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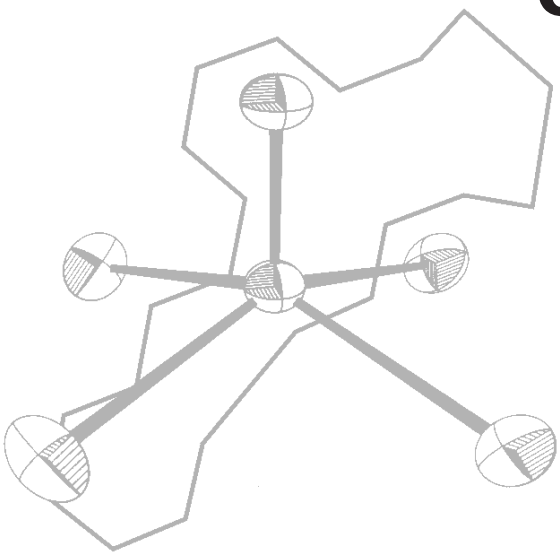

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The Synthesis of Novel Hybrid Monomers

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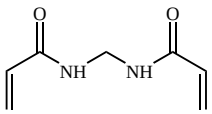
Novel hybrid amide–ester crosslinking monomers were prepared by using methodology which utilizes the differential functionalities present within a convenient amino alcohol. Modification of the procedure to a simple one-pot reaction enables the generation of these unique monomers to be scaled to commercial levels.

Introduction

Monomers which contain two vinyl functionalities have the potential to undergo crosslinking reactions to form polymeric network systems. In particular, free-radical copolymerizations performed with acryloyl-derived crosslinking agents are able to afford a variety of dimensionally stable network polymers which may range from soft and porous hydrogels to the hard and brittle materials of some methacrylate-derived polymers. Such polymers have found use in a variety of applications of commercial significance and many examples exist of their use in the manufacture of biocompatible materials such as contact lenses, permeable membranes, dental cements, electrophoresis gels and resins for solid-phase synthesis.[1–4]

The majority of commercially available acryloyl-derived crosslinking agents currently used for the formation of three-dimensional crosslinked polymers typically possess identical vinyl functionalities. These include monomers such as *N,N′*-methylenebisacrylamide (1), which is traditionally used for the generation of network polymers in aqueous environments, and 1,2-ethylene glycol dimethacrylate (2), which is suited for polymerization in organic solvents.



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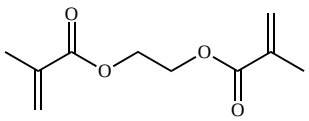

(2)

Network polymers formed with crosslinking agents such as (1) and (2) in a copolymerization with the monovinyl monomers acrylamide and methyl methacrylate respectively, may be viewed as being composed of linear chains of polymer with crosslinking monomer incorporated at statistical intervals dictated by their relative reactivities. However, due to the structural similarity of the vinyl units in both the monovinyl and crosslinking comonomers, the resultant network polymer is often regarded as a highly complex structure which encapsulates regions of high- and low-crosslink density and moieties arising from, for example, intramolecular cyclizations.[5–7]

Many researchers have attempted to change the physical properties of the networks by modifying the central alkyl portion of the crosslinking monomers. Such an approach may alter the occurrence of events such as intramolecular cyclizations during the polymerization process but not necessarily the manner in which the network is constructed. In an attempt to impart a degree of control over the crosslinking reaction and resultant polymerization exotherm, we desired to synthesize a range of new monomeric systems containing differentiated vinylic units which are expected to exhibit individual reactivity profiles under free radical conditions. The approach described in this paper uses amide and ester functionalities as well as variation in the acryloyl and methacryloyl moieties to induce a reactivity differential.

It is proposed that these amide–ester crosslinking monomers may eventually be used to afford network polymers which are different to those currently available, and this paper describes the synthesis of these novel crosslinking agents by a commercially viable route.

