

## Supporting Information

# Tacticity control approached by electric-field assisted free radical polymerization - the case of sterically hindered monomers

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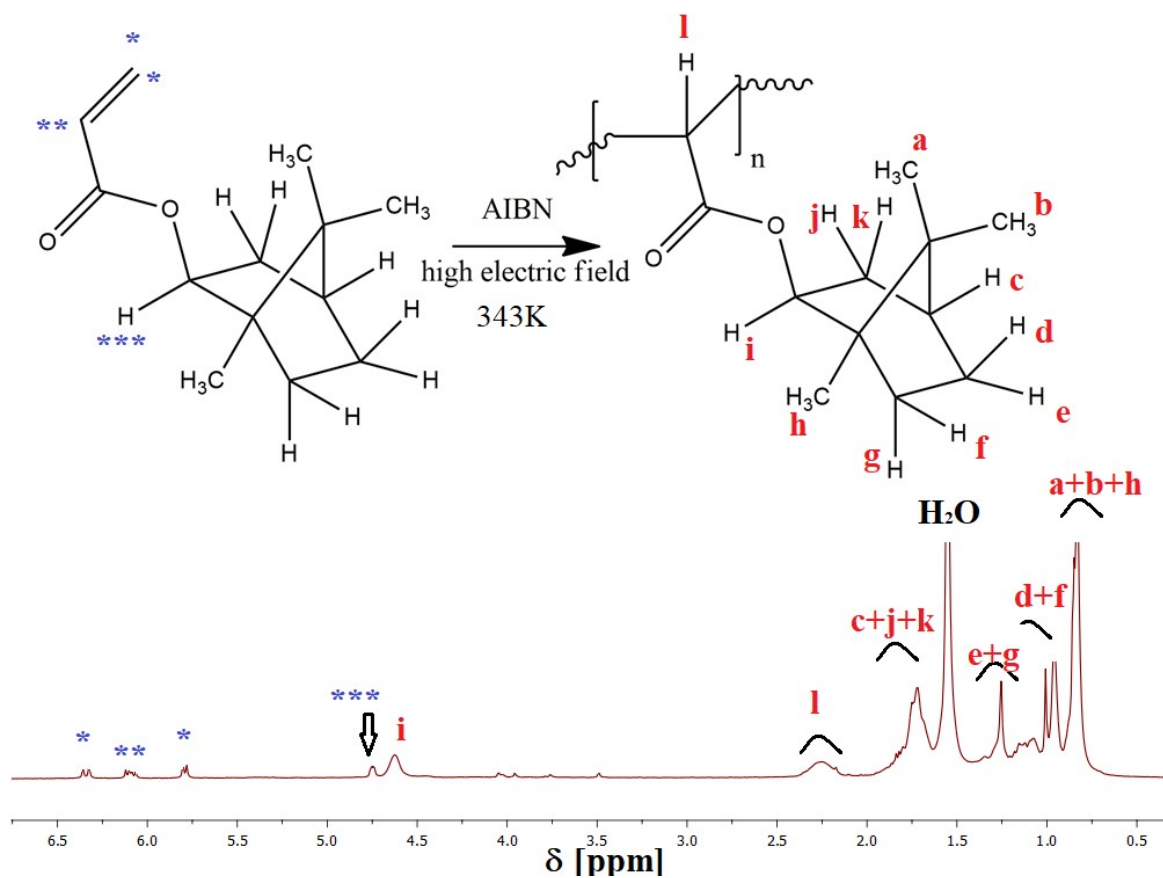


Figure S1.  $^1\text{H}$  NMR spectrum of the polymerization mixture (600 MHz,  $\text{CDCl}_3$ ).

