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Self-reinforcing hydrogels comprised of hydrophobic methyl methacrylate macromers copolymerised with either *N*-vinyl-2-pyrrolidone or 2-hydroxyethyl acrylate

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Methyl methacrylate macromers have been synthesised by catalytic chain transfer polymerization with M_n values ranging from 565 to 25 392. These macromers were subsequently copolymerized with either 2-hydroxyethyl acrylate or *N*-vinyl-2-pyrrolidone, in bulk, by γ-radiation to yield xerogel materials. Copolymerization was confirmed by NMR analyses and by subsequent aqueous extraction of the resultant copolymers. The xerogels containing 2-hydroxyethyl acrylate and macromers below 10 000 (M_n) molecular weight yielded popcorn polymers. All other xerogel materials were transparent. On swelling in deionised water, compositions containing 2-hydroxyethyl acrylate became white and opaque indicating phase segregation. In contrast all of the hydrogels based on *N*-vinyl-2-pyrrolidone retained transparency. Hydrogels were formed that had significantly higher Young's moduli than hydrogels based on random copolymers of equivalent composition.

Introduction

Hydrogels have found widespread application in the biomedical industries, predominantly as contact lenses, wound dressings and skin contact adhesives. The unique properties of hydrogels stem from the combined properties imbued by the polymeric and aqueous phases. One problem often encountered on optimising hydrogel formulations for specific end-uses is poor mechanical strength, which can restrict the utility of the materials. This is evident in membranes applications where hydrogels have many favourable and attractive properties but the fragility of the hydrogels often precludes their adoption. The origin of this problem is quite simple, *viz*, a significant proportion of the material is water which does not contribute to the mechanical integrity of the gel. Thus, the mechanical strength of hydrogels is generally improved by the addition of a crosslinking agent or hydrophobic monomer to the copolymer mixture. However, this strategy always results in a concomitant reduction in the equilibrium water content (EWC). Therefore, the final choice of hydrogel formulation is a compromise between optimising the hydrophilicity and maintaining mechanical strength.

One method of achieving an optimal balance between mechanical strength and water content is to formulate a hydrogel composition based on a graft copolymer comprised of a hydrophobic macromer and a hydrophilic monomer. Yamashita[1,2] showed that high strength hydrogels are possible using this approach, and he used the term 'self-reinforcing gel' to describe the materials he made. Friends *et al.*[3] have published work on synthetic strategies followed in modern contact lens design, including the use of siloxane-containing macromers and crosslinking agents for inducing high oxygen permeability.

In recent work from this laboratory,[4] it was shown that hydrogels made from a hydrophilic polymer backbone substituted with long perfluoro side-chains display very high oxygen permeabilities by providing two pathways for oxygen transmission. As with conventional hydrogel materials, the water provides one route *via* dissolved oxygen. The second route is surmised to be *via* a co-continuous fluorine-rich polymeric phase. Thus hydrogels composed of distinct hydrophilic and hydrophobic regions offer great promise for many applications. Other work[5] has found that macromers of methyl methacrylate, made by catalytic chain transfer polymerization can be readily copolymerized with *N*,*N*-dimethylacrylamide (DMA) to yield transparent xerogels. On swelling in water, hydrogels were formed with significantly higher Young's moduli than the equivalent composition random copolymers.

The aim of this current paper is to describe synthetic work on two alternative hydrogel systems applying the same macromer methodology, using either *N*-vinyl-2-pyrrolidone or 2-hydroxyethyl acrylate as the hydrophilic comonomers.

Experimental

Materials

N-Vinylpyrrolidone (NVP) (Aldrich Pty. Ltd), 2-hydroxyethyl acrylate (HEA) (Aldrich Pty. Ltd) and methyl methacrylate (MMA) (Aldrich Pty. Ltd) were all purified by passing over a short column of basic alumina to remove the inhibitor. Deionised water was used for all swelling measurements. The catalytic chain transfer agent, bis[(difluoroboryl)dimethylglyoximato]cobalt(II) (COBF), was prepared according to the method described by Bakac *et al.*[6]

Macromer preparation

A stock solution of COBF in toluene was prepared by charging COBF (~4 mg) into a dry Schlenk flask, subsequently adding toluene. Conventional Schlenk techniques were used to ensure that an oxygen free environment was maintained throughout the CCT polymerization procedure.