Results and Discussion

The amide–ester compounds of interest in this synthetic approach can, in principle, be synthesized from any available amino alcohol. Here the methodology is exemplified by using ethanolamine as the starting material. The amine and alcohol functionalities of this precursor have a sufficient reactivity differential

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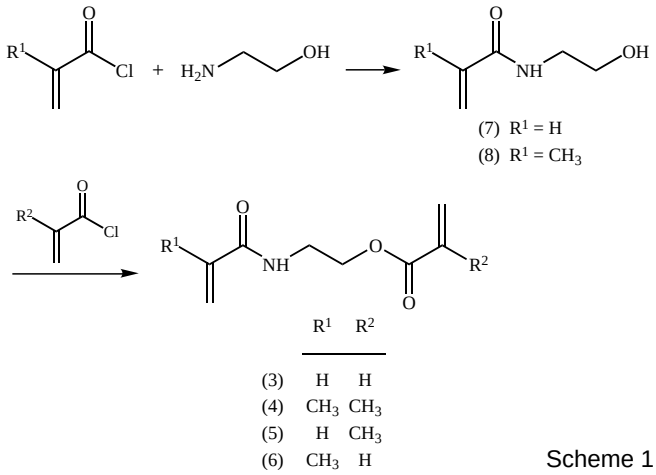
to selectively produce an amide-derived intermediate before further elaboration to give the ester functionality. By using this strategy, four different crosslinking monomers may be readily produced; two containing identical vinyl units, (3) and (4), and two with non-identical vinyl units, (5) and (6).

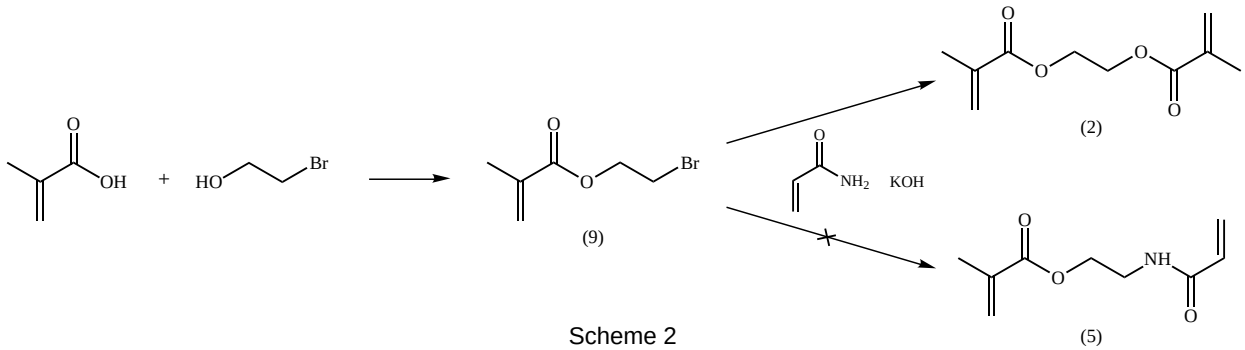


Scheme 1

The initial approach in the generation of the required monomers involved the reaction of equimolar amounts of ethanolamine with an acid chloride (acryloyl or methacryloyl chloride) in the presence of an amine base such as pyridine or triethylamine. However, complex reaction mixtures were produced which required extensive purification before isolation of the intermediate product. The use of aqueous alkali was also attempted, but there was difficulty in the ensuing isolation of the intermediate compound owing to its hydrophilic nature. A general synthetic procedure was then developed which involved the reaction of 2 molar equivalents of ethanolamine with 1 molar equivalent of an acid chloride (acryloyl or methacryloyl chloride) at 0°C in dry chloroform. During the reaction an ethanolamine monohydrochloride salt precipitated, which was subsequently removed from the required intermediate. Concentration of the resulting filtrates, then, afforded the intermediates *N*-(2-hydroxyethyl)acrylamide (7) and *N*-(2-hydroxyethyl)methacrylamide (8) in excellent yields of 87 and 96% respectively. Reaction of the intermediate (7) with a molar equivalent of acryloyl or methacryloyl chloride in the presence of triethylamine then gave the ester–amide crosslinking monomers (3) and (5) in yields of 50 and 61% respectively. Similarly, the reaction of (8) with 1·1 molar equivalents of acryloyl or methacryloyl chloride under the same reaction conditions afforded the monomers (4) and (6) yields of 31 and 48% after purification (Scheme 1).

