

## Supporting information

### Scalable synthesis of methacrylate – based vitrimer powders by suspension polymerization

Laura Ballester-Bayarri <sup>a</sup>, Elodie Limousin <sup>a</sup>, Mercedes Fernández <sup>a</sup>, Robert Aguirresarobe <sup>a</sup> and  
Nicholas Ballard <sup>a,b</sup>

<sup>a</sup> POLYMAT and Department of Polymers and Advanced Materials: Physics, Chemistry and Technology, Faculty of Chemistry, Basque Country University (UPV/EHU), 20018 Donostia-San Sebastián (Spain).

<sup>b</sup> Ikerbasque, Basque Foundation for Science, 48013 Bilbao (Spain)

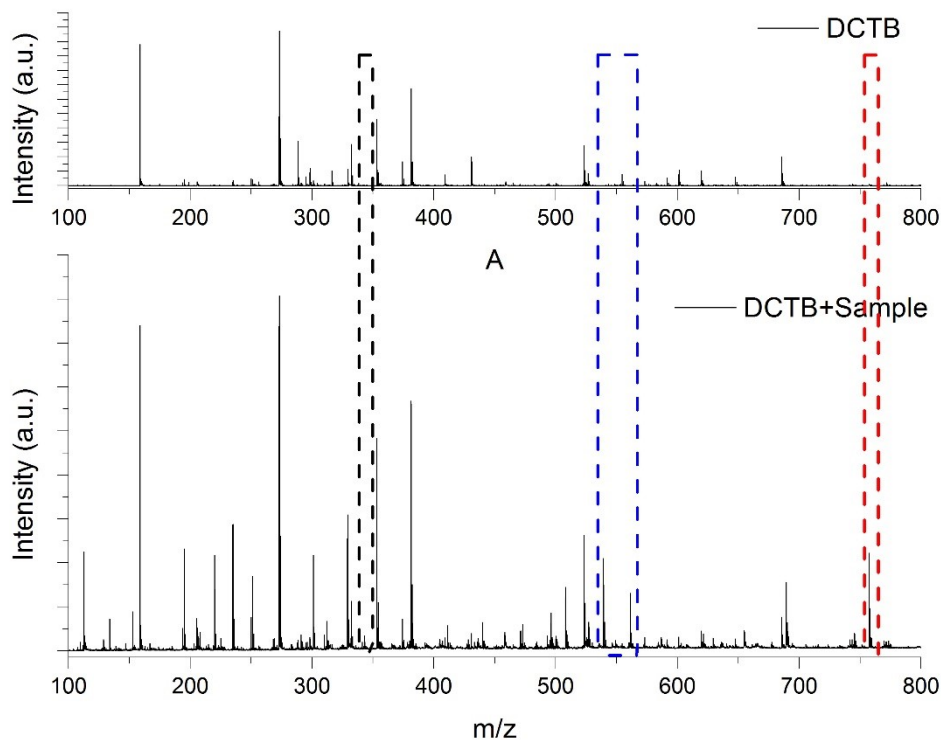


Figure S1. MALDI-ToF spectra of reaction mixture of TREN and AAEMA. The top panel shows the MALDI spectra of the matrix (DCTB). The bottom panel shows the spectra of the matrix with the sample. There is considerable overlap with the matrix but three distinct species can be observed as highlighted in the figure; TREN with reaction of one acetoacetoxy molecule ( $[M+H]^+$   $m/z_{\text{theory}} = 343.2$ ,  $m/z_{\text{exp}} = 343.2$ ), TREN with reaction of two acetoacetoxy molecules ( $[M+H]^+$   $m/z_{\text{theory}} = 539.3$ ,  $m/z_{\text{exp}} = 539.3$ ,  $[M+Na]^+$   $m/z_{\text{theory}} = 561.3$ ,  $m/z_{\text{exp}} = 561.3$ ), TREN with reaction of three acetoacetoxy molecules ( $[M+Na]^+$   $m/z_{\text{theory}} = 757.4$ ,  $m/z_{\text{exp}} = 757.4$ ),

