

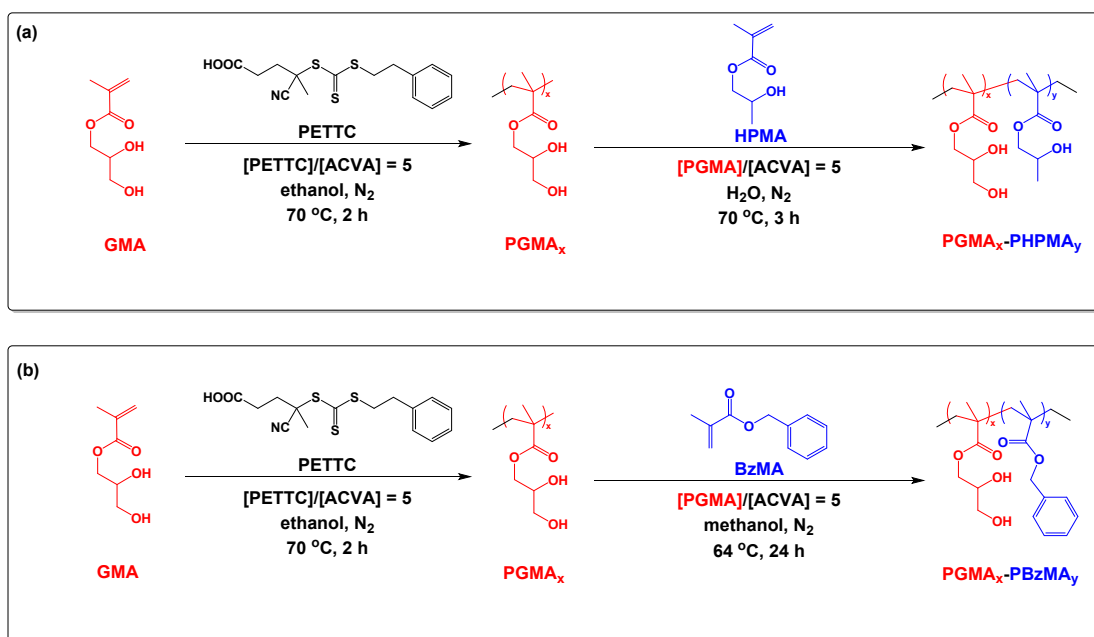
Electronic Supplementary Information for:  
**Preparation and characterisation of graphene oxide containing block copolymer worm gels**

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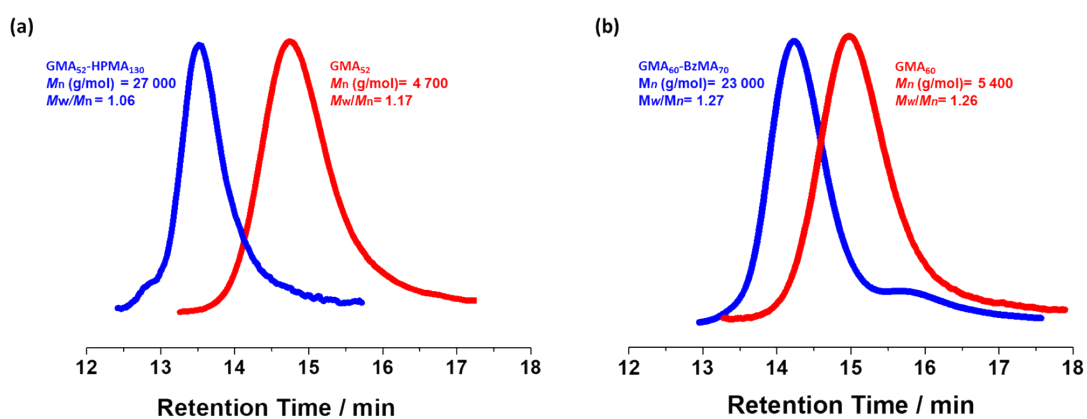


