10.1071/CH12161_AC
©CSIRO 2012 Australian Journal of Chemistry 2012, 65(7), 931-934

Supplementary Material for:

The Synthesis of PHEMA sponges *via* ARGET ARTP

Stefan M. Paterson,[a] David H. Brown,[a,b] Jeremy A. Shaw,[c] Traian V. Chirila[d,e,f,g] and Murray V. Baker[a,d,*]

[a] *Chemistry M313, School of Biomedical, Biomolecular and Chemical Sciences, The University of Western Australia, Crawley, W.A. 6009, Australia*

[b] *Nanochemistry Research Institute, Department of Chemistry, Curtin University of Technology, Kent St, Bentley, W.A. 6102, Australia*

[c] *Centre for Microscopy, Characterisation and Analysis, The University of Western Australia, Crawley, WA 6009, Australia*

[d] *Queensland Eye Institute, 41 Annerley Road, South Brisbane, Queensland 4101, Australia*

[e] *Faculty of Science and Technology, Queensland University of Technology, Brisbane, Queensland 4001, Australia*

[f] *Australian Institute for Bioengineering and Nanotechnology, University of Queensland, St Lucia, Queensland 4072, Australia*

[g] *Faculty of Health Science, University of Queensland, Herston, Queensland 4006, Australia*

Contents

1. Materials

HEMA (Bimax, Inc, USA > 99.0%), $CuBr_2$ (98%, Ajax), methanol (Ajax), diethyl ether (BDH), ascorbic acid (Ajax), tetraethyleneglycol dimethacrylate (TEGDMA, Fluka) and hydrazine monohydrate (> 99%, Fluka) were all used as received. Tris(2-pyridylmethyl)amine (TPMA)[1] and Na{Cu(H_2-Gly3)}[2] were synthesized using literatures procedures. The PEG-based initiator (MeO-PEG-Br) were synthesized using a modified literature procedure;[3] the MeO-PEG-Br initiator used in this study contained MeO-PEG-OH 550 (Simga). For polymerisation, aqueous stock solutions of hydrazine monohydrate (7.1 mg/mL, 6.9 μL/mL) and MeO-PEG-Br (233 mg/mL), and methanol stock solutions of $CuBr_2$/TPMA (4.00 mg/mL $CuBr_2$, 25.0 mg/mL TPMA) were used. For ^{1}H NMR conversion studies, hydrazine monohydrate (7.1 mg/mL, 6.9 μL/mL) and MeO-PEG-Br (233 mg/mL) were made up as solutions in D_2O.

2. Synthesis of PHEMA sponges.

HEMA was polymerised in a 80:20 H_2O:HEMA solvent system using $CuBr_2$/TPMA or Na{Cu(H_2-Gly3)} as catalyst, MeO-PEG-Br as the initiator, TEGDMA as a crosslinking agent, and hydrazine as the reducing agent. As an example, the procedure for entry 1, Table 1 is provided. A solution prepared from HEMA (100 μL, 0.82 mmol), TEGDMA (6 μL, 0.02 mmol) H_2O (360 μL), and stock solutions of MeO-PEG-Br (25 μL, 10.5 μmol) and $CuBr_2$/TPMA (2.2 μL, 42.0 nmol $CuBr_2$, 0.21 μmol TPMA) in a quartz vial (I.D. 10 mm), was capped with a septum and deoxygenated by bubbling the reaction mixture with argon for 20 minutes. Hydrazine stock solution (24 μL, 3.36 μmol) was then added and the reaction mixture was swirled to ensure thorough mixing. After polymerisation, the septum was removed and the specimen was carefully removed and placed into a vial containing water. The samples were stored in water, and the water was replaced every 24 hours for one week to remove any unreacted monomers, hydrazine and catalyst salts.

3. Monomer conversion Using ^{1}H NMR

Determination of monomer conversion by ^{1}H NMR was carried out using a Bruker Avance 500 MHz spectrometer at 25 °C with D_2O solutions. As an example, the procedure for entry 1, Table 1 is provided. A solution prepared from HEMA (100 μL, 0.82), D_2O (360 μL), and D_2O stock solutions of MeO-PEG-Br (25 μL, 10.5 μmol) and $CuBr_2$/TPMA (2.2 μL, 42.0 nmol $CuBr_2$, 0.21 μmol TPMA) along with 5 μL of DMF (acting as an internal standard) were injected into a NMR tube (I.D. 5 mm). The tube was capped with a septum and argon was bubbled through the reaction mixture for 20 minutes to deoxygenate the reaction mixture. A spectrum was recorded and the D_2O hydrazine stock solution (24 μL, 3.36 μmol) was added and thoroughly mixed by inverting the NMR tube twice. The sample was then placed back into the spectrometer and spectra were recorded every 5 minutes using 4 scans. The integrals for the vinylic protons at δ 6.15 (between the region δ 6.4-6.0) and δ 5.52 (between the region δ 5.9-5.6) were normalized to the integral for the DMF resonance at δ7.95. DMF was also used to calibrate the spectrum.

4. Characterisation of the internal morphologies using SEM

All polymer samples were cut into 300 μm thick cross-sections (Vibratome 3000) and these sections were further cut into disks using a 5 mm biopsy cutter. After sectioning, the samples were placed in a conventional freezer at -20 °C until frozen. Samples were then freeze-dried (Dynavac FD2) until a constant mass was reached. Dehydrated samples were mounted on double-sided carbon tabs and coated with a layer of carbon (approximately 30 nm thick) using a carbon evaporator (Speedivac 12E6/1178, Edwards High Vacuum LTD). The samples were then imaged using a Zeiss 1555 VF-FESEM SEM at 3 kV, using a working distance of 6 mm and an aperture of 10 μm. To acquire an image, frame integration was used to prevent charging on the surface of the polymer.

4. References

1 Tyeklar Z, Jacobson RR, Wei N, Murthy NN, Zubieta J and Karlin KD, *J. Am. Chem. Soc.* **115**: 2677-2689 (1993).

2 Manyak AR, Murphy CB and Martell AE, *Arch Biochem Biophys* **59**: 373-382 (1955).

3 Wang X-S, Lascelles SF, Jackson RA and Armes SP, *Chem. Comm.*: 1817-1818 (1999).