While this procedure is viable for small-scale preparation and is necessary for the synthesis of the first functionalized monomer, scale-up of the reaction led to difficulty during the isolation of the intermediate compounds (7) and (8); a highly viscous oil formed upon concentration of the solution. Attempts to dissolve the oil in chloroform for further reaction were unsuccessful, producing a tacky substance which may be a result of significant hydrogen bonding between molecules of the intermediate. As an alternative approach, a one-pot procedure was developed which was appropriate for the scale-up of compounds (3)–(6), whereby the intermediate compounds (7) and (8) were not isolated after removal of the monohydrochloride salt. Immediate reaction of the resulting filtrates containing the intermediates with further amounts of acid chloride at 0°C followed by subsequent purification by column chromatography then afforded the monomers (3)–(6).

Other synthetic approaches to the formation of these amide–ester monomers were also attempted, but proved to be unsuccessful. It was envisaged that the formation of an ester-derived intermediate with a readily displaced substituent would also enable access to the target monomers. The reaction of 2-bromoethanol with methacrylic acid, according to literature procedure,[8] afforded the ester-derived intermediate 2-bromoethyl methacrylate (9) in a yield of 55%. However, efforts to form the monomer (5) by the treatment of this intermediate with acrylamide under the conditions described by Itoh[9] did not produce any of the expected material. Instead, the only monomer isolated from the reaction mixture was the diester ethylene glycol dimethacrylate (2) (Scheme 2). A possible mechanism for the formation of this molecule is base-assisted cleavage of the ester functionality of 2-bromoethyl methacrylate (9) to give methacrylic acid which then reacts with further units of the intermediate (9).



Scheme 2

Although briefly mentioned in the literature as by-products isolated from different chemical processes,[10–14] no characterization data exists for the target compounds and little, if any, interest has been shown in their potential as crosslinking agents for network formation. In this report, not only were these compounds synthesized in a direct manner, but their formation was demonstrated to be possible by a viable commercial pathway.

Conclusion

In the past few decades we have seen a rise in the importance of new monomers for the formation of network polymers, with the design and synthesis of new molecules with unique attributes for particular applications. The amide–ester crosslinking agents described in this report may be applied to situations where solubility in both organic and aqueous systems is required, or where the presence of a readily hydrolysable moiety for the controlled degradation of the network polymer is desired. Moreover, the intermediates (7) and (8) generated during the course of this work are also worthy of consideration as monomers in their own right, and it is envisaged that the free-radical polymerization of these intermediates would give novel polymers which may readily undergo further elaboration to produce functionalized polymers, or participate in condensation reactions to afford different crosslinked materials with specific properties.

Experimental

Instrumentation

N.m.r. spectra were obtained in (D)chloroform (99·9%) (Cambridge Isotope Laboratories) by using a Varian Unity Plus 400 spectrometer unless otherwise specified. Mass spectrometric data were obtained with a V. G. Micromass 7070F spectrometer or on a Kratos Analytical Concept ISQ. Infrared (i.r.) spectra were recorded on a Bio-Rad FTS-60A Fourier-transform i.r. spectrometer. Microanalyses were performed by Central Science Laboratory, Hobart, or Chemical and Microanalysis Services Pty Ltd, Melbourne.

Flash chromatography and vacuum liquid chromatography were performed by using Merck Kieselgel 60 (230–400 mesh) and Merck Kieselgel 60 GF_{254}, respectively. The eluent used was diethyl ether/hexane/methanol (7 : 2·5 : 0·5). The components were located under a 254 nm u.v. lamp and visualization was achieved by using a 1 : 1 solution of 2% potassium permanganate and 4% sodium bicarbonate.