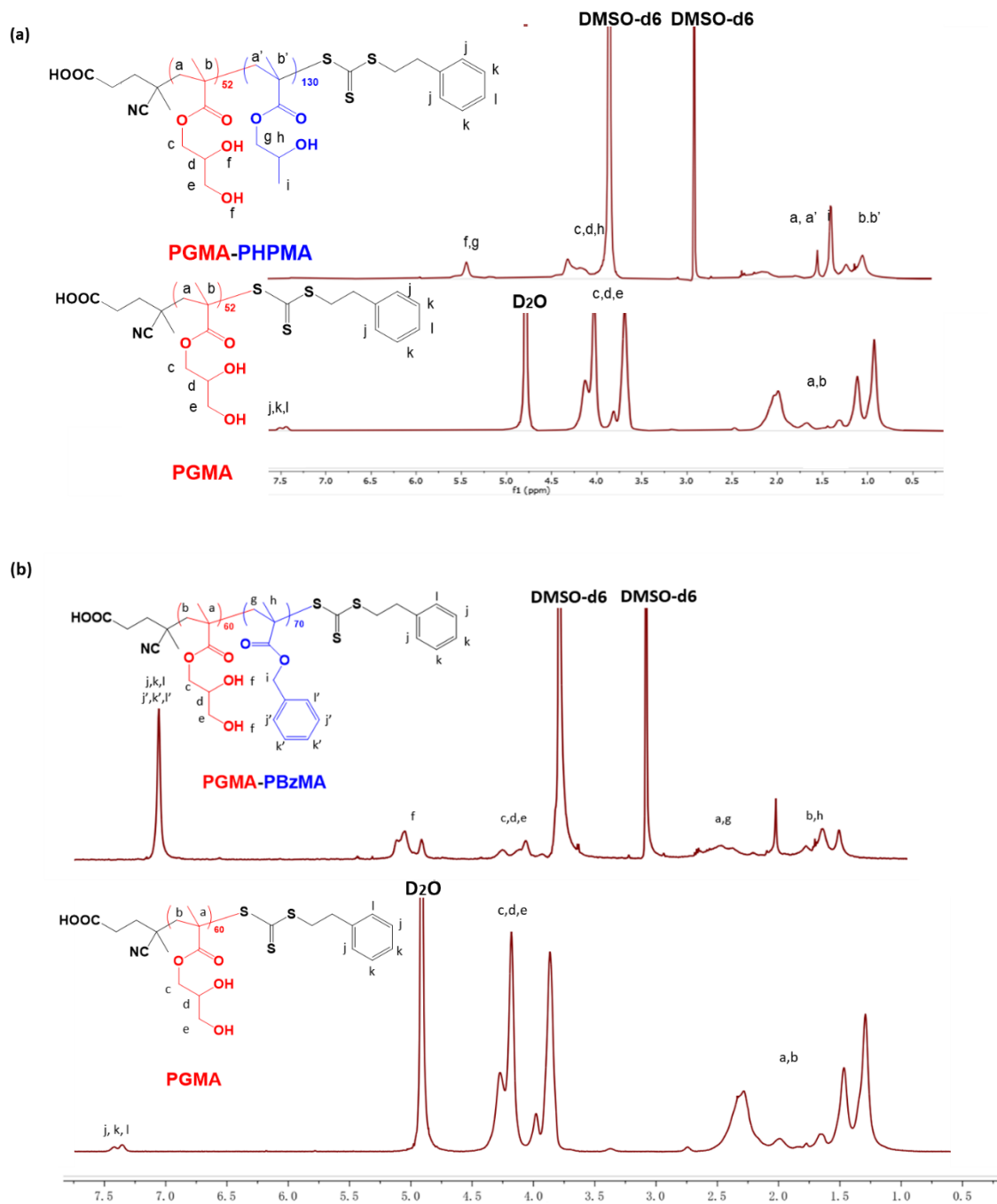
**Figure S1.** (a) Synthesis of PGMA<sub>x</sub> macromolecular chain-transfer agent (macro-CTA) *via* RAFT solution polymerisation in ethanol at 70 °C and PGMA<sub>x</sub>-PHPMA<sub>y</sub> (G<sub>x</sub>-H<sub>y</sub>) diblock copolymer *via* RAFT aqueous dispersion polymerisation at 70 °C and 20 % w/w. Glycerol monomethacrylate (GMA) and 2-hydroxypropyl methacrylate (HPMA) were used as monomers, 4-cyano-4-(2-phenylethane sulfanylthiocarbonyl)sulfanylpentanoic acid (PETTC) was used as a RAFT agent, and 4,4-azobis(4-cyanovaleric acid) (ACVA) as a free-radical initiator. (b) Synthesis of PGMA<sub>x</sub> macromolecular chain-transfer agent (macro-CTA) *via* RAFT solution polymerisation in ethanol at 70 °C and PGMA<sub>x</sub>-PBzMA<sub>y</sub> (G<sub>x</sub>-B<sub>y</sub>) diblock copolymer *via* RAFT dispersion polymerisation in methanol at 64 °C and 20 % w/w. GMA and benzyl methacrylate (BzMA) were used as monomers, PETTC was used as a RAFT agent, and ACVA as a free-radical initiator.