A solution of MMA (20 ml) in toluene (40 ml) and AIBN (0.12 g) was purged with nitrogen for 1 hour. Subsequently, the COBF solution (6 ml) was added utilising standard vacuum and syringe techniques. The flask was then placed in an oil bath at 60 °C for 24 hours. After completion of polymerization, the toluene was removed and molecular weight analysis was performed by GPC.

Macromers of higher molecular weight ($M_n > \sim 5000$) were further purified by reprecipitation in diethyl ether. The number average molecular weights (M_n) of the macromers produced were 25 392, 12 769, 11 361, 10 021, 4335, 1512, 882, 855, and 565 (*i.e.*, a mixture of dimer, trimer (predominant), tetramer, pentamer and hexamer).

Copolymerization

Mixtures of NVP (or HEA) and MMA macromers were made up gravimetrically, deoxygenated with nitrogen for 10 min and irradiated in sealed polypropylene ampoules. As the different copolymerization compositions are designated by weight, this means that the total amount of MMA (repeat unit) remains constant for any given wt% designation. A consequence of this is that the number of MMA or MMA macromer double bonds in the monomer mixture decreases as the macromer molecular weight increases. In all cases the γ-irradiation dose was 1 Mrad obtained from a ^{60}Co source at UNSW, the dose rate being 0.01 Mrad h^{-1} as determined by Fricke dosimetry. The resultant solid rods of xerogel were post-cured at 90 °C for 24 h and then lathe cut to produce thin discs (diameter 10 mm; thickness 1 mm) for swelling measurements and cylindrical pellets (diameter 10 mm; thickness 20 mm) for mechanical testing. In all cases conversions were close to 100% and so the final copolymer composition is defined by the original feed composition.

Gel permeation chromatography

Molecular weight distributions of the macromers were determined by gel permeation chromatography using a GBC Instruments LC1120 HPLC pump, a Shimadzu SIL-10AD VP Autoinjector, a column set consisting of a Polymer Laboratories 3.0 μm bead-size guard column (50 × 7.5 mm) followed by three linear PL columns (10^5, 10^4 and 10^3) and a Shimadzu RID-10A differential refractive index detector. Tetrahydrofuran (BDH, HPLC grade) was used as eluent at 1 ml min^{-1}. Calibration of the GPC equipment was effected with narrow poly(methyl methacrylate) standards (Polymer Laboratories, molecular weight range: 200–1.6 × 10^6).

Nuclear magnetic resonance (NMR)

^{1}H nuclear magnetic resonance (NMR) spectra were acquired on two instruments in the UNSW NMR Facility: a Bruker DMX-500 operating at 500.13 MHz for ^{1}H and 125.47 MHz for ^{13}C, and a Bruker ACF-300 operating at 300.13 MHz for ^{1}H and 75.47 MHz for ^{13}C, both recording at 298 K. Samples were prepared as solutions in deuterated chloroform ($CDCl_3$).

Equilibrium water content

Dimensions of the dry discs and pellets were measured with Vernier calipers and the weighed samples were equilibrated in deionised water at room temperature, the times to attain equilibrium being 2–4 weeks. During this time the water was changed at frequent intervals to allow for the removal of water-soluble material from the samples.

The equilibrium water content (EWC) of the hydrogels is defined by eqn. (1),

$$\mathrm{EWC} = \frac{m_s - m_o}{m_s} \times 100 \quad (1)$$

where m_s = mass of swollen sample, m_o = mass of dry sample.