Reagents

Acryloyl and methacryloyl chloride were obtained from Aldrich Chemical Company and were filtered over basic alumina and distilled prior to use. Ethanolamine was distilled under reduced pressure before use. All organic solvents were of analytical grade unless otherwise specified. Dry benzene and dry and ethanol-free chloroform was prepared according to the method described by Vogel.[15]

N-*(2-Hydroxyethyl)acrylamide (7)*

Acryloyl chloride (25 mmol, 2·0 ml) in chloroform (25 ml) was added dropwise to a stirred solution of ethanolamine (50 mmol, 3·0 ml) in chloroform (50 ml) at 0°C. After the addition was complete, the reaction mixture was stirred at 0°C for a further 2 h. The ethanolamine monohydrochloride precipitate was removed by filtration and the filtrate evaporated under reduced pressure to give the crude product as a yellow oil. This was then taken up in a slurry of basic alumina in chloroform, and stirred at room temperature for 18 h. Removal of the alumina and concentration of the solution then gave (7) as a clear colourless *oil* (2·5 g, 87%) (Found: C, 52·4; H, 8·1; N, 12·0. $C_5H_9NO_2$ requires C, 52·2; H, 7·9; N, 12·2%). ν_{max} (NaCl)/cm^{-1} 3296, 3088, 2491, 2881, 1660, 1623, 1554. ^{1}H n.m.r. δ ($CDCl_3$) 7·06, br s, NH; 6·24, dd, *J* 17·0, 1·8 Hz, CH=C**H**$_a$H$_b$; 6·17, dd, *J* 17·0, 9·8 Hz, C**H**=CH$_2$; 5·62, dd, *J* 9·9, 1·8 Hz, CH=CH$_a$**H**$_b$; 4·13, s, OH; 3·69, t, *J* 5·1 Hz, C**H**$_2$OH; 3·43, dt, *J* 5·4, 5·3 Hz, NHC**H**$_2$. ^{13}C n.m.r. δ ($CDCl_3$) 166·8, C=O; 130·5, **C**H=CH$_2$; 126·7, CH=**C**H$_2$; 61·5, CH_2OH; 42·3, $NHCH_2$. *m/z* (c.i., NH_4) 116 ($(MH)^+$, 100%), 85 (21), 72 (29), 55 (43) (Found: $(MH)^{+\bullet}$, 116·07123. $C_5H_{10}NO_2$ requires $(MH)^{+\bullet}$, 116·07114).

N-*(2-Hydroxyethyl)methacrylamide (8)*

Methacryloyl chloride (25 mmol, 2·4 ml) in chloroform (25 ml) was added dropwise to a stirred solution of ethanolamine (50 mmol, 3·0 ml) in chloroform (50 ml) following the same reaction and workup conditions as outlined for (7). The product (8) was then isolated as a clear colourless *oil* (3·17 g, 96%) (Found: C, 55·9; H, 8·7; N, 10·6. $C_6H_{11}NO_2$ requires C, 55·8; H, 8·6; N, 10·8%). ν_{max} (NaCl)/cm^{-1} 3332, 2929, 2878, 1656, 1616, 1539. ^{1}H n.m.r. δ ($CDCl_3$) 6·88, br m, NH; 5·69, br m, $(H_3C)C=C\mathbf{H}_aH_b$; 5·30, br m, $(H_3C)C=CH_a\mathbf{H}_b$; 4·29, s, OH; 3·66, t, *J* 5·1 Hz, C**H**$_2$OH; 3·40, dt, *J* 5·3, 5·1 Hz, NHC**H**$_2$; 1·90, br m, CH_3. ^{13}C n.m.r. δ ($CDCl_3$) 166·5, C=O; 139·2, $(H_3C)\mathbf{C}=CH_2$; 120·1, $(H_3C)C=\mathbf{C}H_2$; 61·2, CH_2OH; 42·3, $NHCH_2$; 18·4, CH_3. *m/z* (c.i., NH_4) 130 ($(MH)^+$, 100%) (Found: $(MH)^{+\bullet}$, 130·08651. $C_6H_{12}NO_2$ requires $(MH)^{+\bullet}$, 130·08679).