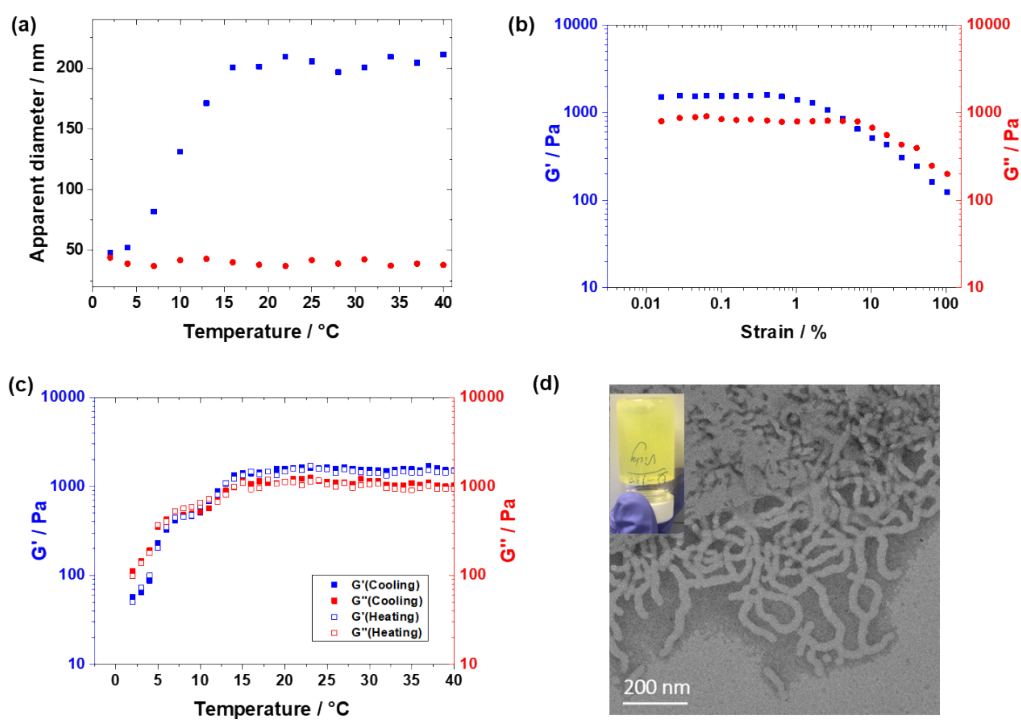
**Table S1** Summary of GPC molecular weight data obtained for PGMA macro-CTAs and copolymers.<sup>a</sup>

Composition	$M_n / \text{g mol}^{-1}$	$M_w / M_n$
PGMA <sub>52</sub> <sup>b</sup>	4 700	1.17
PGMA <sub>60</sub> <sup>b</sup>	5 400	1.26
GMA <sub>52</sub> -HPMA <sub>130</sub> <sup>c</sup>	27 000	1.06
GMA <sub>60</sub> -BzMA <sub>70</sub> <sup>d</sup>	23 000	1.27

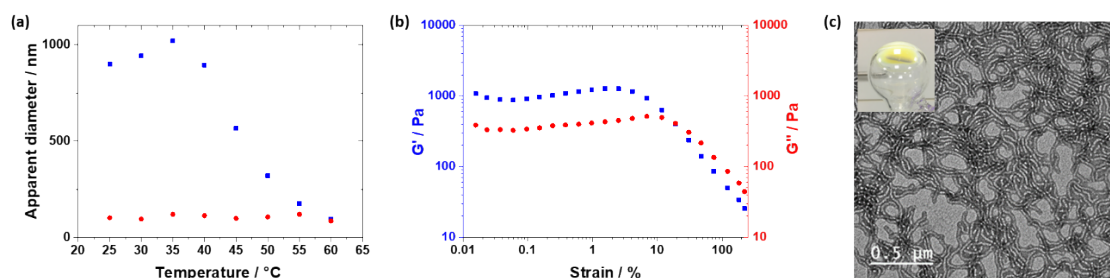
<sup>a</sup> Molecular weight distributions were determined using DMF eluent, a refractive index detector and polystyrene calibration standards. <sup>b</sup> Prepared by RAFT solution polymerisation in ethanol at 70 °C, 50 % w/w GMA and PETTC/ACVA molar ratio = 5:1. <sup>c</sup> Prepared by RAFT dispersion polymerisation in water at 70 °C, 20 % w/w and PGMA<sub>52</sub> macro-CTA/ACVA molar ratio = 5:1. <sup>d</sup> Prepared by RAFT dispersion polymerisation in methanol at 64 °C, 20 % w/w and PGMA<sub>60</sub> macro-CTA/ACVA molar ratio = 5:1.