This EWC measurement needs to be based on the xerogel weight after sol fraction extraction, in the aqueous medium [eqn. (2)],

$$\%\ \text{sol fraction} = \frac{m_o - m_E}{m_o} \times 100 \quad (2)$$

where m_E = dry mass of extracted sample.

The volume fraction of polymer within a hydrogel is given by eqn. (3),

$$\phi_2 = \left(\frac{D_o}{D}\right)^3 \quad (3)$$

where D and D_o are the diameters of the hydrogel and xerogel respectively.

Mechanical testing

The elastic moduli of the hydrogels were determined by stress (compression)–strain measurements. The compression rig consisted of a micrometer dial gauge capable of measuring displacement accurately to 0.01 mm. A cylindrical block of Teflon was fastened to the lower end of a shaft that was attached to this gauge. The hydrogel sample was placed centrally on a set of electronic balances inside a Petri dish containing deionised water. The Teflon compressor was moved into contact with the material and the mass recorded as a function of deformation of the sample. The sample was allowed to relax for at least 30 min before re-testing. All samples were tested in triplicate.

Results and discussion

Macromer synthesis

The molecular weight analysis results are given in Table 1. The macromers range in molecular weight from about 500 to 25 000. Typical GPC chromatograms are shown in Fig. 1 for three of the macromers. A MALDI analysis showing the molecular weight distribution of PMMA generated in a CCT reaction is given in Fig. 2. Each peak mass (m) is consistent with the expression $m = (100.1 \times n) + 23.0$; where n is the degree of polymerization, 100.1 is the mass of the repeat unit and 23.0 is the mass of the sodium counterion. There are no chains evident with an AIBN initiator fragment (mass = 68). This result is concordant with a polymerization process dominated by catalytic chain transfer. Finally an NMR analysis of the lowest molecular weight macromer is given in Fig. 3(a), clearly showing the vinyl peaks consistent with a typical macromer structure.

Macromer reactivity

Proof of macromer reactivity in the copolymerization reaction was obtained by ^{1}H-NMR. Fig. 3 shows three NMR spectra corresponding to the macromer (3a), HEA (3b) and a copoly-

Table 1 Molecular weight of macromers

Macromer	M_n	M_w	PD
MMA(1)	565	1834	3.244
MMA(2)	855	1532	1.790
MMA(3)	882	1648	1.869
MMA(4)	1512	3665	2.423
MMA(5)	4335	9091	2.097
MMA(6)	10021	13648	1.362
MMA(7)	11361	21158	1.862
MMA(8)	12769	19183	1.502
MMA(9)	25392	42571	1.677

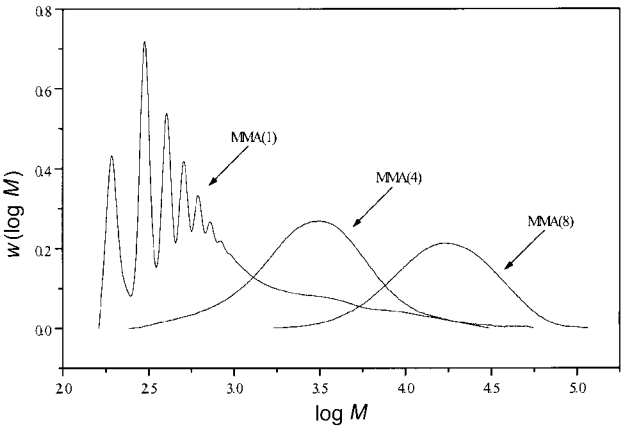

Fig. 1 Typical GPC chromatograms for three of the MMA macromers.