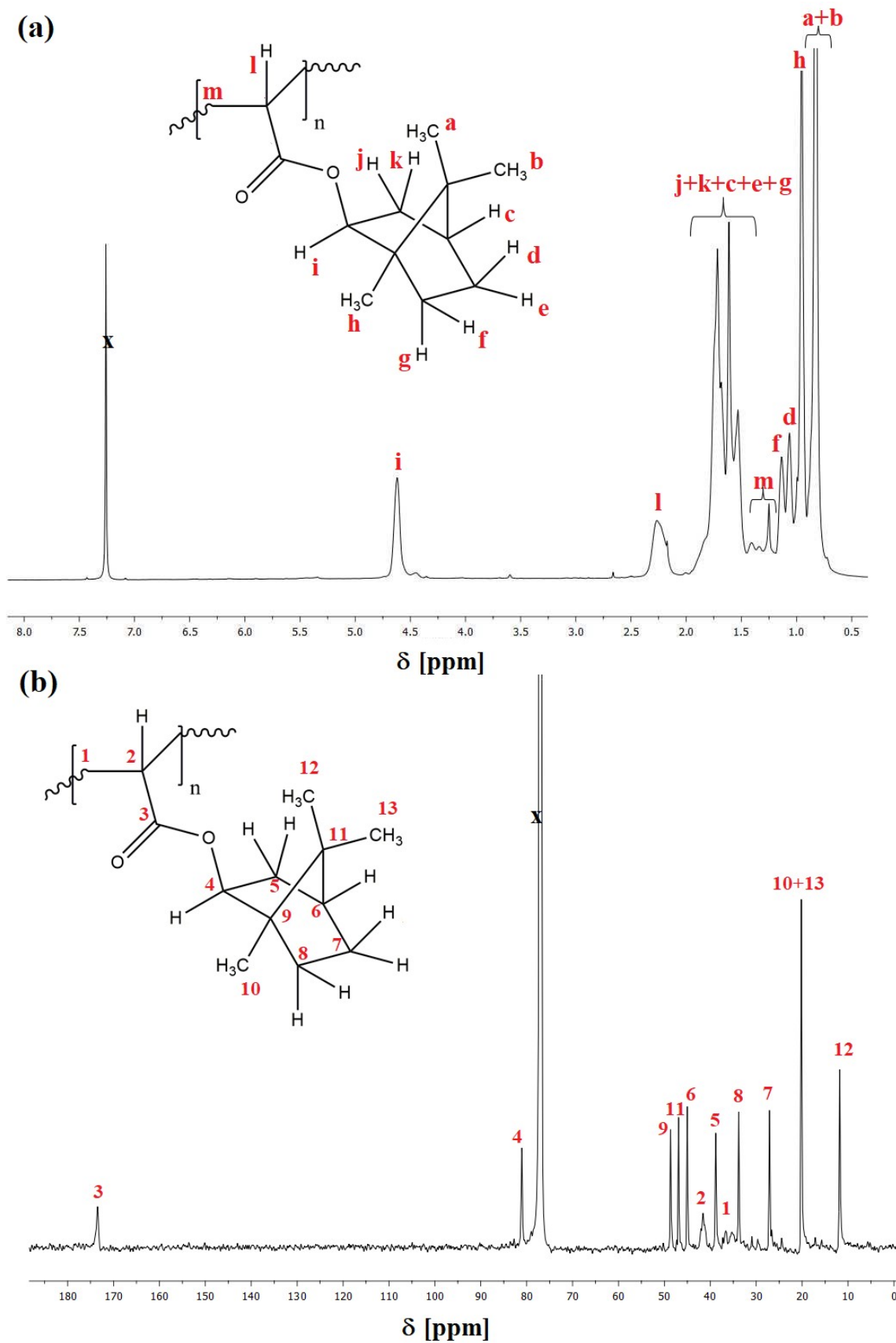


Figure S2. Representative  $^1\text{H}$  NMR (a) and  $^{13}\text{C}$  NMR (b) spectra of PIBA samples produced via field assisted FRP.