**Figure S2.** DMF GPC data recorded for (a) PGMA<sub>52</sub> and PGMA<sub>52</sub>-HPMA<sub>130</sub> and (b) PGMA<sub>60</sub> and PGMA<sub>60</sub>-PBzMA<sub>70</sub>.  $M_n$  and  $M_w/M_n$  values were determined against polystyrene calibration standards.

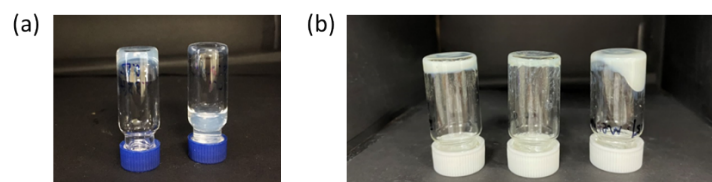




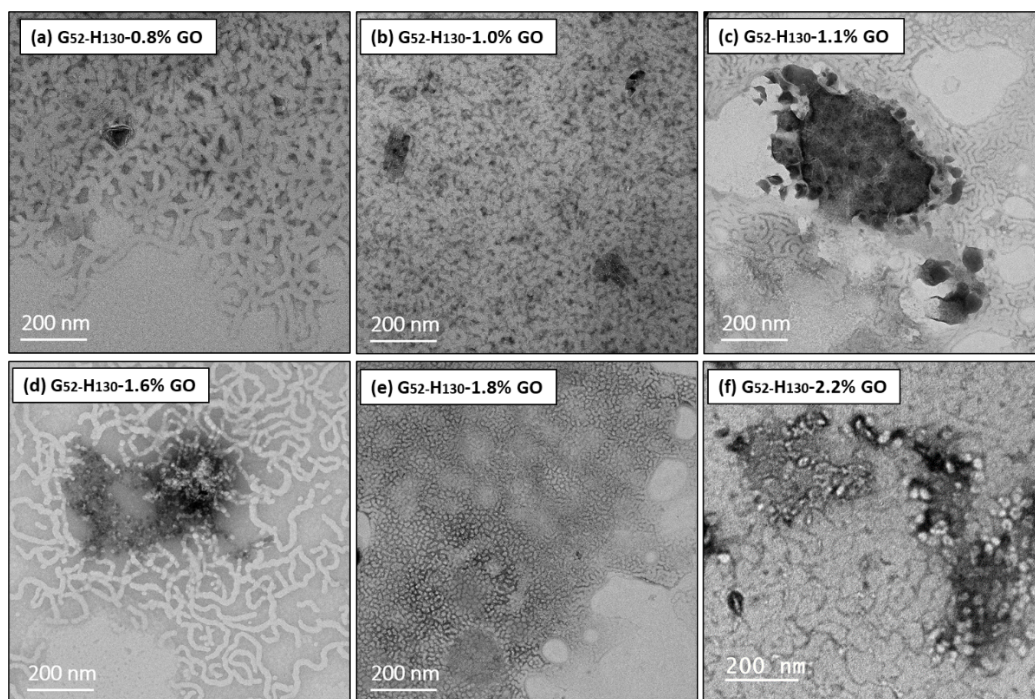
**Figure S4.** (a) Dynamic light scattering studies as a function of temperature for 0.1 % w/w aqueous dispersions of PGMA<sub>52</sub>-PHPMA<sub>130</sub>. The sample was cooled from 40 to 2 °C (blue data) and subsequently heated from 2 to 40 °C (red data). Sphere equivalent diameters (Z-average) were recorded at 3 °C intervals. (b) Storage modulus ( $G'$ , blue data) and loss modulus ( $G''$ , red data) versus % strain obtained by oscillatory rheology on 20 % w/w G<sub>52</sub>-H<sub>130</sub>. Measurements were conducted at 10 rad s<sup>-1</sup> at 25 °C. (c) Temperature-dependent oscillatory rheology studies obtained for 20 % w/w aqueous dispersions of G<sub>52</sub>-H<sub>130</sub>. Measurements were conducted with an angular frequency of 10 Hz and an applied strain amplitude of 1.0 %. (d) TEM image of diluted dispersion of G<sub>52</sub>-H<sub>130</sub> worm gel prepared at 20 % w/w. The inset shows a digital photograph of the 20 % w/w copolymer dispersion at room temperature.