2-Acrylamidoethyl Acrylate (3)

To a stirred solution of (7) (20 mmol, 2·32 g) and triethylamine (22 mmol, 2·8 ml) in chloroform (80 ml), at room temperature and under a nitrogen atmosphere, was added dropwise a solution of acryloyl chloride (22 mmol, 1·8 ml) in chloroform (40 ml). Upon completion of the addition, the mixture was stirred for an additional 17 h. The reaction mixture was then washed with dilute hydrochloric acid (0·5 M, 3×60 ml), and the organic fraction collected and concentrated under reduced pressure to give the crude product as an oil. Purification by flash vacuum chromatography afforded (3) as a clear colourless *oil* (1·7 g, 50%) (Found: C, 56·8; H, 6·7; N, 8·3. $C_8H_{11}NO_3$ requires C, 56·8; H, 6·6; N, 8·3%). ν_{max} (NaCl)/cm^{-1} 3285, 3075, 2959, 1726, 1661, 1627, 1547. ^{1}H n.m.r. δ ($CDCl_3$) 6·44, dd, *J* 17·3, 1·3 Hz, $ROOCCH=C\mathbf{H}_aH_b$; 6·30, dd, *J* 17·1, 1·4 Hz; $RHNCOCH=C\mathbf{H}_cH_d$; 6·14, dd, *J* 17·5, 10·3 Hz, $RHNCOC\mathbf{H}=CH_cH_d$; 6·10, dd, *J* 16·4, 9·7 Hz, $RO_2CC\mathbf{H}=CH_aH_b$; 6·00, br m, NH; 5·88, dd, *J* 10·4, 1·3 Hz, $RO_2CCH=CH_a\mathbf{H}_b$; 5·67, dd, *J* 10·0, 1·6 Hz, $RHNCOCH=CH_c\mathbf{H}_d$; 4·30, t, *J* 5·3 Hz, OCH_2; 3·65, dt, *J* 5·4, 5·2 Hz, NHC**H**$_2$. ^{13}C n.m.r. δ ($CDCl_3$) 166·0, C=O; 165·8, C=O; 131·3, $RO_2CCH=\mathbf{C}H_2$; 130·5, $RHNCO\mathbf{C}H=CH_2$; 127·8, $RO_2C\mathbf{C}H=CH_2$; 126·4, $RHNCOCH=\mathbf{C}H_2$; 63·0, OCH_2; 38·5, $NHCH_2$. *m/z* (c.i., NH_4) 170 ($(MH)^+$, 100%), 98 (33) (Found: $(MH)^{+\bullet}$, 170·08195. $C_8H_{12}NO_3$ requires $(MH)^{+\bullet}$, 170·08170).

2-Methacrylamidoethyl Methacrylate (4)

To a stirred solution of (8) (10 mmol, 1·3 g) and triethylamine (11 mmol, 1·5 ml) in chloroform (40 ml) and under a nitrogen atmosphere, was added dropwise a solution of methacryloyl chloride (11 mmol, 1·1 ml) in chloroform (20 ml) at room temperature. The workup procedure and chromatography as described for (3) yielded the crosslinking monomer (4) as a colourless *oil*