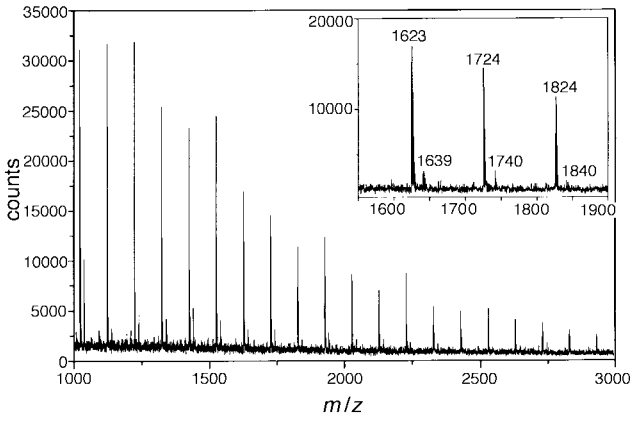

Fig. 2 MALDI analysis showing the molecular weight distribution of PMMA generated in a CCT reaction.

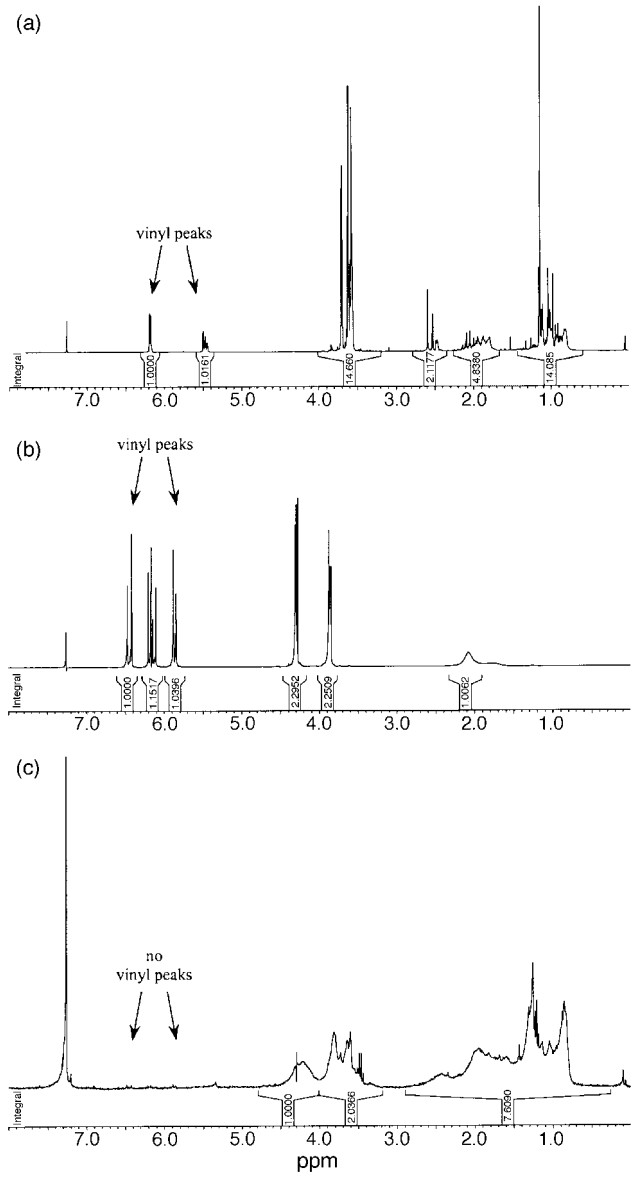

Fig. 3 ^{1}H-NMR spectra for (a) MMA(1), (b) HEA and (c) copolymer, MMA(1)-30–DMA-70.

mer (3c) dissolved in $CDCl_3$. The vinyl peaks are evident in spectra 3a and 3b and plainly absent in 3c. The spectrum 3c also shows the presence of peaks from both the macromer and HEA. Some limited data are available on the reactivity of the macromer double bonds in copolymerization reactions. Cacioli *et al.*[7] showed that MMA macromers prepared *via* CCT copolymerized with ethyl acrylate. In more recent work Abbey *et al.*[8] estimated reactivity ratios for MMA dimers (made by CCT) with styrene. A number of patents[9–11] have also been published on synthesising comb and star polymers using macromers produced by CCT *via* copolymerization with acrylate monomers. In summary, it seems clear from the NMR analysis that copolymerization is indeed occurring—a result which is quite consistent with previous studies.

