ABA triblock copolymers: from controlled synthesis to controlled function†

Simon J. Holder,*[a] Nicholas A. A. Rossi,[a] Chert-Tsun Yeoh,[a] Geraldine G. Durand,[a] Mark J. Boerakker[b] and Nico A. J. M. Sommerdijk[b]

[a]*Functional Materials Group, School of Physical Sciences, University of Kent, Canterbury, Kent, UK CT2 7NR. E-mail: S.J.Holder@kent.ac.uk; Fax: +44 (0)1227 827724; Tel: +44 (0)1227 823547*
[b]*Laboratory for Macromolecular and Organic Chemistry, Eindhoven University of Technology, Post Office Box 513, 5600 MB Eindhoven, The Netherlands*

The ABA amphiphilic block copolymers, poly(hydroxyethyl methacrylate-*block*-methylphenylsilane-*block*-hydroxyethyl methacrylate) (PHEMA–PMPS–PHEMA) and poly[oligo(ethylene glycol) methyl ether methacrylate-*block*-methylphenylsilane-*block*-oligo(ethylene glycol) methyl ether methacrylate] (POEGMA–PMPS–POEGMA) were successfully synthesised *via* atom transfer radical polymerisation (ATRP). Macroinitiators suitable for the ATRP of oligo(ethylene glycol) methyl ether methacrylate and 2-hydroxyethyl methacrylate were synthesised from the condensation reaction of α,ω-dihalopolymethylphenylsilane and 2′-hydroxyethyl 2-bromo-2-methylpropanoate. The copolymers were characterised using ^{1}H NMR and ^{13}C NMR spectroscopy and molecular weight characteristics were determined using size exclusion chromatography and ^{1}H NMR. The aggregation behaviour of some of the copolymers in water was studied using transmission and scanning electron microscopy and dynamic light scattering. These revealed the prevalent aggregate species to be micelles. Larger aggregates of 300–1000 nm diameter were also observed. The UV induced degradation of the aggregates was studied by UV-Vis spectroscopy. The thermal behaviour of selected copolymers was studied by differential scanning calorimetry and microphase separation of the two components was demonstrated.

1 Introduction

In the fifty years since the first syntheses of linear block copolymers were described they have proven to posses a fascinating range of properties.[1] Many of these properties have become increasingly amenable to general study over the past two decades with the increased accessibility of ever more sophisticated analytical techniques to researchers in the field.[2] The two most intriguing and most studied of these properties are self-assembly and self-organisation. The former is best exemplified by the ability of amphiphilic block copolymers to self-assemble in solutions where there is a preferential solvation of one block into well-defined aggregate structures such as vesicles,[3] micelles,[4] and micellar fibres. Whilst such colloidal aggregates share many of the behavioural characteristics of low molecular weight surfactants their behaviour is not simply an extension of that observed for these species.[5] Applications of block copolymers include their use as encapsulants for drug delivery[6] and templates for inorganic synthesis.[7]

Thin films of self-organising block copolymers undergoing microphase separation and adopting highly ordered 3-dimensional morphologies are of increasing theoretical and practical interest.[8] Their design and application offer a host of opportunities in the field of smart and nanotechnological materials, particularly in the form of thin films.[9]

It has been demonstrated, that the self-assembly and/or self-organisation of block copolymers might be used for the imposition of increased order to fine-tune the performance of conjugated polymers and facilitate the preparation of nanoscale devices for molecular electronics.[10] Polysilanes as σ-conjugated polymers are therefore ideal targets for investigating self-organising and assembling block copolymer systems. Block copolymers of polysilanes and carbon chain polymers have been synthesised by a number of methodologies, including ring-opening mechanisms,[11] the anionic polymerisation of masked-disilylenes[12] and *via* condensation reactions involving halogenated chain ends.[13] Previously, we have demonstrated the coupling of α,ω-dihaloPMPS (PMPS is polymethylphenylsilane) with polyisoprene dianions and with hydroxy terminated poly(ethylene oxide) to give multi-block copolymers.[14] The latter was subsequently demonstrated to self-assemble in different solvents to give vesicles, micellar fibres and super-helices.[15]