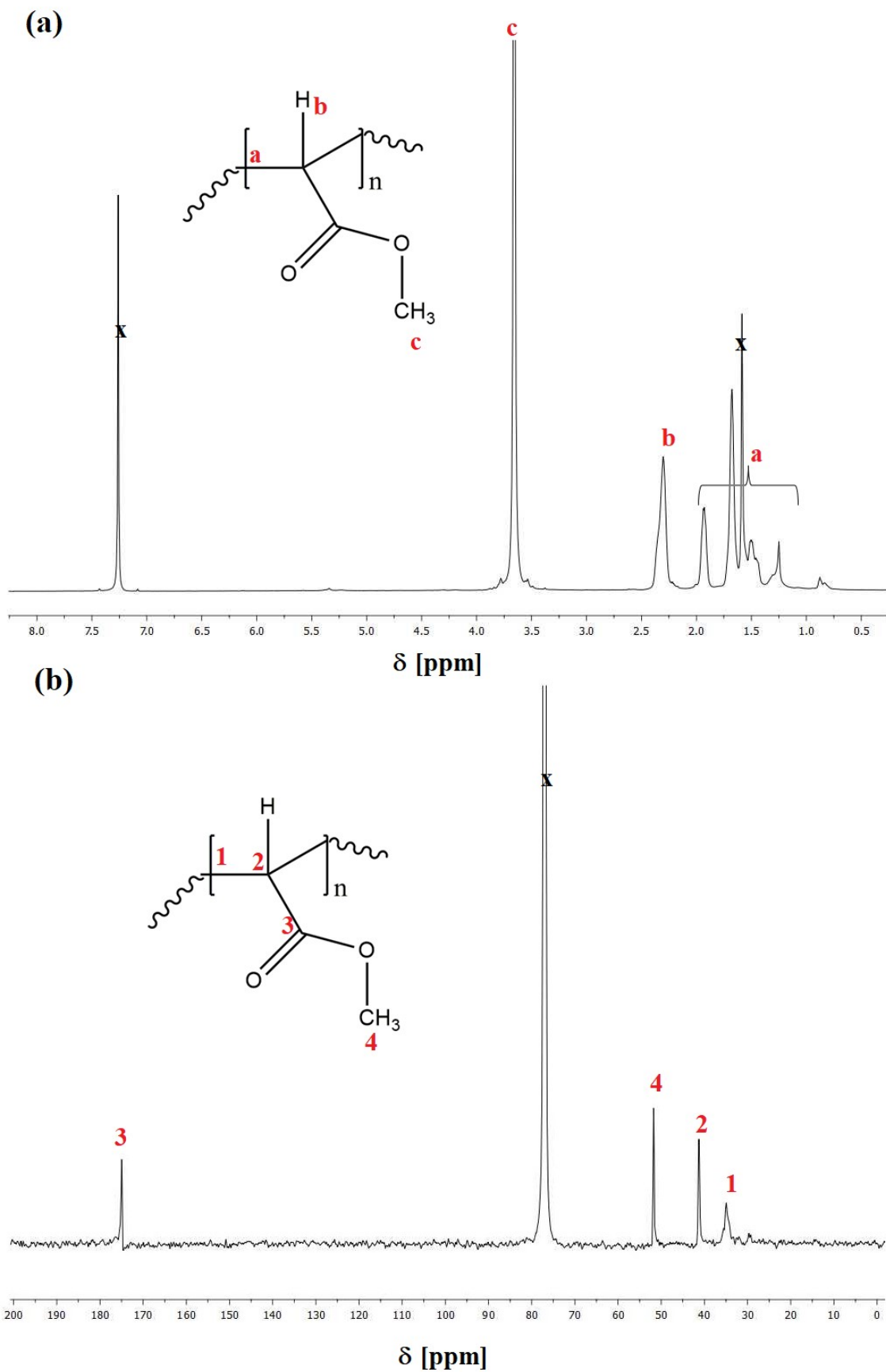


Figure S3. Representative  $^1\text{H}$  NMR (a) and  $^{13}\text{C}$  NMR (b) spectra of PMA samples produced via FRP.