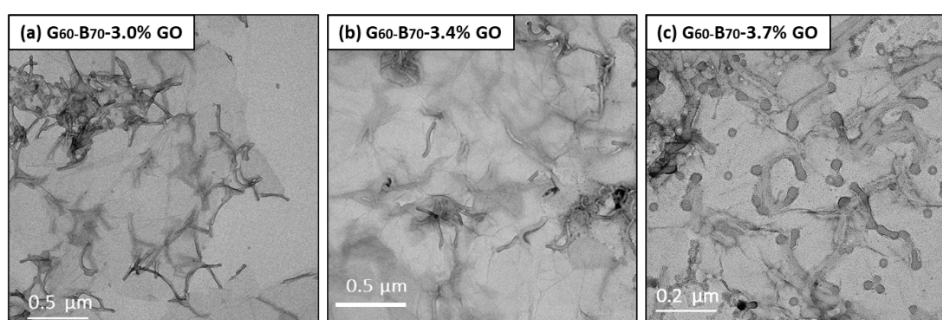
**Figure S5.** (a) Dynamic light scattering studies as a function of temperature for 0.1 % w/w aqueous dispersions of PGMA<sub>60</sub>-PBzMA<sub>70</sub>. The sample was heated from 25 to 60 °C (blue data) and subsequently cooled back to 25 °C (red data). Sphere equivalent diameters (Z-average) were recorded at 5 °C intervals. (b) Storage modulus ( $G'$ , blue data) and loss modulus ( $G''$ , red data) versus % strain obtained by oscillatory rheology for 20 % w/w G<sub>60</sub>-B<sub>70</sub>. Measurements were conducted at 10 Hz at 25 °C. (c) TEM image of diluted dispersion of G<sub>60</sub>-B<sub>70</sub> worm gel prepared at 20 % w/w in methanol. The inset shows a digital photograph of the 20 % w/w copolymer dispersion at room temperature.



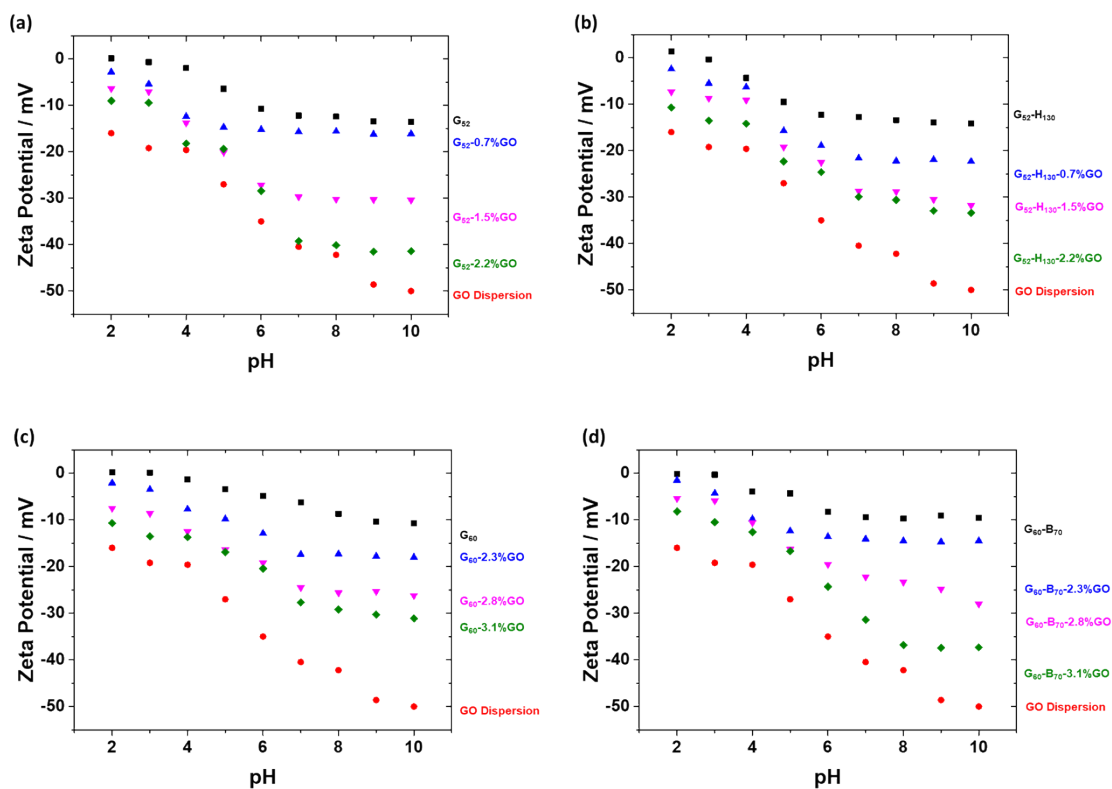
**Figure S6.** (a) Digital photographs of aqueous G<sub>52</sub>-H<sub>130</sub> dispersions after being cooled, diluted with water at approximately 5 °C and re-heated to room temperature for at least 10 minutes. Left = 15 % w/w G<sub>52</sub>-H<sub>130</sub> and right = 10 % w/w G<sub>52</sub>-H<sub>130</sub>. (b) Digital photographs of G<sub>60</sub>-B<sub>70</sub> dispersions after being heated to approximately 56 °C, diluted with methanol or water and cooling to room temperature for at least 10 minutes. Left = original 20 % w/w G<sub>60</sub>-B<sub>70</sub> dispersion in methanol; middle = 15 % w/w G<sub>60</sub>-B<sub>70</sub> diluted with water and right = 15 % w/w G<sub>60</sub>-B<sub>70</sub> diluted with methanol.