Xerogel and hydrogel appearance

MMA–NVP hydrogels. The xerogel rods were lathe cut into pellets and discs. All xerogel rods were transparent in the dry state and maintained their transparency on swelling.

MMA–HEA hydrogels. During the polymerization of MMA macromers with HEA some of the polymers underwent popcorn polymerization. When the molecular weight of the macromers is above $M_n = 10\,000$, popcorn formation does not occur. It appears to increase in severity with decreasing molecular weight of macromer. Furthermore, as the amount of macromer is increased the extent of popcorn formation also decreases. This is consistent with previous observations reported by Bakac *et al.*[6] who found that popcorn polymerization could be suppressed by employing strategies that reduce the molecular weight (and hence mitigate the gel effect) such as increasing the initiator concentration or including a chain transfer agent. Starodubtzev *et al.*[12] also noted that increased concentrations of crosslinker induced popcorn polymerization, again indicating that the origin of the popcorn phenomenon is a strong gel effect, leading to 'hot-spots' within a bulk polymer matrix. In the current work the low propagation rate of the macromer end-group would tend to reduce the severity of the gel-effect, and therefore popcorn polymerization would be suppressed by higher concentrations of macromer double bonds in the initial feed mixture. It is noteworthy that there is no popcorn formation in the random copolymerization of HEA and MMA.

Swelling properties

High water content hydrogels were targeted with the aim of improving the mechanical strength whilst maintaining a high water content. Hydrogels were synthesised based on 5, 10, 20 and 30% by weight of MMA units—utilising all the macromers listed in Table 1. Copolymeric hydrogels based on random MMA–NVP and MMA–HEA copolymers were synthesised to provide a comparison with conventional hydrogel materials.

MMA–NVP hydrogels. The equilibrium water content (EWC) of the materials as a function of total MMA content and macromer chain length is shown in Fig. 4. The inclusion of macromers resulted in reduced swelling—however, the EWC remained above 70 wt% even with the very high molecular weight macromers.

High sol fractions were noted on extraction of the gels with water. The low tendency of NVP to copolymerise with many monomers leads to the presence of uncrosslinked homopolymer material and low molecular weight fractions in the products.[13] The sol fraction could be significantly reduced by the addition of crosslinking agents.

MMA–HEA hydrogels. The equilibrium water content (EWC) of the gels as a function of total MMA content and macromer chain length is shown in Fig. 5. Here, a much lower EWC value is observed for the copolymers with a high macromer content. The sol fractions of the copolymers are all quite low ($\sim$5 wt%).

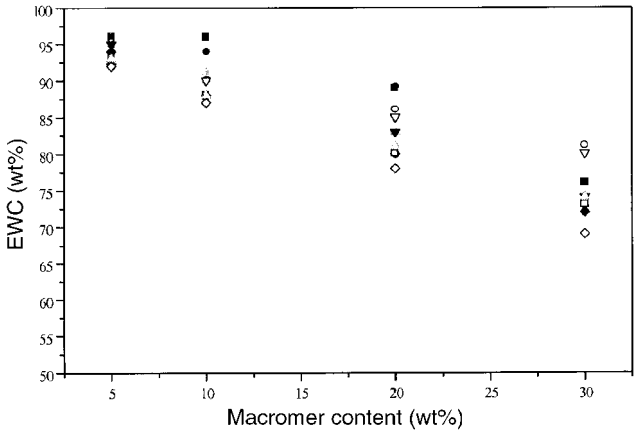

Fig. 4 Equilibrium water content (EWC) of the MMA–NVP hydrogels as a function of total MMA content and macromer chain length. ■ MMA, ● MMA(1), ▲ MMA(2), ▼ MMA(3), ◆ MMA(4), □ MMA(5), ○ MMA(6), △ MMA(7), ▽ MMA(8), ◇ MMA(9).

