

## Molecular Interactions in Coupled PMMA-Bioglass Hybrid Networks

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### $^{13}\text{C}$ NMR

The  $^{13}\text{C}$  NMR spectra of synthesized PMMA-*co*-MPMA copolymers were recorded using chloroform ( $\text{CDCl}_3$ ) as the solvent. The  $^{13}\text{C}$  NMR spectrum of  $\text{P}_{\text{Med}}$  was depicted in Fig. S1 that included the characteristic peaks of carboxyl group (178 ppm), methylene (56 ppm), methoxy (52 ppm), quaternary (45 ppm) and methyl carbons (17 ppm). This data confirmed the successful copolymerization of PMMA and MPMA.<sup>1</sup> Similar spectrum was obtained for  $\text{P}_{\text{Low}}$  and  $\text{P}_{\text{High}}$  samples.

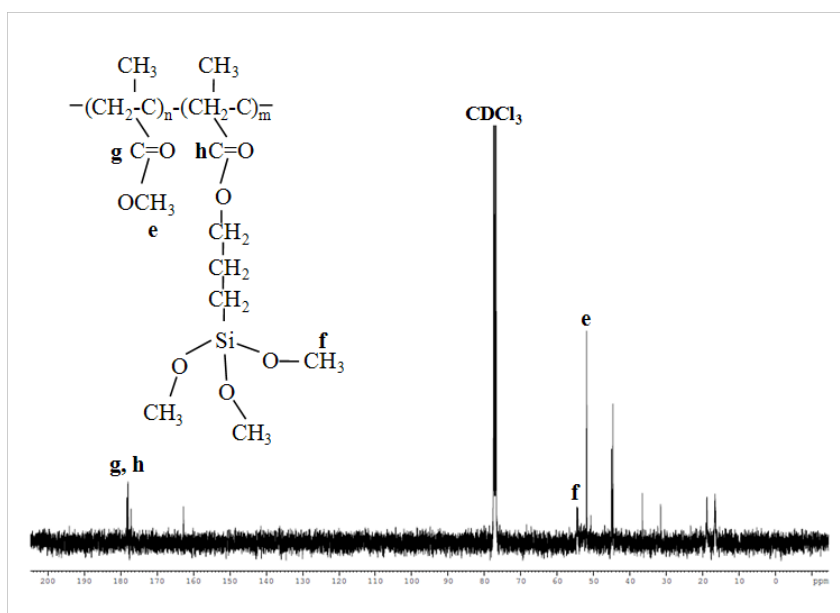


Fig. S1 The  $^{13}\text{C}$  NMR spectrum of  $\text{P}_{\text{Med}}$

### *Differential Scanning Calorimetry (DSC)*

DSC analysis was conducted for pure bioglass, synthesized polymers (i.e.  $\text{P}_{\text{Cont}}$ ,  $\text{P}_{\text{High}}$ ) and the hybrids (i.e.  $\text{H}_{\text{Cont60}}$ ,  $\text{H}_{\text{High60}}$ ). The results in Fig. S2(a,b) show that the glass-transition temperature ( $T_g$ ) of pure PMMA was 105 °C, whereas no thermal effect was observed in DSC profile of highly functionalized PMMA ( $\text{P}_{\text{High}}$ ) below 250 °C. This effect might be due to the covalent bonding of MPMA-PMMA that limited the mobility of PMMA polymer chains. This phenomenon decreased the degree of freedom for PMMA chains and resulted in the absence of  $T_g$  peak for  $\text{P}_{\text{High}}$  copolymer.

The peak at 120 °C which was observed in bioglass DSC profile (Fig. S2(c)) was attributed to the condensation of bioglass silica network. The same trend was also observed in  $\text{H}_{\text{Cont60}}$  and

$H_{High60}$  curves (Fig. S2(d,e)); however, this peak was shifted toward higher temperatures (i.e. to 150 °C) in  $H_{High60}$  due to the covalent bonding of polymer chains to silica network. Therefore, inorganic moieties reduced the polymer chains mobility and the covalent bonds between the phases reduced the free movement of both organic and inorganic chains. Upon increasing the coupling between phases, more energy (heat) was required in hybrid samples to approach the same degree of freedom. It could then be concluded that covalent bonding of silica to PMMA chains enhanced the thermal stability of final product.

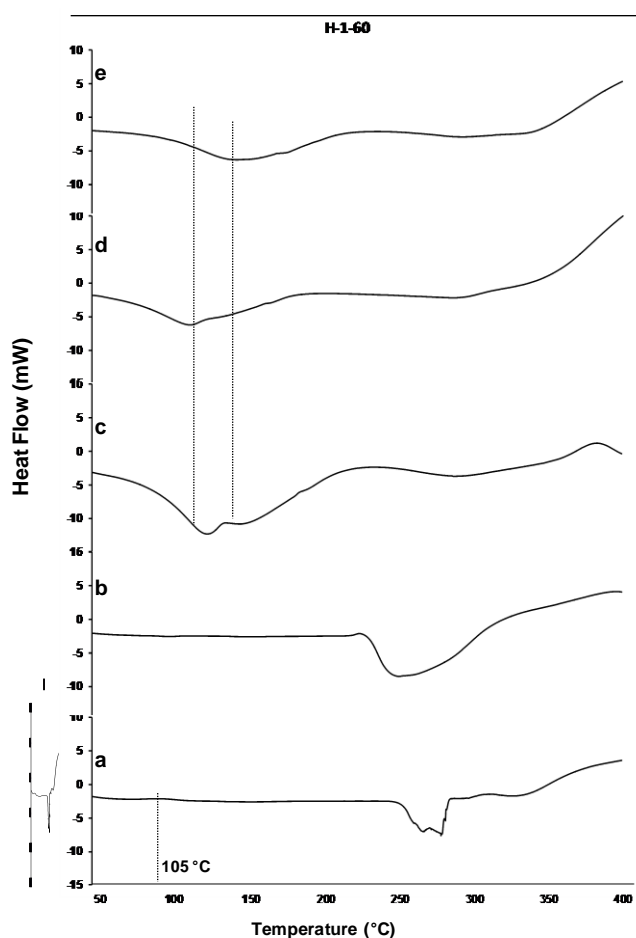


Fig. S2 DSC curves of a) P<sub>Cont</sub>, b) P<sub>High</sub>, c) pure bioglass, d) H<sub>Cont60</sub>, e) H<sub>High60</sub>

### Reference for supporting information

1. Chang, T.C.; Y.T. Wang; Y.S. Hong, and Y.S. Chiu. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, 38, 1972-1980.