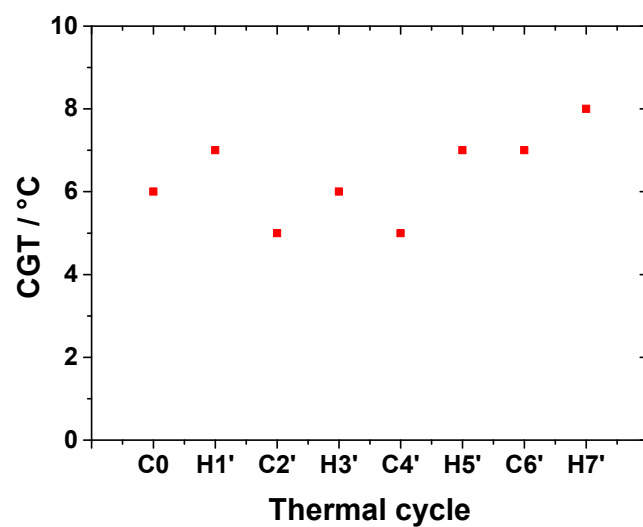
**Figure S7.** TEM images recorded for (a) 15 % w/w G<sub>52</sub>-H<sub>130</sub>-0.8% GO; (b) G<sub>52</sub>-H<sub>130</sub>-1.0% GO; (c) G<sub>52</sub>-H<sub>130</sub>-1.1% GO; (d) G<sub>52</sub>-H<sub>130</sub>-1.6% GO; (e) G<sub>52</sub>-H<sub>130</sub>-1.8% GO and (f) G<sub>52</sub>-H<sub>130</sub>-2.2% GO. Samples were diluted to 0.01 % w/w before being deposited onto carbon coated TEM grids at room temperature and being stained using ruthenium tetroxide vapour.



**Figure S8.** TEM images recorded for 15 % w/w (a) G<sub>60</sub>-B<sub>70</sub>-3.0% GO; (b) G<sub>60</sub>-B<sub>70</sub>-3.4% GO and (c) G<sub>60</sub>-B<sub>70</sub>-3.7% GO. Samples were prepared by mixing methanolic worm gels with aqueous GO at 56 °C before being allowed to return to room temperature. TEM grids were prepared by diluting these samples to 0.01 % w/w before being deposited on to carbon coated TEM grids at room temperature and being stained using ruthenium tetroxide vapour.