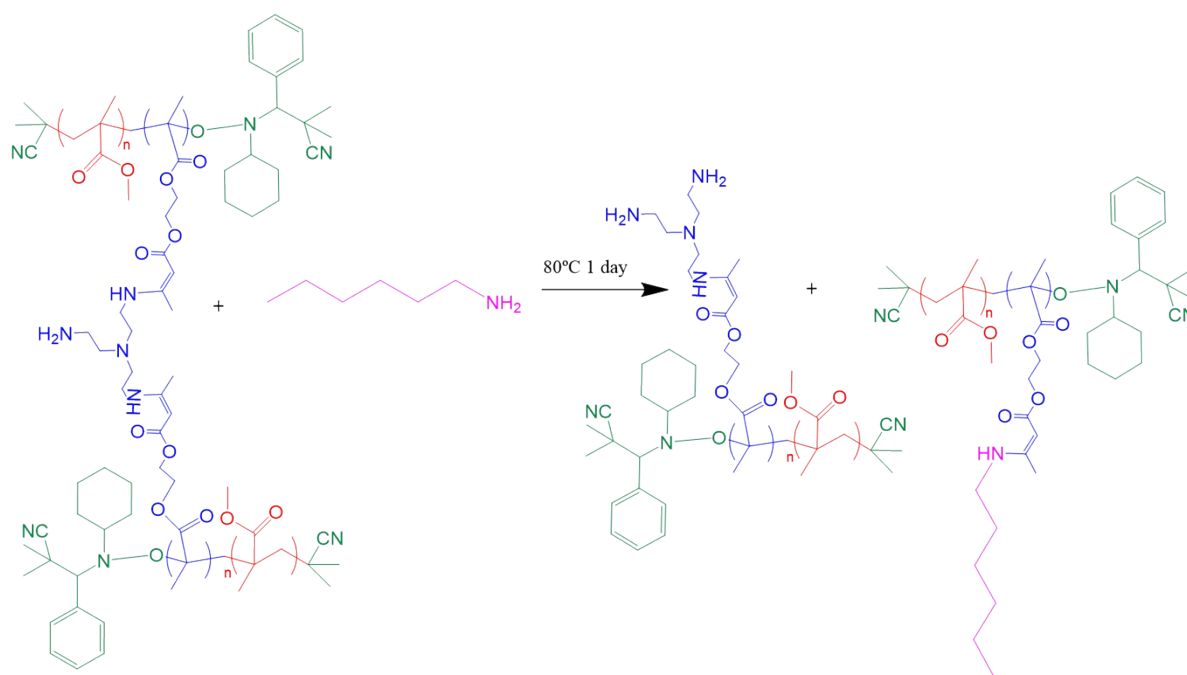


Figure S2. Aminolysis process of the vitrimer powder in presence of hexylamine and excess of THF.