Over the past 10 years the advent of controlled radical polymerisation has resulted in an explosion of interest in the synthesis of block copolymer systems that were hitherto inaccessible.[16] Atom transfer radical polymerisation (ATRP) in particular has allowed for the synthesis of polymers and copolymers from most of the monomers available for standard free radical polymerisations.[17] Whilst many block copolymer syntheses have been successful using ATRP, difficulties can arise through the incompatibility of the blocks and/or monomers resulting in inhomogeneous reaction mixtures. The choice of ligand and solvent is crucial in successful block copolymer syntheses.[18] The first inorganic–organic hybrid copolymer system synthesised *via* ATRP was that of a polystyrene graft grown from bromomethylated PMPS.[19] Recently, we successfully synthesised a range of well-defined poly(methyl methacrylate)-PMPS-poly(methyl methacrylate) block copolymers using a PMPS macroinitiator to initiate ATRP.[20] Here, we describe the synthesis of PMPS amphiphilic block copolymers containing blocks of either poly(2-hydroxyethyl methacrylate) (PHEMA)[21] or poly[oligo(ethylene glycol) methyl ether methacrylate] (POEGMA)[22] *via* ATRP. The methodology follows that of the earlier study.[20] In addition,

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their aggregation behaviour in aqueous solution and the effects of UV irradiation are described. Evidence for microphase separation in the bulk state is also presented.

2 Experimental

2.1 Materials

All solvents were dried using standard procedures. Hexane was pre-dried over magnesium sulfate and calcium hydride, then distilled from calcium hydride immediately prior to use. Toluene and tetrahydrofuran (THF) were pre-dried over magnesium sulfate followed by sodium wire and then distilled from sodium wire and benzophenone immediately prior to use. Dichloromethylphenylsilane (diClMPS) (Aldrich, 98%) was distilled under vacuum and stored under nitrogen over magnesium turnings at -4 °C. 2-Hydroxyethyl methacrylate (99+%) (HEMA) was purchased from Aldrich and distilled under vacuum immediately prior to use. Oligo(ethylene glycol methyl ether) methacrylate (M_n ca. 300, Aldrich) (OEGMA), propanol (AR grade, Fischer), aluminium oxide (Acros Organics, activated, neutral), 2,2-bipyridine (Aldrich, 99%), Cu(I)Cl (Aldrich, 98+%), and Cu(I)Br (Aldrich, 98%) were used as received. N-(n-Propyl)-2-pyridyl(methanimine) and 3-morpholinyl-4-propyl-2-pyridylmethanimine were synthesised according to literature procedures.[23] 2-[(Pyridin-2-ylmethylene)amino]ethanol was synthesised following similar procedures.[24]

2.2 Apparatus

[1]H nuclear magnetic resonance (NMR) spectra were recorded at 30 °C using a JEOL GX-270 spectrometer from solutions in $CDCl_3$. For certain samples a mixture of d_6-DMSO and $CDCl_3$ was used.

Molecular weights of the polymers were estimated relative to polystyrene standards by gel permeation chromatography (GPC) using equipment supplied by Polymer Laboratories Ltd. All determinations were carried out at room temperature using a 600 mm × 5 mm mixed D Plgel column with THF as eluent at a flow rate of 1 ml min^{-1}, and a Knauer variable wavelength detector in series with a refractive index detector.

Transmission electron microscopy was carried out using a JEOL JEM (200-FX) operating at 120 kV. Scanning electron microscopy was carried out using a Cambridge Stereo scan S-200. Samples were deposited onto copper grids (200 mesh, C covered) prior to analysis.

UV degradation was carried out using a Shimadzu photo-diode array spectrophotometer Multispec-1501. Dynamic light scattering measurements were carried out on a Malvern HPPS at 25 °C.

Thermal analysis was carried out on a Perkin Elmer differential scanning calorimeter (PE DSC 7) calibrated against the melting point of indium (156.1 °C).

MWCO 12 000–14 000 Da dialysis tubing was purchased from Spectrapor.

2.3 Synthesis

Preparation of ATRP initiator end-group functionalised polymethylphenylsilane. A typical ATRP macroinitiator was prepared via the reaction of α,ω-dihaloPMPS and 2'-hydroxyethyl 2-bromo-2-methylpropanoate according to the literature procedure.[20] PMPS macroinitiators of varying molecular weights were synthesised and are described in Table 1.