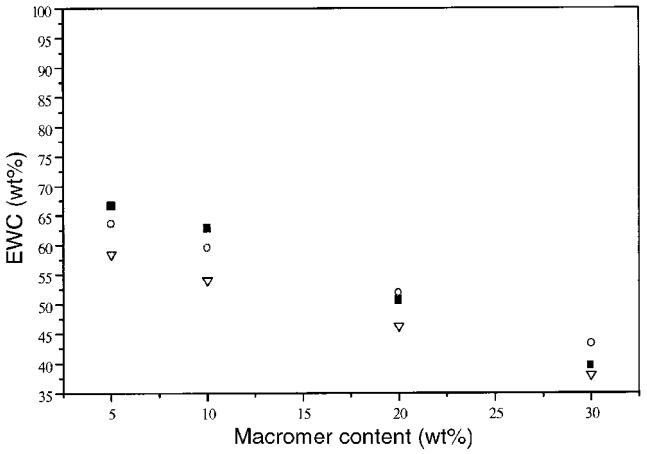

Fig. 5 Equilibrium water content (EWC) of the MMA–HEA hydrogels as a function of total MMA content and macromer chain length. ■ MMA, ○ MMA(6), ▽ MMA(8).

Mechanical properties

MMA–NVP hydrogels. When the MMA component is included as a macromer the hydrogels become less fragile and it is quite clear, even visually, that the mechanical properties are significantly different in comparison with the random copolymeric gels.

An increase in the Young's modulus (E) becomes evident for hydrogels containing macromers with an M_n greater than 850, as can be seen in Fig. 6, and is further improved when the concentration of macromer is at least 10 wt%. In a control experiment we synthesised a poly(2-hydroxyethyl methacrylate) (PHEMA) hydrogel under identical polymerization conditions and found that the Young's modulus was similar to the MMA–NVP gels containing high amounts of the MMA macromers in this work. This is a significant result as the water content of the current MMA–NVP gels is about 80% higher than the PHEMA hydrogel. Thus it is clear that high strength hydrogels can be easily synthesised by this particular macromer approach.

In related work, Michálek *et al.*[14] have also prepared macromers of MMA copolymerised with NVP; the vinyl functionality of the macromer was prepared by copolymerization of MMA with allyl methacrylate. A similar relationship between macromer length and mechanical strength was observed, although crosslinking may also have occurred, so that the increased strength originated from both physical and chemical crosslinking.

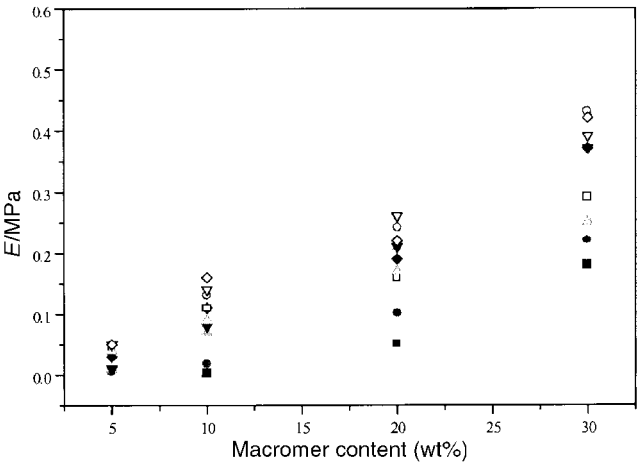

Fig. 6 Young's modulus (E) of the MMA–NVP hydrogels as a function of total MMA content and macromer chain length. ■ MMA, ● MMA(1), ▲ MMA(2), ▼ MMA(3), ◆ MMA(4), □ MMA(5), ○ MMA(6), △ MMA(7), ▽ MMA(8), ◇ MMA(9).