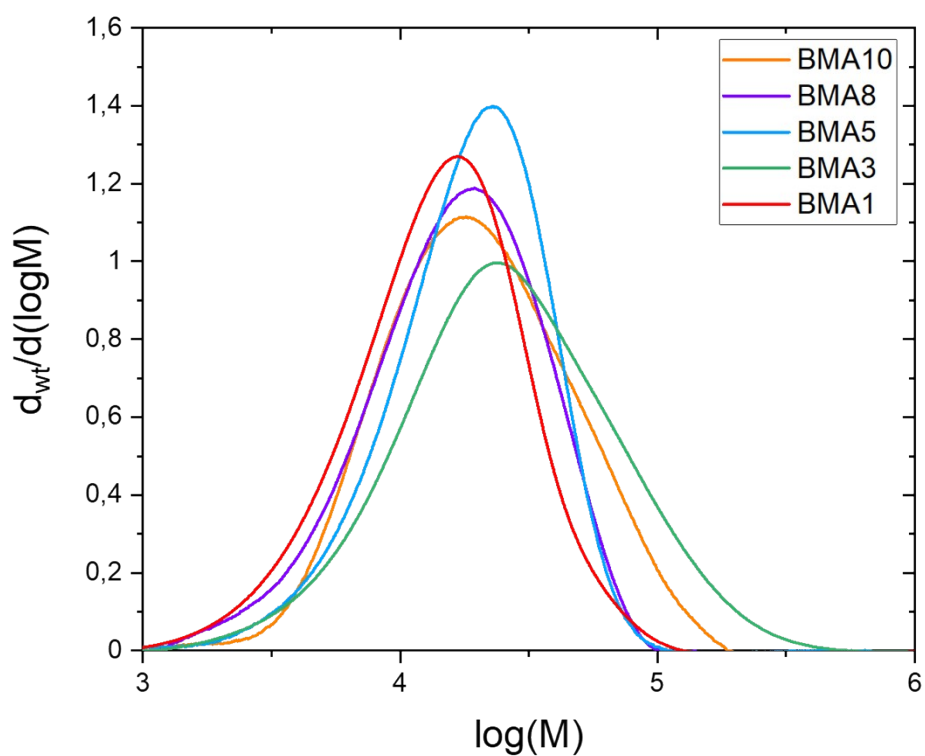


Figure S3. GPC data of primary chains after aminolysis of synthesized powders.

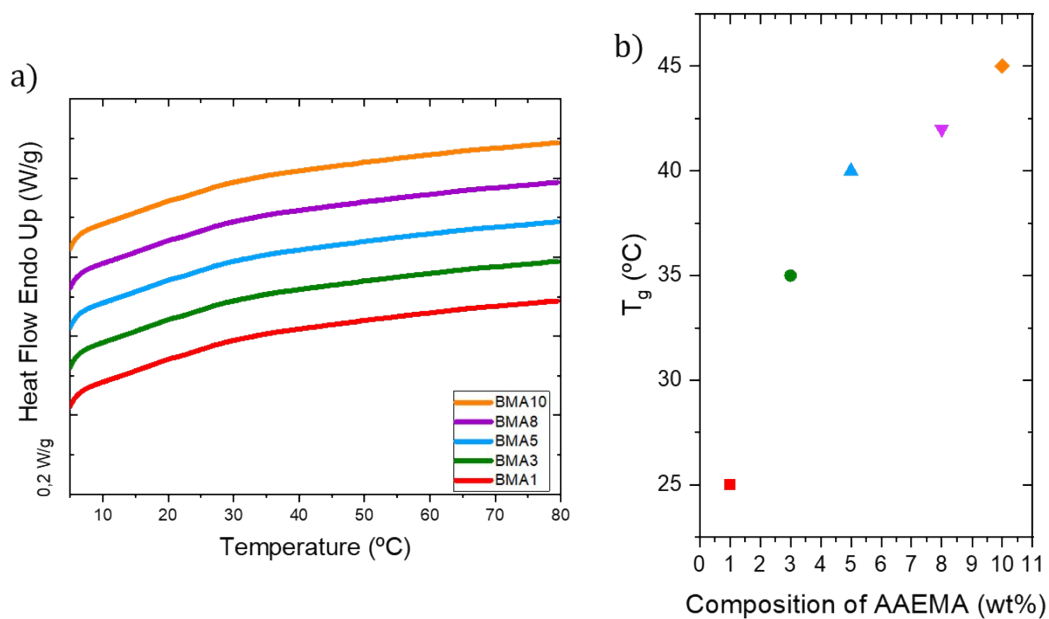


Figure S4. Thermal characterization of the powder a) Differential scanning calorimetry b) Relation between the glass transition temperature and the composition of the polymer powder