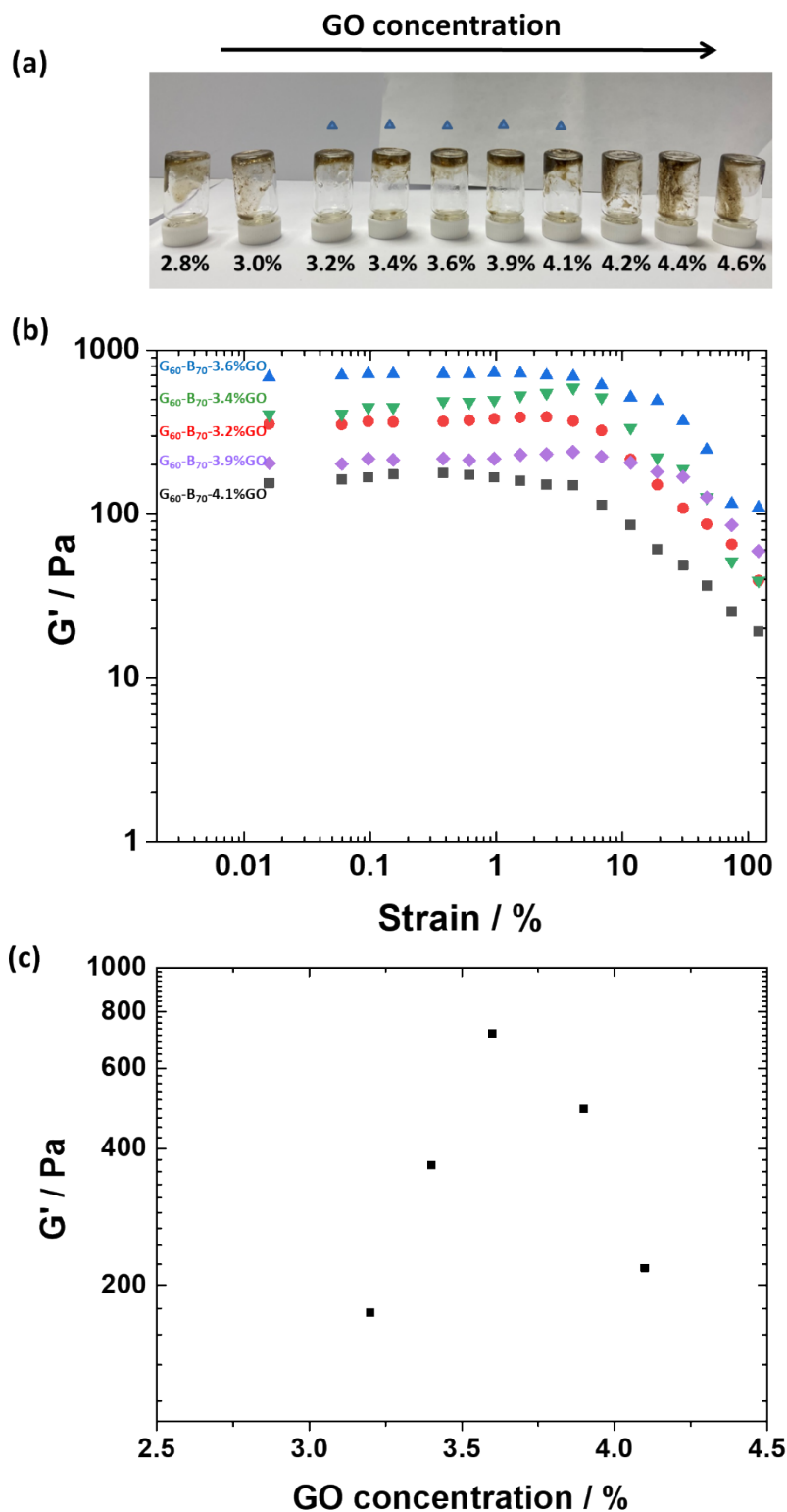


**Figure S9.** Zeta potential versus pH recorded for: (a)  $G_{52}$  solution, GO dispersion ( $4 \text{ mg ml}^{-1}$ ), and  $G_{52}$  mixed with different concentrations of GO (0.7 %, 1.5 % and 2.2 % based on homopolymer); (b)  $G_{52}$ - $H_{130}$  dispersion, GO dispersion ( $4 \text{ mg ml}^{-1}$ ), and  $G_{52}$ - $H_{130}$  mixed with different concentrations of GO (0.7 %, 1.5 % and 2.2 % based on copolymer); (c)  $G_{60}$  solution, GO dispersion ( $4 \text{ mg ml}^{-1}$ ), and  $G_{60}$  mixed with different concentrations of GO (2.3 %, 2.8 % and 3.1 % based on homopolymer); (d)  $G_{60}$ - $B_{70}$  dispersion, GO dispersion ( $4 \text{ mg ml}^{-1}$ ), and  $G_{60}$ - $B_{70}$  mixed different concentrations of GO (2.3 %, 2.8 % and 3.1 % based on copolymer). Samples were diluted in 0.1 mM KCl and titrated from pH  $\sim$ 10 to 2 using HCl.

