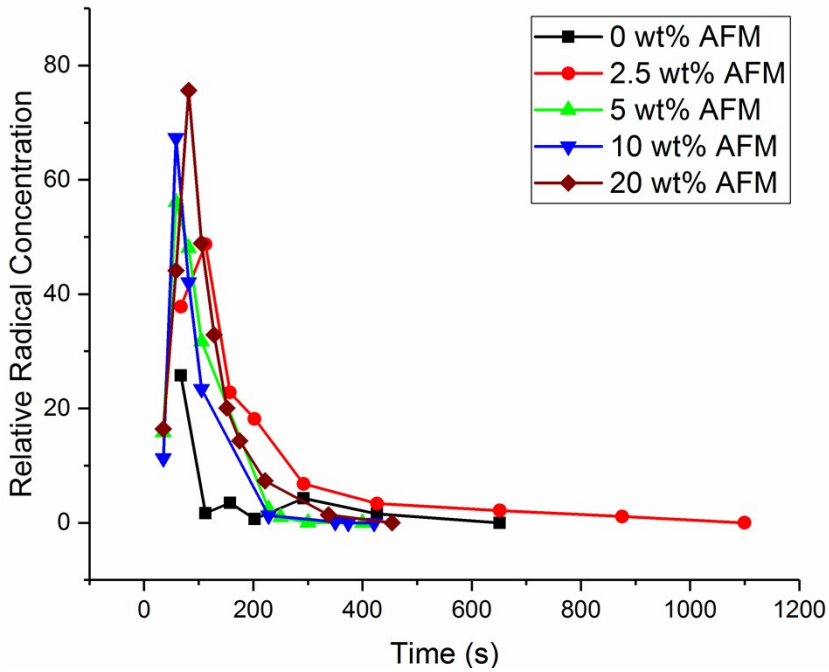


Figure S12 – BisGA/TEGDA series – Low conversion