^{1}H NMR (270 MHz, $CDCl_3$, ppm) δ: -1.0–0. (Si-CH$_3$), 1.8–2.0 (C(CH$_3$)$_2$Br), 3.5–4.1 (-OCH$_2$CH$_2$O-), 6.3–7.3 (Ph). ^{13}C NMR (67.8 MHz, $CDCl_3$, ppm) δ: -8 to -5. (Si-CH$_3$), 31 (C(CH$_3$)$_2$Br), 55.5 (C(CH$_3$)$_2$Br), 61 (CH$_2$O-CO), 67 (CH$_2$O-Si), 127, 135 (Ph), 171 (C=O).

Table 1 Molecular weight characteristics of PMPS macroinitiators as determined by SEC

Macroinitiator	M_n	M_w/M_n	DP$_n$[a]
PMPS 1	3 800	1.6	32
PMPS 2	7 000	1.9	58
PMPS 3	8 400	1.95	70

[a]DP$_n$ = degree of polymerisation.

Poly(hydroxyethyl methacrylate-*block*-methylphenylsilane-*block*-hydroxyethyl methacrylate). A typical synthesis is given for the growth of PHEMA blocks of 50 units on each end of a PMPS macroinitiator (PMPS3, M_n 8400, M_w/M_n 1.95).

CuCl (0.0133 g, 5.68×10^{-5} mol), 2,2'-bipyridine (0.0355 g, 2.27×10^{-4} mol) and HEMA (0.739 g, 5.68×10^{-3} mol) were added to a solution of PMPS3 (0.477 g, 5.68×10^{-5} mol) in THF (2 ml). The solution was degassed by three freeze–thaw cycles. The mixture was stirred at 65 °C using an oil bath, and progress of the reaction was monitored using SEC. After 24 hours, the reaction mixture was cooled and diluted with THF (3 ml) and filtered through alumina using THF as the eluent. The product was precipitated into a 50 : 50 v/v mixture of hexane and propanol. The product was filtered and recovered as an off white solid which was dried under vacuum at 65 °C.

$M_n = 10 300$, $M_w/M_n = 1.9$. ^{1}H NMR (270 MHz, $CDCl_3$–d$_6$-DMSO, ppm) δ: 6.2–7.2 (Si-C$_6$H$_5$), 4.6–4.8 (OCH$_2$CH$_2$OH), 3.8–4.1 (OCH$_2$CH$_2$OH), 3.1–3.55 (OCH$_2$CH$_2$OH), 1.7–1.9 (-CH$_2$C(CH$_3$)-), 0.85–1.3 (-CH$_2$C(CH$_3$)-), -1.1–0.1 (Si-CH$_3$). ^{13}C NMR (67.8 MHz, $CDCl_3$–d$_6$-DMSO, ppm) δ: 177 (C=O), 126, 134 (Si-C$_6$H$_5$), 65 (OCH$_2$CH$_2$OH), 58 (OCH$_2$CH$_2$OH), 44 (-CH$_2$C(CH$_3$)-), 22 (-CH$_2$C(CH$_3$)-), 16 (-CH$_2$C(CH$_3$)-), -8 (Si-CH$_3$).

This procedure was repeated using ligands N-(n-propyl)-2-pyridyl(methanimine), 3-morpholinyl-4-propyl-2-pyridylmethanimine, or 2-[(pyridin-2-ylmethylene)amino]ethanol, other copper halides (CuBr), and various monomer to macroinitiator ratios (Table 2)

Poly[(oligoethylene glycol methyl ether methacrylate)-*block*-methylphenylsilane-*block*-(oligoethylene glycol methyl ether methacrylate)]. A typical synthesis is given for the growth of POEGMA blocks of 30 units on each end of the PMPS macroinitiator (PMPS3, M_n 8400, M_w/M_n 1.95).