(0·94 g, 48%) (Found: C, 60·9; H, 7·6; N, 6·9. $C_{10}H_{15}NO_3$ requires C, 60·9; H, 7·7; N, 7·1%). ν_{max} (NaCl)/cm^{-1} 3338, 2958, 1720, 1661, 1623, 1533. ^{1}H n.m.r. δ ($CDCl_3$) 6·29, br s, NH; 6·11, br m, $RO_2C(H_3C)C{=}C\mathbf{H}_aH_b$; 5·68, br m, $RHNCO(H_3C)C{=}C\mathbf{H}_cH_d$; 5·58, br m, $RO_2C(H_3C)C{=}CH_a\mathbf{H}_b$; 5·33, br m, $RHNCO(H_3C)C{=}CH_c\mathbf{H}_d$; 4·28, t, J 5·4 Hz, OCH_2; 3·63, dt, J 5·5, 5·3 Hz, $NHC\mathbf{H}_2$; 1·94, br m, CH_3; 1·92, br m, CH_3. ^{13}C n.m.r. δ ($CDCl_3$) 168·4, HNC=O; 167·4, OC=O; 139·6, $RHNCO(H_3C)\mathbf{C}{=}CH_2$; 135·7, $RO_2C(H_3C)\mathbf{C}{=}CH_2$; 126·0, $RO_2C(H_3C)C{=}\mathbf{C}H_2$; 119·6, $RHNCO(H_3C)C{=}\mathbf{C}H_2$; 63·1, OCH_2; 36·9, $NHCH_2$; 18·4, $RHNCO(H_3\mathbf{C})C{=}CH_2$; 18·1, $ROOC(H_3\mathbf{C})C{=}CH_2$. *m/z* (c.i., NH_4) 198 ($(MH)^+$, 74%), 128 (22), 112 (100), 111 (27) (Found: $(MH)^{+\bullet}$, 198·11318. $C_{10}H_{16}NO_3$ requires $(MH)^{+\bullet}$, 198·11300).

2-Acrylamidoethyl Methacrylate (5)

To a stirred solution of (7) (7·0 mmol, 0·8 g) and triethylamine (7·7 mmol, 1·1 ml) in chloroform (30 ml) at room temperature, was added dropwise a solution of methacryloyl chloride (7·7 mmol, 0·8 ml) in chloroform (15 ml) under an atmosphere of nitrogen. The workup and chromatography as described for (3) then afforded (5) as a clear colourless *oil* (0·78 g, 61%) (Found: C, 59·0; H, 7·2; N, 7·6. $C_9H_{13}NO_3$ requires C, 59·0; H, 7·2; N, 7·6%). ν_{max} (NaCl)/cm^{-1} 3287, 3076, 2959, 1720, 1662, 1630, 1548. ^{1}H n.m.r. δ ($CDCl_3$) 6·29, dd, J 17·0, 1·4 Hz, $RHNCOCH{=}C\mathbf{H}_aH_b$; 6·11, dd, J 17·2, 10·2 Hz, $RHNCOC\mathbf{H}{=}CH_aH_b$; 6·10, br m, $RO_2C(H_3C)C{=}C\mathbf{H}_cH_d$; 6·09, br s, NH; 5·66, dd, J 10·3, 1·3 Hz, $RHNCOCH{=}CH_a\mathbf{H}_b$; 5·60, m, $RO_2C(H_3C)C{=}CH_c\mathbf{H}_d$; 4·28, t, J 5·3 Hz, OCH_2; 3·63, q, J 5·5 Hz, $NHC\mathbf{H}_2$; 1·94, br m, CH_3. ^{13}C n.m.r. δ ($CDCl_3$) 167·3, C=O; 165·8, C=O; 135·7, $RO_2C(H_3C)\mathbf{C}{=}CH_2$; 130·6, $RHNCO\mathbf{C}H{=}CH_2$; 126·3, $RHNCOCH{=}\mathbf{C}H_2$; 126·0, $RO_2C(H_3C)C{=}\mathbf{C}H_2$; 63·1, OCH_2; 38·6, $NHCH_2$; 18·1, CH_3. *m/z* (c.i., NH_4) 184 ($(MH)^+$, 100%), 116 (20), 98 (61), 72 (22) (Found: $(MH)^{+\bullet}$, 184·09661. $C_9H_{14}NO_3$ requires $(MH)^{+\bullet}$, 184·09735).

