

SUPPLEMENTARY INFORMATION

Swelling and Mechanical Properties of Hydrogels Composed of Binary Blends of Inter-linked pH-Responsive Microgel Particles

Amir H. Milani^{a,*}, Jane Bramhill^b, Anthony J. Freemont^c and Brian R. Saunders^{a,*}

^a*Polymer Science Research Group, School of Materials, University of Manchester, Grosvenor Street, Manchester, M13 9PL, U.K.*

^b*Gelexir Healthcare Ltd, C/o- Ward Hadaway, The Observatory, Chapel Walks, UK, M2 1HL.*

^c*Regenerative Medicine, Developmental Biomedicine Research Group, School of Medicine, Stopford Building, University of Manchester, Oxford Road, Manchester, M13 9PT*

Glycidyl oligo(ether ester) acrylate characterisation

Glycidyl oligo(ether ester) acrylate (GOE) was prepared from HOE (Fig .S1a) and is reported here for the first time to our knowledge. The first step was synthesis of hydroxyl oligo(ether ester) acrylate (HOE), which followed the method of Gibas et al.¹ Our GOE design strategy involved achieving a balance between two opposing effects. A high n was expected to give longer strand lengths between inter-linked MGs and increased ductility. However, a high n could also cause the vinyl groups to become buried within ether ester chains and restrict the bimolecular free-radical coupling required to achieve inter-linking of neighbouring MG particles. Oligomeric GOE was the specific target for this work. As oligomerisation involved a step-growth process, via a Michael addition, lower molecular weight products (oligomers) could be obtained at lower conversions, and this approach was used to achieve a low ether ester chain length (n)². The conditions used here (Fig. S1a) gave an optimum conversion and value of n for GOE as judged by the mechanical properties of the gels (See Results and Discussion section).

The ¹H NMR spectra for HOE and GOE (Fig .S1b) were used to determine values for n . For HOE, the appearance of the OH resonance with a shift of 2.6 ppm, which had the same integrated area as

each of the vinyl resonances (a , 5.8 – 6.4 ppm), together with the methylene proton signals (c , 3.6 ppm), enabled end group analysis to calculate a value for n of 6 for HOE (Table. S1). Appearance of new peaks in the range of 2.5 - 4 ppm (f and g) confirmed the presence of the epoxide group in GOE (Fig .S1b). By integrating the total signal areas for the three vinyl protons (A_a), and also methylene protons in repeat unit (A_d), the value of n using for GOE was calculated using:

$$n = \frac{3A_d}{2A_a} \quad (1)$$

The conversion of glycidylisation (α_G) for GOE was calculated by determining the epoxide peak area (A_f) and equation 2.

$$\alpha_G = \frac{3A_f}{A_a} \quad (2)$$

The values for n and α_G for GOE were found to be 7 and 20 mol.%, respectively. The α_G value was kept low to minimise chain growth during the glycidylisation reaction because both processes occurred simultaneously as evidenced by GPC data (below). This meant that the final product consisted of a mixture of GOE (20 mol.%) and HOE (80 mol.%). Residual HOE was removed during the MG vinyl functionalisation step (later).

GOE and HOE had monomodal size distributions (Fig .S1c). A shift in the chromatogram for GOE toward higher molecular weights occurred compared to HOE (Fig .S1c) which is in agreement with ^1H NMR data (Table S1) and is due to oligomer growth. The values for M_n determined for GOE and HOE from GPC were higher than those determined from ^1H NMR data. Gibas et al¹ reported much higher differences between the M_n values determined by GPC and ^1H NMR than observed here. These discrepancies may be due to the differences between the hydrodynamic volumes occupied by GOE and HOE and the PMMA standards used here for GPC. We used the M_n values determined from ^1H NMR for this study.