MMA–HEA hydrogels. MMA–HEA random copolymers possess a relatively high modulus compared to the random MMA–NVP hydrogels. It is evident that the incorporation of macromers further increases the mechanical strength of the hydrogels as shown in Fig. 7. These MMA-macromer–HEA hydrogels have a modulus of 2–3 times that measured for uncrosslinked PHEMA (prepared under identical conditions), which has a comparable water content.

Network parameters

The effective cross-link density, v_e, was obtained from compression-strain results *via* eqn. (4),

$$\tau = RTv_e\phi_2^{1/3}\left(\lambda - \frac{1}{\lambda^2}\right) \quad (4)$$

where τ is the force per cross-sectional area, R is the gas constant, T the absolute temperature and v_e, the effective cross-link density (mol m^{-3}).

Values of the polymer–water interaction parameter, χ, were calculated from eqn. (5), valid at swelling equilibrium,

$$\ln(1-\phi_2)+\phi_2+\chi\phi_2^2+v_eV_1(\phi_2^{1/3}-2\phi_2 f^{-1})=0 \quad (5)$$

where f = crosslinking functionality of crosslinking agent and V_1 = molar volume of water (dm^3 mol^{-1}).

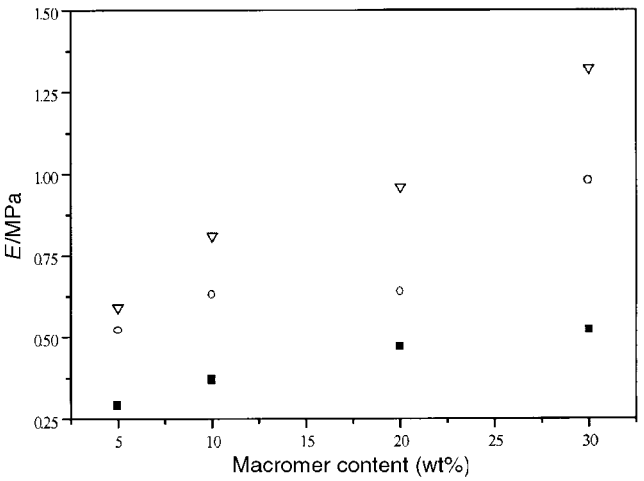

Fig. 7 Young's modulus (E) of the MMA–HEA hydrogels as a function of total MMA content and macromer chain length. ■ MMA, ○ MMA(6), ▽ MMA(8).

Table 2 Network parameters obtained from swelling and modulus data for MMA–NVP hydrogels

Material	v_e/mol m^{-3}	M_c/kg mol^{-1}	χ
MMA-5–NVP-95	0.97	1206.19	0.510
MMA-10–NVP-90	1.18	991.53	0.509
MMA-20–NVP-80	12.8	91.41	0.537
MMA-30–NVP-70	34.04	34.37	0.593
MMA(1)-5–NVP-95	1.6	731.25	0.508
MMA(1)-10–NVP-90	5.73	204.19	0.517
MMA(1)-20–NVP-80	25.22	46.39	0.524
MMA(1)-30–NVP-70	45.48	25.73	0.569
MMA(2)-5–NVP-95	3.45	339.13	0.509
MMA(2)-10–NVP-90	17.62	66.40	0.523
MMA(2)-20–NVP-80	47.35	24.71	0.557
MMA(2)-30–NVP-70	81.06	14.43	0.615
MMA(3)-5–NVP-95	4.79	244.26	0.512
MMA(3)-10–NVP-90	20.92	55.93	0.527
MMA(3)-20–NVP-80	43.19	27.09	0.564
MMA(3)-30–NVP-70	71.27	16.42	0.610
MMA(4)-5–NVP-95	9.14	128.01	0.518
MMA(4)-10–NVP-90	26.54	44.08	0.547
MMA(4)-20–NVP-80	35.74	32.74	0.598
MMA(4)-30–NVP-70	63.38	18.46	0.655
MMA(5)-5–NVP-95	11.98	97.66	0.515
MMA(5)-10–NVP-90	24.61	47.54	0.536
MMA(5)-20–NVP-80	30.85	37.93	0.582
MMA(5)-30–NVP-70	52.72	22.19	0.624
MMA(6)-5–NVP-95	13.61	85.97	0.520
MMA(6)-10–NVP-90	30.02	38.97	0.534
MMA(6)-20–NVP-80	46.96	24.91	0.596
MMA(6)-30–NVP-70	71.44	16.38	0.667
MMA(7)-5–NVP-95	9.82	119.14	0.518
MMA(7)-10–NVP-90	20.87	56.06	0.538
MMA(7)-20–NVP-80	30.43	38.45	0.582
MMA(7)-30–NVP-70	43.46	26.92	0.625
MMA(8)-5–NVP-95	12.47	93.83	0.521
MMA(8)-10–NVP-90	31.76	36.84	0.539
MMA(8)-20–NVP-80	49.59	23.59	0.596
MMA98)-30–NVP-70	67.73	17.27	0.681
MMA(9)-5–NVP-95	13.24	88.37	0.520
MMA(9)-10–NVP-90	38.69	30.24	0.536
MMA(9)-20–NVP-80	43.23	27.06	0.591
MMA(9)-30–NVP-70	77.19	15.16	0.640