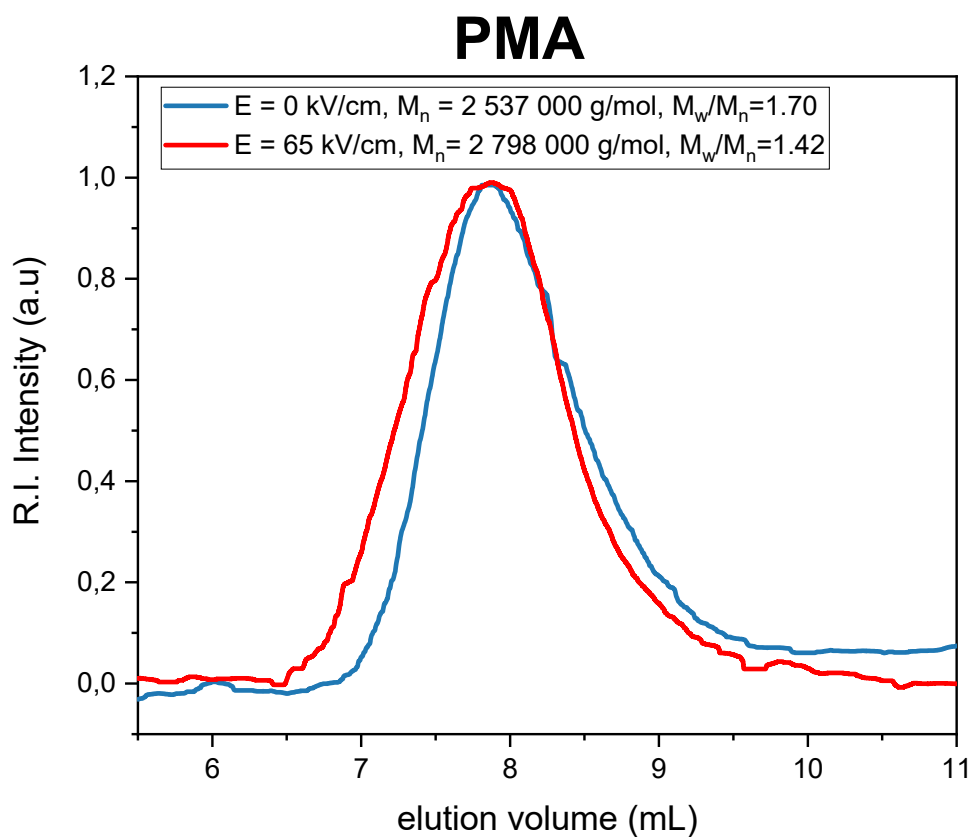


Figure S4. SEC-LALLS trace of poly(methyl acrylate) obtained via FRP in the presence and absence of high electric field.

Table S1. Characteristics of PMA obtained by FRP in the presence and the absence of high electric field

Electric field [kV/cm]	$\alpha$ [%] <sup>a</sup>	$M_n$ [g/mol] <sup>b</sup>	$M_w$ [g/mol]	$\mathcal{D}^b$	$dn/dc$
0	>99	2 537 000	5 374 100	1.70	0.012
65	>99	2 798 000	3 973 160	1.42	0.019

<sup>a</sup>determined by  $^1\text{H}$  NMR after 4h; <sup>b</sup>determined by SEC-LALLS (DMF, 10 mM LiBr)

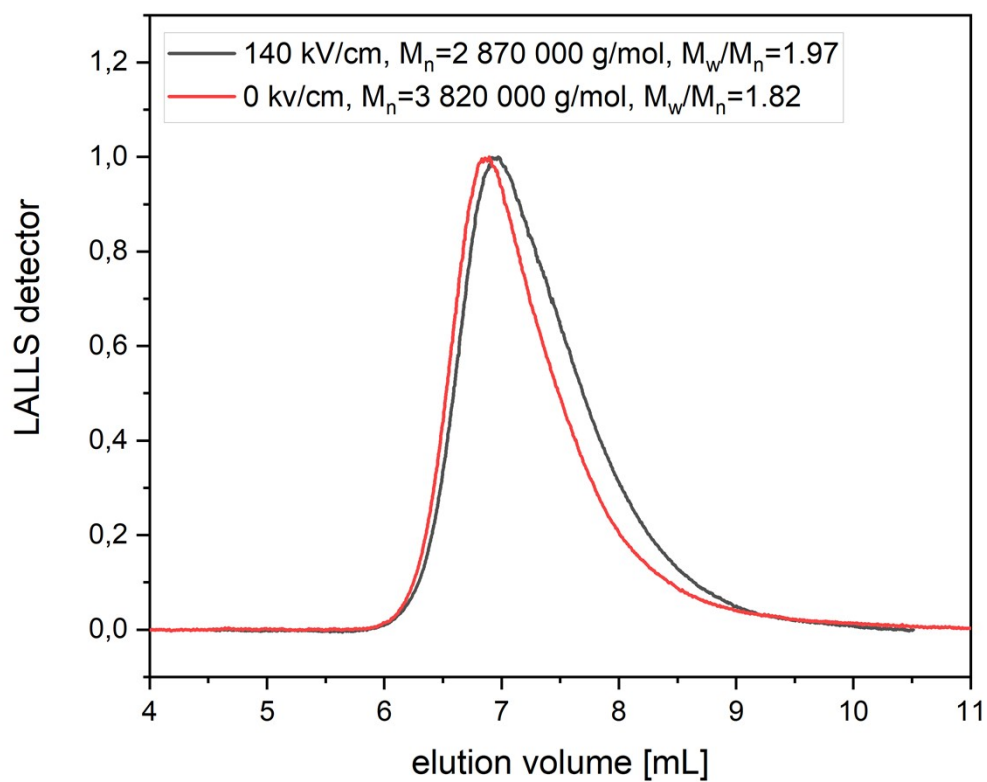
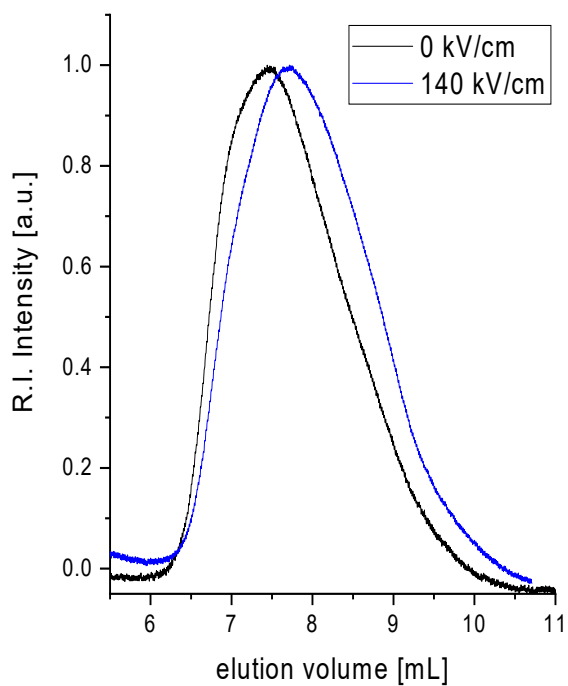