2-Methacrylamidoethyl Acrylate (6)

To a stirred solution of (8) (10 mmol, 1·3 g) and triethylamine (11 mmol, 1·5 ml) in chloroform (40 ml), was added dropwise a solution of acryloyl chloride (11 mmol, 0·9 ml) in chloroform (20 ml) at room temperature under a nitrogen atmosphere. After the addition was complete, the reaction mixture was stirred for a further 30 h. The workup as for (3) followed by chromatography then gave the hybrid crosslinking agent (6) as a clear colourless *oil* (0·57 g, 31%) (Found: C, 59·0; H, 7·2; N, 7·5. $C_9H_{13}NO_3$ requires C, 59·0; H, 7·2; N, 7·6%). ν_{max} (NaCl)/cm^{-1} 3337, 2958, 1725, 1662, 1622, 1533. ^{1}H n.m.r. δ ($CDCl_3$) 6·42, br s, NH; 6·38, dd, J 17·4, 1·2 Hz, $RO_2CCH{=}C\mathbf{H}_aH_b$; 6·08, dd, J 17·4, 10·5 Hz, $RO_2CC\mathbf{H}{=}CH_aH_b$; 5·82, dd, J 10·4, 1·1 Hz, $RO_2CCH{=}CH_a\mathbf{H}_b$; 5·66, br m, $RHNCO(H_3C)C{=}C\mathbf{H}_cH_d$; 5·29, br m, $RHNCO(H_3C)C{=}CH_c\mathbf{H}_d$; 4·25, t, J 5·5 Hz, OCH_2; 3·58, dt, J 5·5, 5·5 Hz, $NHC\mathbf{H}_2$; 1·91, br m, CH_3. ^{13}C n.m.r. δ ($CDCl_3$) 168·5, HNC=O; 166·1, OC=O; 139·5, $RHNCO(H_3C)\mathbf{C}{=}CH_2$; 131·2, $RO_2CCH{=}\mathbf{C}H_2$; 127·7, $RO_2C\mathbf{C}H{=}CH_2$; 119·5, $RHNCO(H_3C)C{=}\mathbf{C}H_2$; 62·9, OCH_2; 38·7, $NHCH_2$; 18·4, CH_3. *m/z* (c.i., NH_4) 184 ($(MH)^+$, 100%), 112 (83), 111 (34), 98 (32), 97 (33), 96 (27), 95 (22) (Found: $(MH)^{+\bullet}$, 184·09677. $C_9H_{14}NO_3$ requires $(MH)^{+\bullet}$, 184·09735).

One-Pot Synthesis of (5)

Acryloyl chloride (38 mmol, 3·1 ml) in chloroform (38 ml) was added dropwise to a stirred solution of ethanolamine (75 mmol, 4·5 ml) in chloroform (75 ml) at 0°C and under a nitrogen atmosphere. After the addition was complete, the reaction mixture was stirred at 0°C for a further 2 h. The ethanolamine monohydrochloride precipitate was removed by filtration. The filtrate was then cooled to 0°C, and to this stirred solution was added triethylamine (38 mmol, 5·3 ml) under an atmosphere of nitrogen. A solution of methacryloyl chloride (34 mmol, 3·3 ml) in chloroform (65 ml) was then introduced dropwise. The workup as described for (3) and purification by chromatography afforded (5) as a colourless oil (2·32 g, 33%). Spectroscopic evidence for this compound was consistent with (5) prepared by the two-step method.

Similarly, this methodology was used to afford the crosslinking monomers (3), (4) and (6) in yields of 15, 23 and 26% respectively.

2-Bromoethyl Methacrylate (9)