Table 3 Network parameters obtained from swelling and modulus data for MMA–HEA hydrogels

Material	v_e/mol m^{-3}	M_c/kg mol^{-1}	χ
MMA-5–HEA-95	51	24.31	0.618
MMA-10–HEA-90	64	19.38	0.654
MMA-20–HEA-80	75	16.53	0.743
MMA-30–HEA-70	74	16.76	0.902
MMA(6)-5–HEA-95	91	13.63	0.639
MMA(6)-10–HEA-90	112	11.07	0.664
MMA(6)-20–HEA-80	87	14.25	0.734
MMA(6)-30–HEA-70	155	8.00	0.827
MMA(8)-5–HEA-95	104	11.92	0.672
MMA(8)-10–HEA-90	140	8.86	0.699
MMA(8)-20–HEA-80	159	7.80	0.776
MMA(8)-30–HEA-70	187	6.63	0.886

From the values of v_e the molar mass per crosslink, M_c was calculated *via* eqn. (6).

$$M_c = \rho / v_e \quad (6)$$

The network parameters, obtained by combining the swelling and compression modulus data, are given in Table 2 and Table 3 for MMA–NVP and MMA–HEA hydrogels respectively. Since no crosslinking agent is added the theoretical crosslinking density is zero. The finite effective crosslinking density can be explained in two ways. Firstly γ-radiation is known to induce crosslinking in HEA and NVP. More importantly, the hydrophobic interactions of the MMA macromers aggregate to form physical crosslinks. This hydrophobic crosslinking approach is clearly enhanced in these graft copolymers in comparison with the random copolymers containing equivalent MMA concentrations. In contact lens applications the challenge is to induce this hydrophilic–hydrophobic segregation without causing excessive phase separation resulting in opacity. In the current work, copolymers based on HEA either formed popcorn polymers or became white and opaque on swelling or became cloudy/white upon swelling. However, the MMA-macromer–NVP copolymers retained transparency. This result for MMA-macromers copolymerised with NVP is perhaps not too surprising as previous studies have clearly demonstrated the high compatibility of these two components both in copolymers and in polymer blends.[15]

It may be possible to offset the phase separation in the HEA based gels by suppressing the gel effect by restricting molecular weight development in the copolymerization process. This would permit the use of smaller macromer chain lengths to synthesise self-reinforcing hydrogels that may retain transparency on swelling.

Conclusions

This work indicates that self-reinforcing hydrogels can be easily synthesised using MMA-macromers made by catalytic chain transfer polymerization. The judicious selection of comonomers enables high modulus, clear xerogel compositions to be made in bulk, suitable for machining to lens materials.

Acknowledgements

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