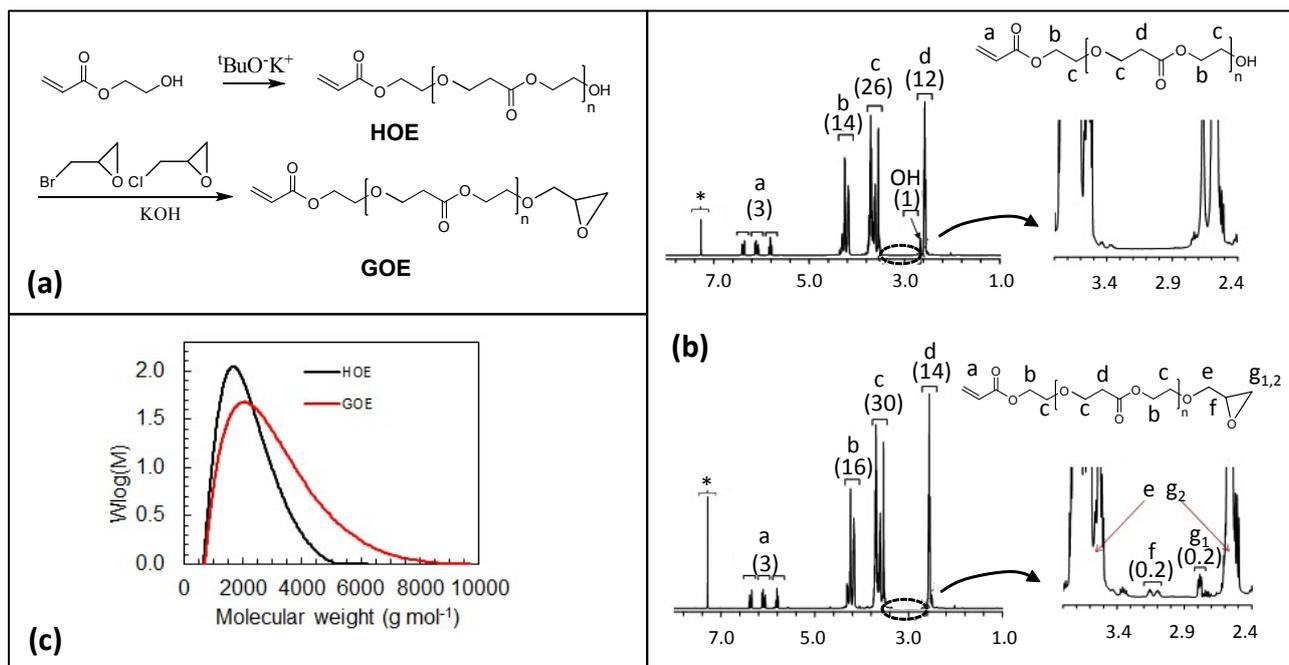


Fig. S1. Synthesis and characterisation data of glycidyl oligo(ether ester) acrylate. (a) Depiction of the method used to prepare GOE. (b) ^1H NMR spectra for hydroxyl oligo(ether ester) acrylate (HOE) (upper) and GOE (lower). The numbers in brackets show the integral values. For the spectrum of GOE, the protons (e) and (g_2) overlap. (c) GPC chromatograms for HOE and GOE.

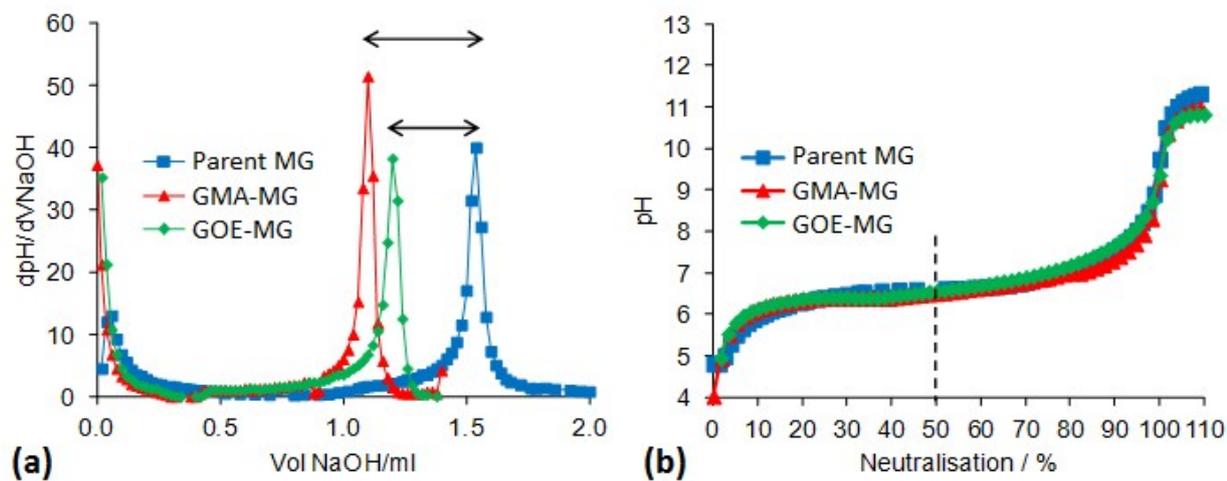


Fig. S2. Potentiometric titration data for vinyl functionalised microgels. (a) shows the first derivative from the pH vs. NaOH addition data and (b) shows the variation of pH as a function of neutralisation. The maxima for (a) were used to determine the MAA contents.