2-Bromoethanol (3·5 ml, 50 mmol) was heated with methacrylic acid (5·1 ml, 60 mmol) in the presence of *p*-toluenesulfonic acid (0·2 g, 1·1 mmol) and benzene (13 ml). The water produced during the reaction was removed azeotropically by using a Dean–Stark trap. After completion of the reaction, the reaction mixture was washed with water (15 ml), saturated sodium carbonate (2×15 ml) and water (15 ml). The organic layer was collected, dried and evaporated under reduced pressure to yield 2-bromoethyl methacrylate (9) as a clear, pale yellow *liquid* (5·3 g, 55%) (Found: C, 37·0; H, 4·9. $C_6H_9BrO_2$ requires C, 37·3; H, 4·7). ν_{max} (NaCl)/cm^{-1} 3104, 1724, 1637. ^{1}H n.m.r. δ ($CDCl_3$, 300 MHz) 6·16, br m, $(H_3C)C{=}C\mathbf{H}_aH_b$; 5·60, br m, $(H_3C)C{=}CH_a\mathbf{H}_b$; 4·44, t, J 6·1 Hz, CH_2O; 3·54, t, J 6·1 Hz, $C\mathbf{H}_2Br$; 1·95, br m, CH_3. ^{13}C n.m.r. δ ($CDCl_3$, 75·4 MHz) 166·8, C=O; 135·8, $(H_3C)\mathbf{C}{=}CH_2$; 126·2, $(H_3C)C{=}\mathbf{C}H_2$; 63·9, CH_2O; 28·7, CH_2Br; 18·2, CH_3. *m/z* (e.i., 70 eV) 193 (M^+, 19%), 113 (39), 109 (81), 107 (84), 69 (100).

Attempted Syntheses of 2-Acrylamidoethyl Methacrylate (5) from (9)

(A) To a suspension of potassium hydroxide (1·4 g, 25 mmol) in *N,N*-dimethylformamide (15 ml) maintained at 40°C, were added acrylamide (1·4 g, 19·7 mmol), 2-bromoethyl methacrylate (9) (3·8 g, 19·7 mmol) and phenothiazine (0·05 g, 0·3 mmol). The reaction mixture was then stirred for 4 h. The solution was filtered and the solvent removed under reduced pressure (freeze dryer). To the resulting residue were added benzene (10 ml) and water (5 ml). The mixture was then stirred thoroughly at room temperature and the resulting phases were separated. The aqueous layer was then extracted with benzene (2×5 ml). The organic fractions were combined, dried and evaporated under reduced pressure to afford only ethylene glycol dimethacrylate (2) as a clear liquid (0·6 g, 32%). ^{1}H n.m.r. δ ($CDCl_3$, 300 MHz) 6·03, br m, $(H_3C)C{=}C\mathbf{H}_aH_b$; 5·50, br m, $(H_3C)C{=}CH_a\mathbf{H}_b$; 4·31, s, CH_2O; 1·85, br m, CH_3. ^{13}C n.m.r. δ ($CDCl_3$, 75·4 MHz) 166·89, C=O; 135·8, $(H_3C)\mathbf{C}{=}CH_2$; 125·8, $(H_3C)C{=}\mathbf{C}H_2$; 62·2, CH_2; 18·1, CH_3.

(B) A mixture of potassium hydroxide (0·3 g, 4·8 mmol), 2-bromoethyl methacrylate (9) (1·0 g, 5·0 mmol) and phenothiazine (0·05 g, 0·3 mmol) in *N,N*-dimethylformamide (10 ml) was maintained at 40°C for 4 h. The solution was then filtered and the solvent removed under reduced pressure (freeze dryer). The same workup as in (A) then afforded only ethylene glycol dimethacrylate (2) as a clear liquid (0·4 g, 86%). The ^{1}H and ^{13}C n.m.r. spectra obtained for the product were identical with those obtained in (A).

(C) To a suspension of potassium hydroxide (0·8 g, 14·5 mmol) in *N,N*-dimethylformamide (10 ml) maintained at 40°C, were added methacrylic acid (0·9 ml, 10·0 mmol), 2-bromoethyl methacrylate (9) (1·9 g, 10·0 mmol) and phenothiazine (0·05 g, 0·3 mmol). The reaction mixture was then stirred for 4 h. By following the workup as described in (A), the only product obtained was ethylene glycol dimethacrylate (2) as a clear liquid (1·7 g, 83%). The ^{1}H and ^{13}C n.m.r. spectra obtained for the product were identical with those obtained in (A).

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