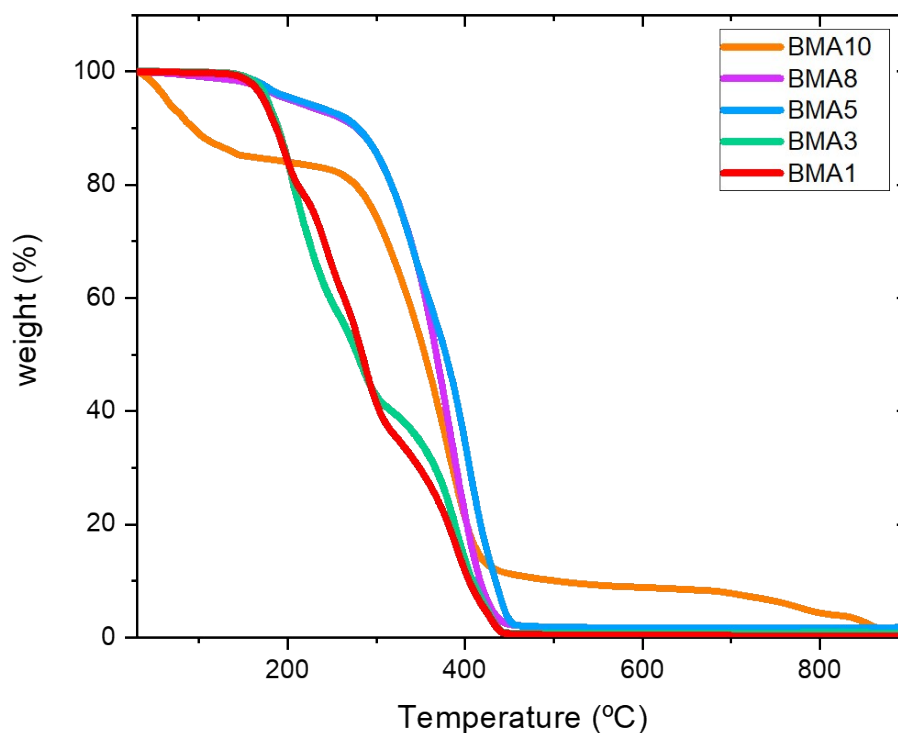


Figure S5. Thermogravimetric analysis of the powder vitrimer with BMA as main monomer at different compositions of AAEMA. Note in the case of BMA3 and BMA1 some early onset is observed which may be due to residual BMA which is difficult to remove from these non-crosslinked samples.