CuCl (0.0113 g, 5.68×10^{-5} mol), 2-(2-pyridylmethanimine) aminoethoxyethanol (0.0441 g, 2.27×10^{-4} mol), and OEGMA (1.02 g, 3.41×10^{-3} mol) were added to a solution of PMPS (0.477 g, 5.68×10^{-5} mol) in THF (2 ml). The reaction mixture was subjected to three freeze–thaw cycles and heated to 65 °C using an oil bath. After 24 hours, the reaction was allowed to cool and was then diluted with THF (3 ml). The

Table 2 Molecular weight characteristics of ABA block copolymers as determined by SEC using polystyrene standards

Copolymer	Init.	Monomer	M_n[e]	M_n	M_w/M_n
1	PMPS1	HEMA[a]	40	8 300	1.75
2	PMPS1	HEMA[b]	50	6 600	1.5
3	PMPS1	HEMA[c]	40	9 600	1.5
4	PMPS1	HEMA[b]	20	6 000	1.5
5	PMPS3	HEMA[b]	50	10 300	1.9
6	PMPS3	HEMA[d]	30	12 500	1.55
7	PMPS1	OEGMA[b]	30	11 100	1.85
8	PMPS1	OEGMA[b]	20	12 600	1.8
9	PMPS1	OEGMA[b]	10	10 900	1.5
10	PMPS2	OEGMA[b]	25	18 700	1.75
11	PMPS3	OEGMA[b]	30	16 900	1.6
12	PMPS3	OEGMA[d]	30	21 000	2.1

[a]CuBr–2,2'-bipyridine. [b]CuCl–2,2'-bipyridine. [c]CuCl–3-morpholinyl-4-propyl-2-pyridylmethanimine. [d]CuCl–2-[(pyridin-2-ylmethylene)amino]ethanol. [e]Molecular weights calculated from [M$_0$]/[I].

mixture was then passed through alumina using THF as the eluent and precipitated into a 50 : 50 v/v mixture of propanol and hexane. The product was isolated and dried overnight under vacuum at 60 °C.

M_n = 21 000, M_w/M_n = 2.1. ^{1}H NMR (270 MHz, CDCl$_3$–d$_6$-DMSO, ppm) δ: 6.2–7.2 (Si-C$_6$H$_5$), 4.1 (CO$_2$CH$_2$CH$_2$O-), 3.5–3.8 (-OCH$_2$CH$_2$-), 3.35 (-OCH$_3$), 1.65–2.1 (-CH$_2$C(CH$_3$)-), 0.8–1.3 (-CH$_2$C(CH$_3$)-), 0.1–1.1 (Si-CH$_3$). ^{13}C NMR (67.8 MHz, CDCl$_3$–d$_6$-DMSO, ppm) δ: 177 (C=O), 127, 134 (Si-C$_6$H$_5$), 60–72 (-OCH$_2$CH$_2$-), 54 (-OCH$_3$), 45 (-CH$_2$C(CH$_3$)-), 25 (-CH$_2$C(CH$_3$)-), 16 (-CH$_2$C(CH$_3$)-), −8 (Si-CH$_3$).

Several other reactions were carried out using similar procedures, and are given in Table 2.

2.4 Techniques

Dialysis. A sample of copolymer (20 mg) was dissolved in THF (2 ml) and water (8 ml) was added drop-wise over a one-hour period. The samples were transferred to dialysis tubing, sealed and dialysed against water for 24 hours, away from any sources of UV light.[25] The water in the beaker (3 l) surrounding the bags was replaced three times. After dialysis, the samples were transferred to vials, sealed and stored in the dark.

Transmission electron microscopy (TEM). Small drops of the dialysed aqueous solutions of the block copolymers were deposited on copper grids. Two grids were prepared for each sample. The first grid was prepared by depositing a 20 μl drop on the grid, after which the drop was removed almost immediately using filter paper. The second grid was prepared in a similar way but with the droplet allowed to remain on the grid for sixty seconds prior to removal. The grids were then wrapped in foil and left overnight to dry under vacuum in a desiccator.

Further TEM experiments led to the grids (which had been prepared and analysed previously) being stained using a yellow coloured dye—uranyl acetate dihydrate (1% w/v in water). The dye (20 μl) was dropped onto each of the grids and left for 30 seconds. Excess dye which had not been soaked up by the grids was then removed using filter paper and the grids dried overnight under vacuum in a desiccator at room temperature.

Scanning electron microscopy (SEM). The samples prepared for TEM were also used for SEM analysis.