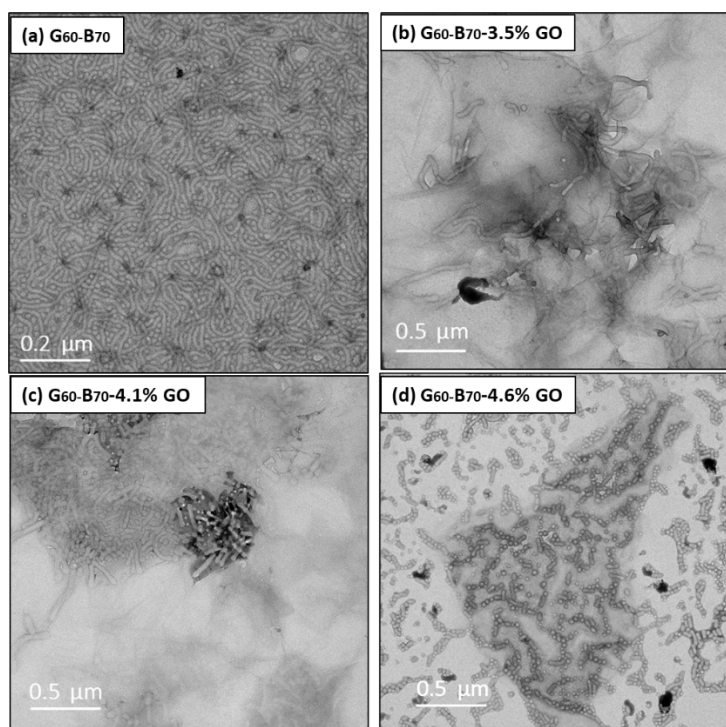


**Figure S10.** Critical gelation temperature (CGT) recorded by oscillatory rheology over several cooling-heating cycles for  $G_{52}$ - $H_{130}$ -1.5% GO based on copolymer. Measurements were conducted at an angular frequency of  $1 \text{ rad s}^{-1}$  and an applied strain amplitude of 1.0 %. Samples were heated/cooled between  $2^\circ\text{C}$  and  $22^\circ\text{C}$  in  $1^\circ\text{C}$  intervals with an equilibration time of 3 min at each temperature. Between each heating/cooling cycle samples were allowed to recover for 30 minutes.

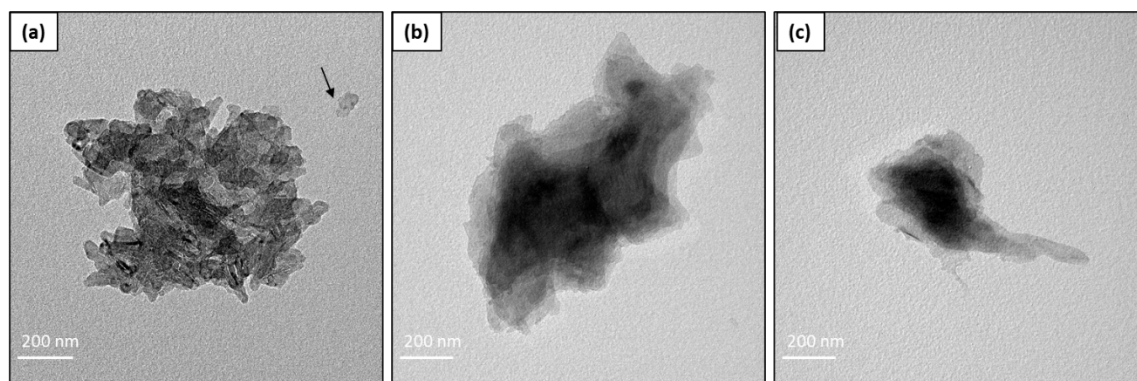




**Figure S11.** (a) PGMA<sub>60</sub>-PBzMA<sub>70</sub> block copolymer dispersions in methanol after mixing with graphene oxide dispersed in methanol (2.8 to 4.6 % w/w based on copolymer) at 56 °C and equilibration overnight at room temperature. (b) Storage modulus ( $G'$ ) versus % strain for 15 % w/w G<sub>60</sub>-B<sub>70</sub> with various GO concentrations (3.2 - 4.1 % w/w based on copolymer) in methanol. (c) Average storage modulus measured between 0.01 and 2 % strain for different GO-containing G<sub>60</sub>-B<sub>70</sub> copolymer methanolic dispersions. All oscillatory rheology measurements were conducted at a frequency of 10 Hz, a strain of 1.0 % and at room temperature.



**Figure S12.** TEM images recorded for 15 % w/w (a) G<sub>60</sub>-B<sub>70</sub>, (b) G<sub>60</sub>-B<sub>70</sub>-3.5% GO, (c) G<sub>60</sub>-B<sub>70</sub>-4.1% GO and (d) G<sub>60</sub>-B<sub>70</sub>-4.6% GO prepared in methanol. Samples were diluted to 0.01 % w/w before being deposited on to carbon coated TEM grids at room temperature and being stained using ruthenium tetroxide vapour.



**Figure S13.** TEM images recorded for GO dispersion. TEM grids were prepared by diluting the dialysed and sonicated GO dispersion to 0.01 % w/w before being deposited on to carbon-coated TEM grids at room temperature and being stained using ruthenium tetroxide vapour.