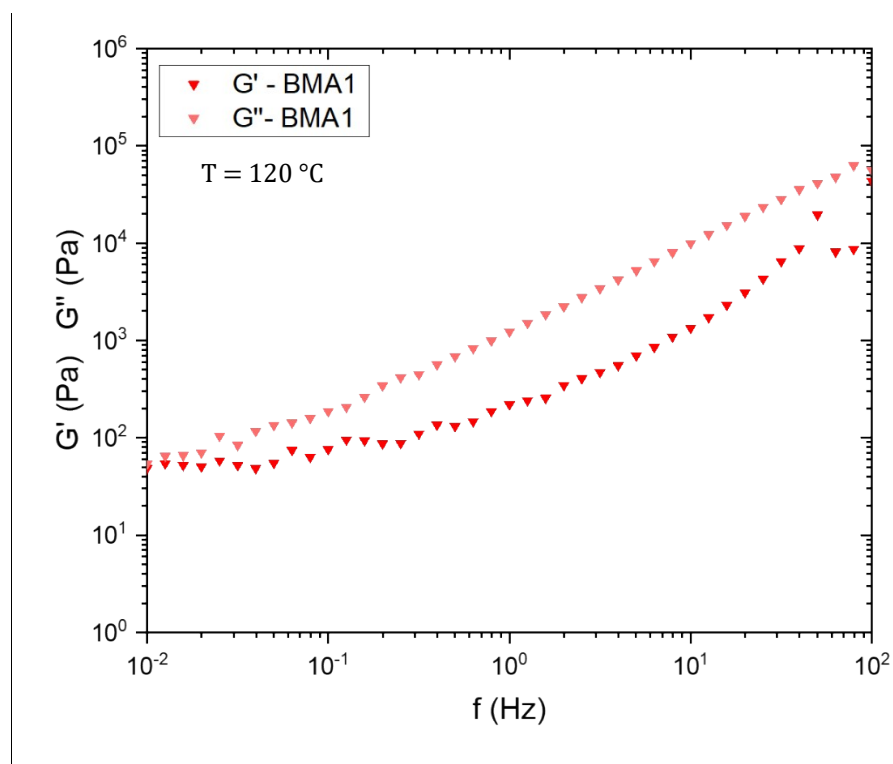


Figure S6. Storage modulus and loss modulus of BMA1 (1 wt% of AAEMA with BMA as main monomer) at 120 °C as a function of frequency.

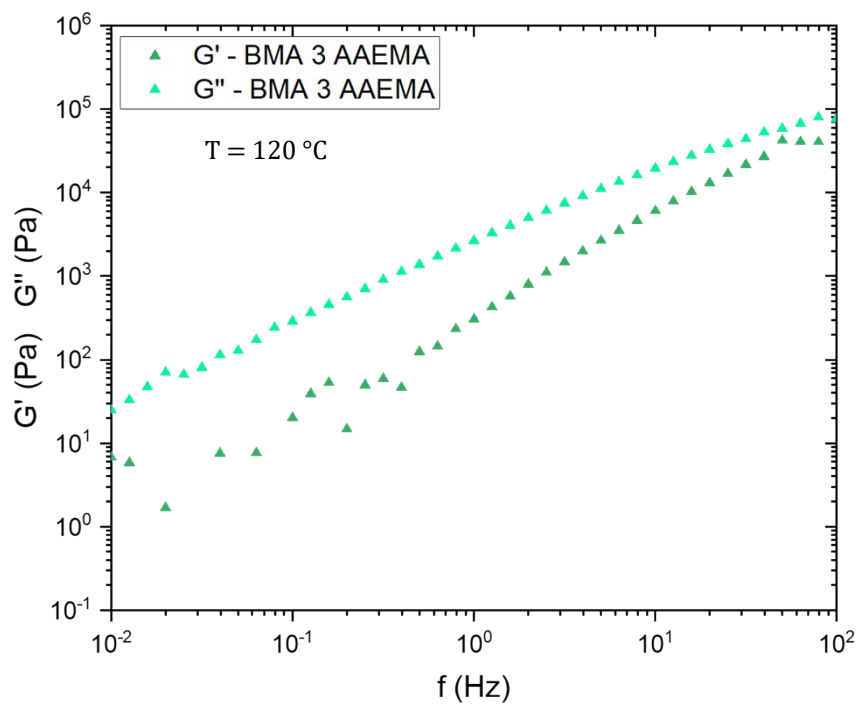


Figure S7. Storage modulus and loss modulus of BMA3 (3 wt% of AAEMA with BMA as main monomer) at 120 °C as a function of frequency.