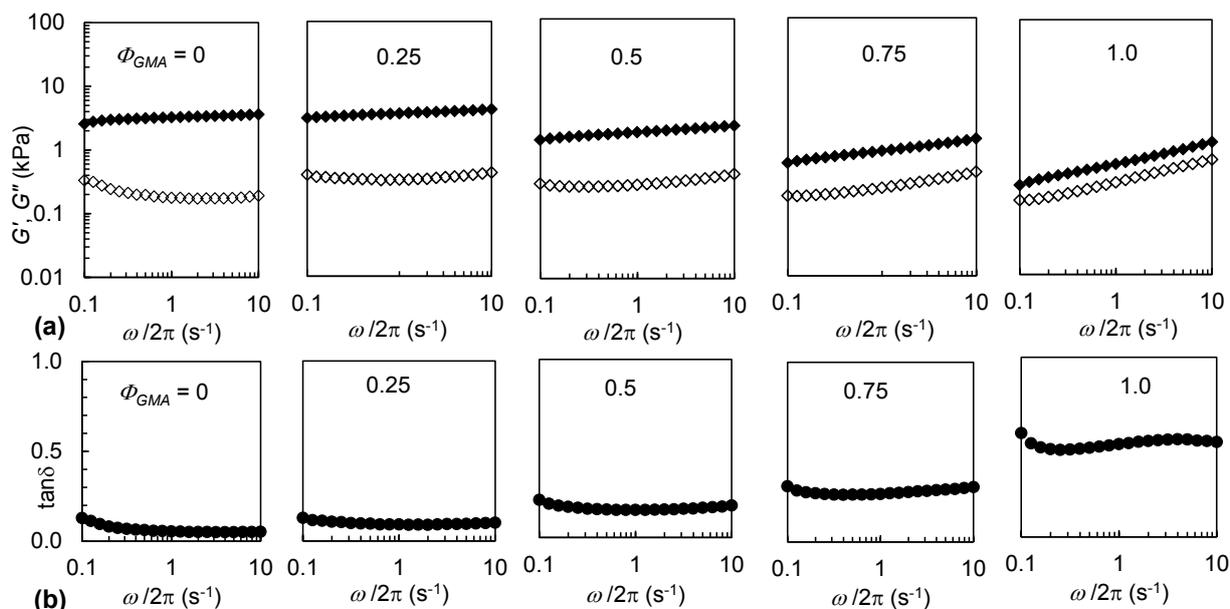


Fig S3. Physical gel mechanical properties studied by frequency-sweep dynamic rheology. (a) shows dynamic storage (G' , closed symbols) and loss (G'' , open symbols) against frequency measured using different Φ_{GMA} values (shown). The y-axis scale is the same for all of the graphs. (b) shows the variation of $\tan\delta$ with frequency

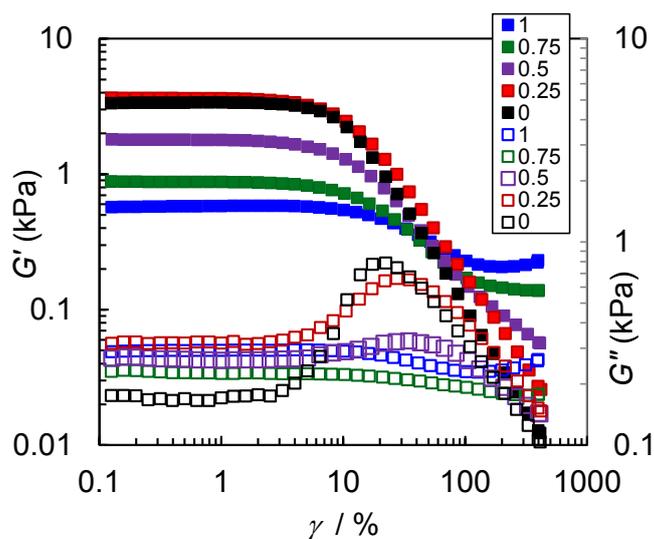


Fig. S4. Variation of dynamic storage (G' , closed symbols) and loss (G'' , open symbols) against strain (γ) measured using different Φ_{GMA} values (shown) for GOE/GMA physical gels. The legend shows values for Φ_{GMA} .

Table S1. Characterisation data for HOE and GOE

name ^c	NMR		GPC	
	n	M_n (g/mol)	M_n (g/mol)	PD
HOE	6	812	1570	1.2
GOE	7	984	1880	1.3

References

1. M. Gibas, and A. Korytkowska-Walach. *Polymer Bulletin* 2003, **51**, 17-22.
2. A. J. Peacock, and A. Calhoun (2006) *Polymer chemistry : properties and applications*, Hanser, Munich.