UV degradation. Solutions were taken from the dialysed samples prepared previously and diluted in water (10% v/v in water) to correspond to an absorbance (at 334 nm) of approx. 0.8 au. UV spectra were recorded over time as the UV lamp irradiated the block copolymer samples. A time scan was run for each of the samples for 2–4 hour runs in order to show the degradation at both 270 nm and 334 nm. Two methods were used to achieve irradiation. Firstly, the copolymers were degraded using a wavelength set at either 334 nm, 270 nm or 210 nm. Secondly, using a wavelength range *via* a diode lamp, polymer degradation was also investigated. After degradation had occurred, the copolymers were analysed *via* aqueous GPC. Water from the irradiated POEGMA–PMPS–POEGMA **8** sample was removed under reduced pressure at 70 °C, THF was added and the solution was analysed with SEC using THF as the eluent.

Differential scanning calorimetry. Samples of approximately 10–20 mg were deposited in aluminium sample pans and heated at 120 °C under vacuum for 24 h prior to analysis. Thermograms were recorded at 10 °C min^{-1} for 2 heating and 1 cooling runs.

3. Results and discussion

3.1 Synthesis

PMPS macroinitiators. A range of macroinitiators were synthesised for use in the subsequent polymerisations of hydrophilic monomers, HEMA and OEGMA (Table 1). The macroinitiators were successfully characterised using ^{1}H NMR and ^{13}C NMR spectroscopy as well as IR spectroscopy in accordance with the literature.[20] NMR results showed the PMPS chains had been successfully endcapped with 2′-hydroxyethyl 2-bromo-2-methylpropanoate. Over 95% end-capping was observed in all cases.[20]

Synthesis of PHEMA–PMPS–PHEMA. A number of PHEMA–PMPS–PHEMA block copolymers (**1–6**) were synthesised using different macroinitiator to monomer ratios,
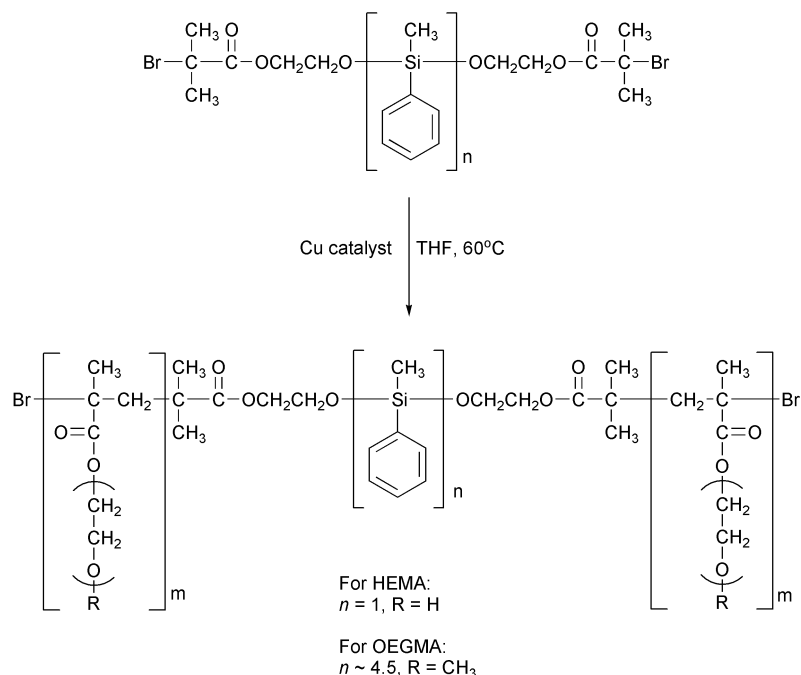
Scheme 1

copper complexes, ligands, and solvents (Scheme 1, Table 2). THF was used as a solvent in order to dissolve the PMPS macroinitiator, which was insoluble in HEMA, and consequently improve the heterogeneity of the system.