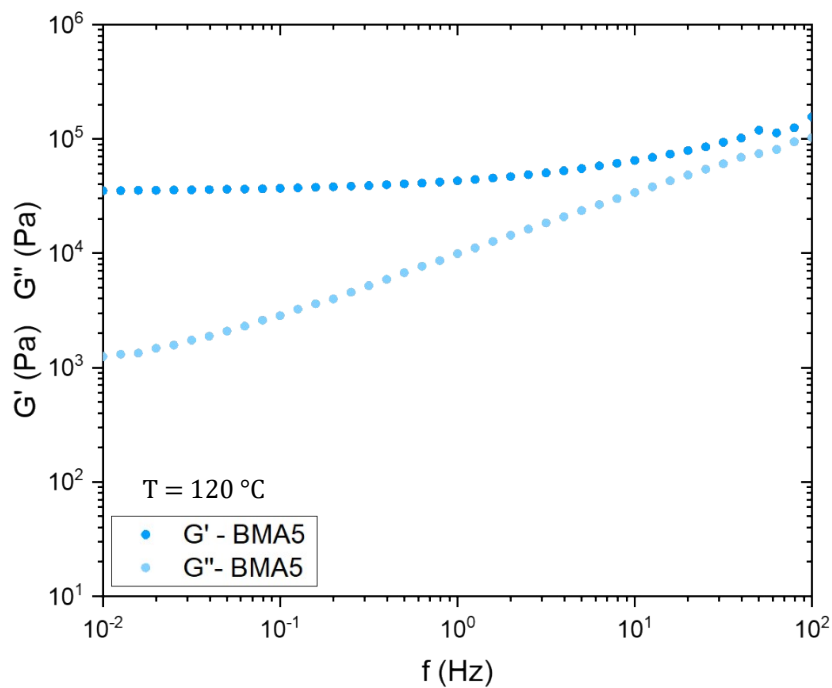


Figure S8. Storage modulus and loss modulus of BMA5 (5 wt% of AAEMA with BMA as main monomer) at 120 °C as a function of frequency.

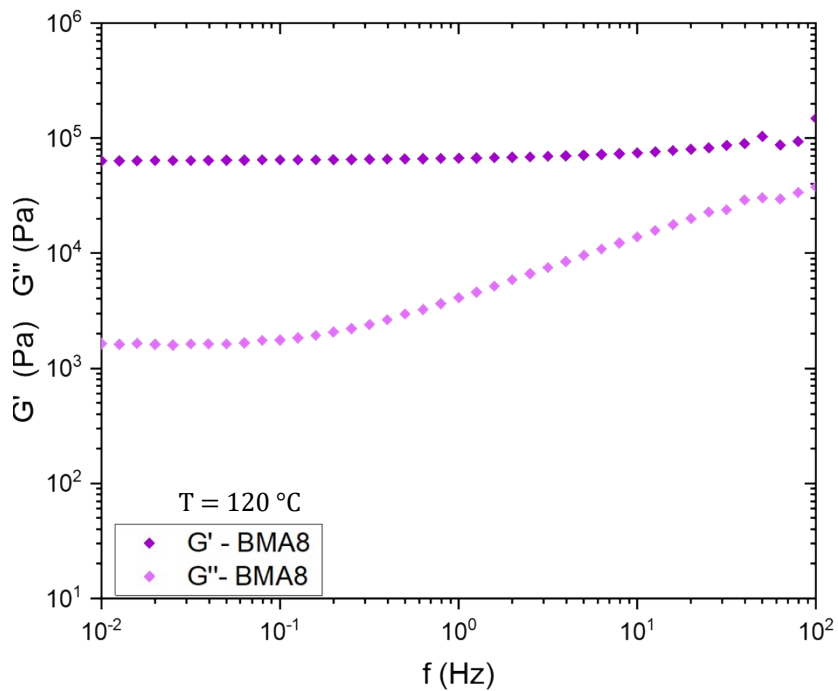


Figure S9. Storage modulus and loss modulus of BMA8 (8 wt% of AAEMA with BMA as main monomer) at  $120\text{ }^{\circ}\text{C}$  as a function of frequency.