Figure S5. SEC-LALLS traces of poly(*n*-butyl acrylate) obtained via FRP in the presence and absence of high electric field.

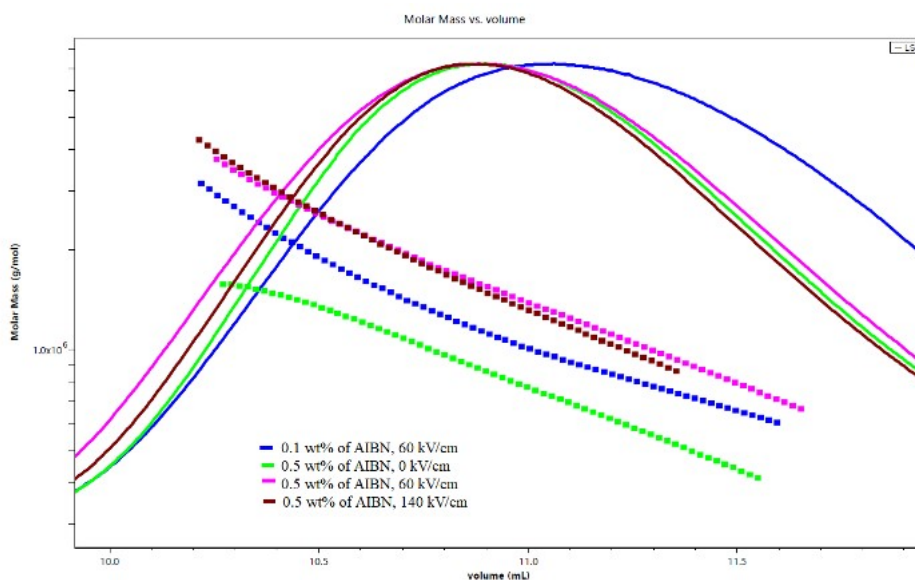


Figure S6 The relationship between elution time (retention time) and the molecular weight determined from SEC-MALLS of PIBA samples obtained at 343 K at different DC field magnitudes. Original SEC-MALLS traces are shown as well.

**Figure S6** presents the corresponding relationship between the molar mass of PIBAs and the elution volume (with the third axis representing the intensity of the chromatographic peak). For a fixed elution volume, the molecular weight increases with DC-field magnitude but decreases with the concentration of the initiator (straight lines in **Figure S6**). Additionally, we found that for the samples obtained at 60 kV/cm and 140 kV/cm with 0.5wt% of AIBN concentration (green and brown lines), the dependence of the molecular weight is almost the same. This indicates a saturation effect, so going further with the field magnitude does not produce a more pronounced effect. Interestingly, we also note wt% concentrations of AIBN affect the dependence between molecular weight and elution volume for PIBA obtained at 60 kV/cm.