Initial syntheses utilised CuBr and bipyridine as the catalyst system and gave reasonable yields of copolymers (e.g. PHEMA–PMPS–PHEMA 1). However, in several reactions involving PMPS macroinitiators of higher molecular weight (i.e. M_n 3 800), no change in molecular weight was observed over time and the reaction mixture appeared to be heterogeneous in comparison to those involving the shorter macroinitiators. Subsequently, an ATRP system involving CuCl and 2,2′-bipyridine was used successfully. It has previously been shown that polymerisations using a CuBr and N-(n-propyl)-2-pyridyl(methanimine) (the Haddleton ligand) complex often give more controlled albeit slower reactions.[26] Unsurprisingly given the hydrophilicity of HEMA, the Haddleton ligand was not successful at dissolving the copper catalyst in the PMPS–HEMA system. The modified Haddleton ligands, 3-morpholinyl-4-propyl-2-pyridylmethanimine and 2-(2-pyridylmethanimine) aminoethoxyethanol were tried in order to aid the reaction by more fully solubilising the copper catalyst in the organic media and creating a more homogeneous reaction mixture.[27] Little difference from the CuCl–bipy catalyst system was observed however, either in control of the reaction or in monomer conversion. More systematic studies of ligand suitability for such copolymer syntheses are still underway. The ATRP of HEMA in methanol–water mixtures has previously afforded monodisperse polymers in high yields.[28] However the use of alcohols in our system was precluded by the insolubility of the macroinitiators in the alcohols.

Purification of the block copolymers proved difficult as the copper complex was not easily removed This was particularly true especially in the case of copolymers formed using ligands with hydrophilic functional groups. Repeated precipitations and runs through alumina columns were often required to fully remove the ligand and monomer. Yields of all of the copolymers were correspondingly low. Whereas NMR confirmed the absence of ligand and monomer, a green tint was observable in many of the copolymers due to the presence of copper.
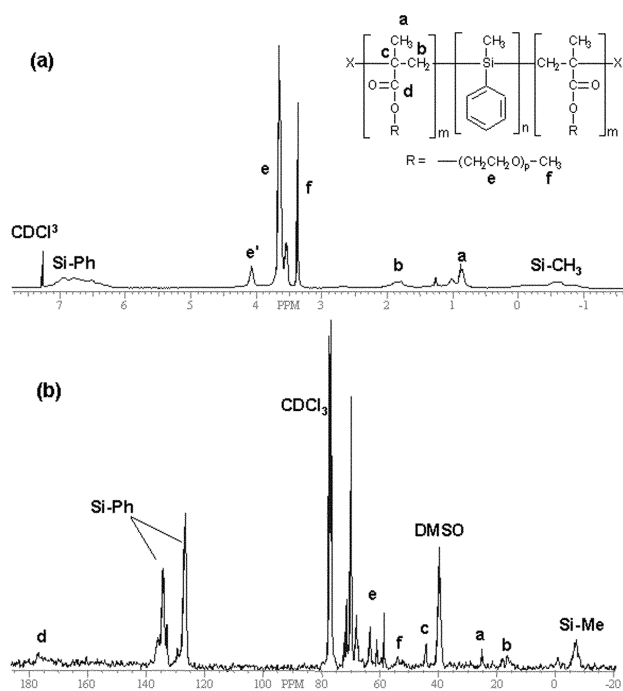

Fig. 1 SEC overlays for (a) PMPS1 and PMPS–PHEMA and (b) PMPS3 and PMPS–POEGMA.

Table 3 Comparison of molecular weight characteristics of a hydrophilic block in ABA block copolymers determined by SEC and ^{1}H NMR spectroscopy

Copolymer	M_n^a	M_w/M_n^a	DP^a	M_n^b	DP^b
2	1 400	1.3	11	950	7
3	2 900	1.4	22	3 650	28
4	1 100	1.2	8	—	—
5	950	1.7	7	650	10
6	2 050	—	16	2 250	17
7	3 650	1.95	12	4 200	14
8	4 400	1.85	15	6 900	23
9	3 550	1.4	12	—	—
10	5 850	1.7	19	7 800	26
11	4 250	1.3	14	5 400	18
12	6 300	2.3	21	8 700	29

^{a}Determined from SEC analysis; polystyrene standards in THF. ^{b}Determined from ^{1}H NMR analysis of solutions in CDCl$_3$–d_6-DMSO.

All copolymers showed a shift in molecular weight by SEC (Fig. 1a). Simultaneous GPC analysis using an RI detector as well as a UV detector (λ 334 nm) confirmed the presence of a copolymer.[19] No PHEMA homopolymer was observed. ^{1}H and ^{13}C NMR spectroscopy confirmed the structures of the PHEMA–PMPS–PHEMA copolymers. The integral data taken from the ^{1}H NMR spectra were used to determine the relative block lengths of the hydrophilic segments (based on the SEC data for the PMPS segment) (Table 3). Generally the NMR data showed that SEC underestimated the molecular weight of the PHEMA segments.