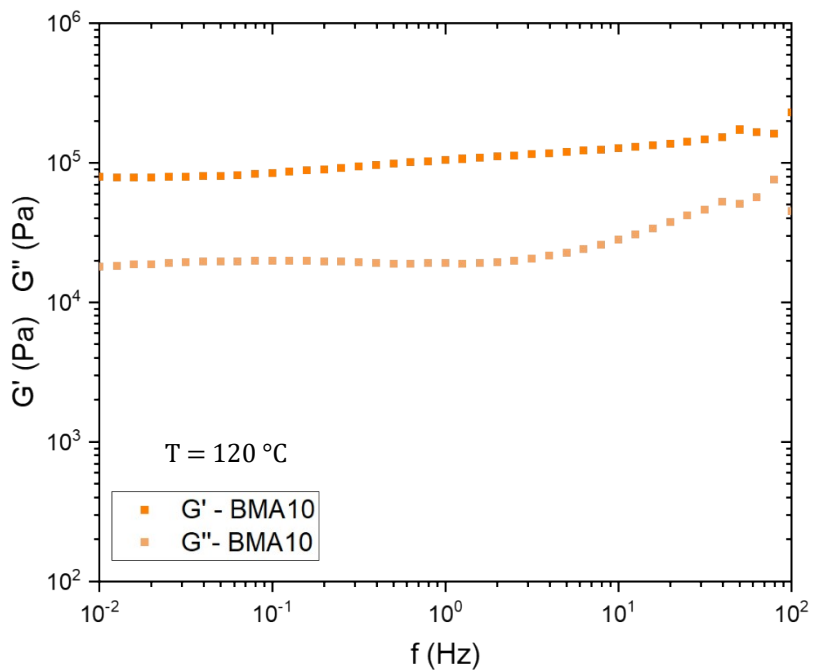


Figure S10. Storage modulus and loss modulus of BMA10 (10 wt% of AAEMA with BMA as main monomer) at  $120\text{ }^{\circ}\text{C}$  as a function of frequency.

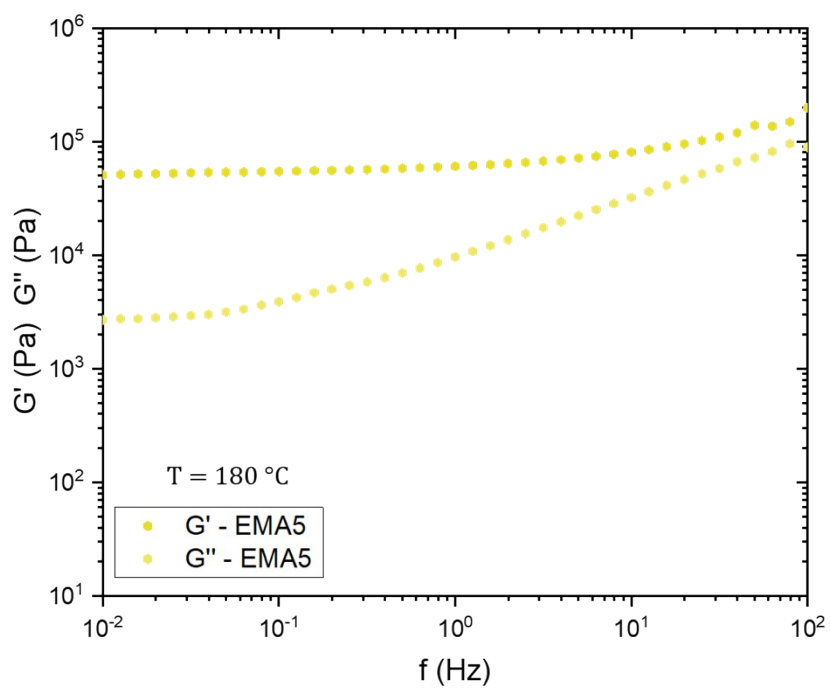


Figure S11. Storage modulus and loss modulus of EMA5 (5 wt% of AAEMA with EMA as main monomer) at  $180\text{ }^{\circ}\text{C}$  as a function of frequency.

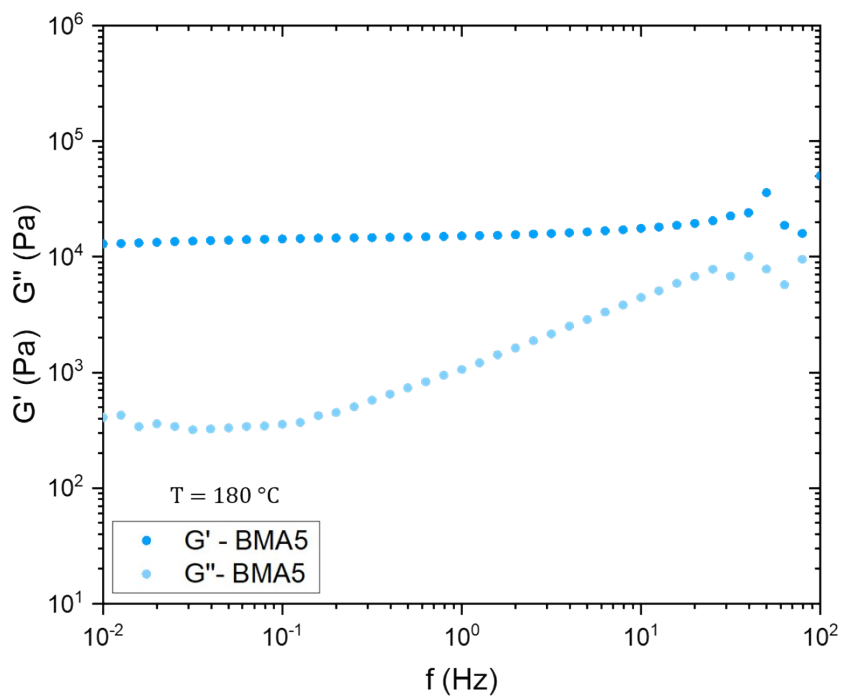


Figure S12. Storage modulus and loss modulus of BMA5 (5 wt% of AAEMA with BMA as main monomer) at  $180\text{ }^{\circ}\text{C}$  as a function of frequency.

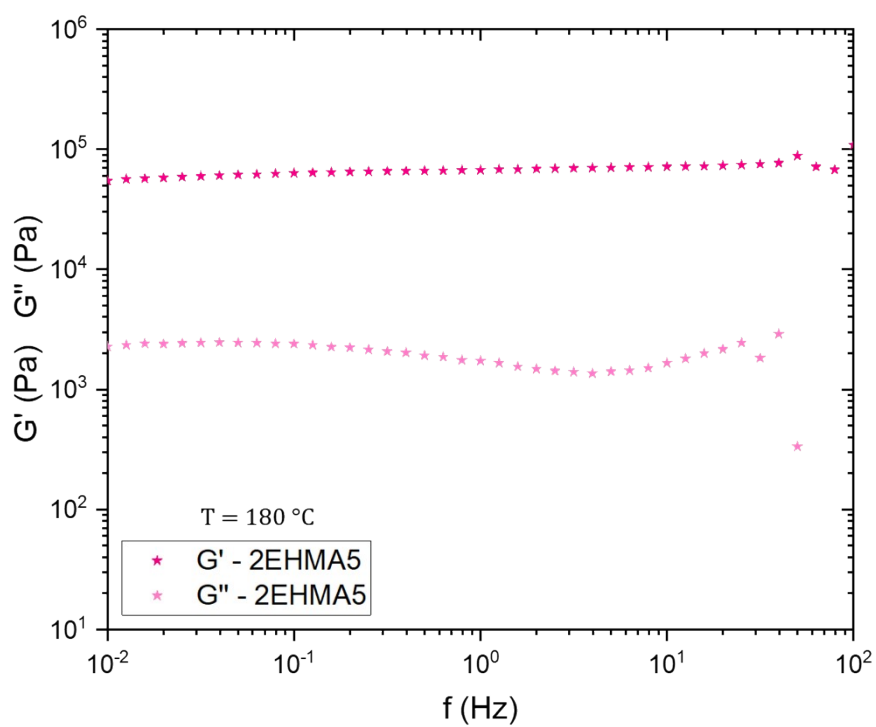


Figure S13. Storage modulus and loss modulus of 2EHMA5 (5 wt% of AAEMA with 2EHMA as main monomer) at 180 °C as a function of frequency.