Synthesis of POEGMA–PMPS–POEGMA. A number of POEGMA–PMPS–POEGMA block copolymers (Table 2) were synthesised using an OEGMA monomer (M_n = 300) containing hydrophilic side chains of an average of 4–5 repeat units in length. In most of the reactions, CuCl and bipyridine were used. The use of an alternative ligand, 2-(2-pyridylmethanimine) aminoethoxyethanol, resulted in a more homogeneous reaction medium and yielded longer POEGMA chains. A slight green tint, due to the copper species, remained in many cases.

On each occasion, SEC analysis revealed a shift in molecular weight and a monomodal distribution (Fig. 1b). The same reaction was repeated several times, each time varying the length of the macroinitiator, the macroinitiator to monomer ratio, the copper complex (CuBr or CuCl), and the type of ligands (2,2′-bipyridine or 2-(2-pyridylmethanimine) amino-ethoxyethanol). ^{1}H and ^{13}C NMR analysis confirmed the structure of the copolymers (an example is shown in Fig. 2). ^{1}H NMR integral data was used to determine the block lengths of the POEGMA segments and were compared to the block lengths determined via SEC (Table 3).

The ^{1}H NMR data shows that the DPs of POEGMA compared to PMPS are consistently higher than the DPs via SEC. This underestimation of the molecular weights by SEC is not uncommon for graft copolymers and results from the difference between their hydrodynamic volumes and those of the polystyrene standards employed in SEC calibration.[29]

A preliminary kinetic analysis of the polymerisation of OEGMA using a PMPS macroinitiator was performed and the results are shown in Fig. 3. As can clearly be seen (Fig. 3a), the early stages of the reaction (up to 2 hours) do not show first order behaviour, however first order kinetics are subsequently obeyed. Similarly M_n does not increase linearly with time during this period ($\sim$15% conversion) (Fig. 3b). The reason for this deviation from linearity is not understood. The initiator end-group on the PMPS has been shown to be an efficient initiator for OEGMA as a monomer and as part of a macroinitiating system. The primary difference between this study and previous ones is the use of an organic solvent (THF) for this polymerisation (typically water and/or alcohols are
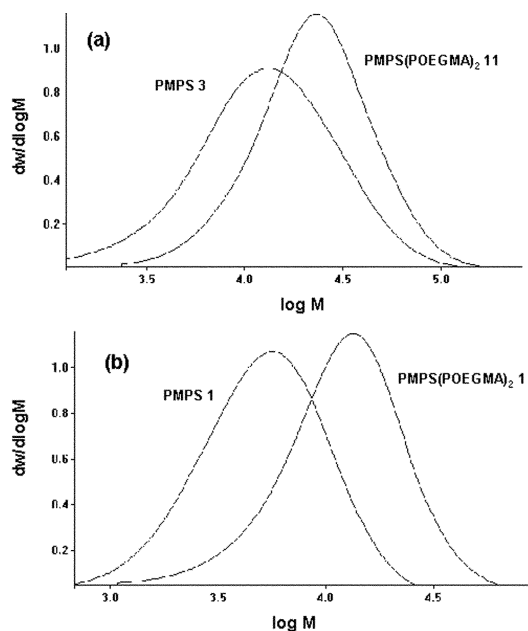
Fig. 2 (a) ^{1}H NMR and (b) ^{13}C NMR spectra for PMPS–POEGMA copolymers in CDCl$_3$ and DMSO.

employed for hydrophilic monomers). Incompatibilities in solvation may be leading to a heterogeneous system in the early stages that becomes gradually more homogeneous as the growing OEGMA chains on the PMPS makes the two polymeric blocks compatible. The lack of control in the early part of the reaction is under further investigation.

3.2 Aggregation behaviour of the block copolymers in water

In total, six copolymer samples were dialysed and were studied using TEM, SEM and dynamic light scattering. These samples were the PHEMA–PMPS–PHEMA copolymers **2** and **6** and the POEGMA–PMPS–POEGMA copolymers **7–9**, and **12**. The results are summarised in Table 4.

Electron microscopy and dynamic light scattering. A number of polysilane block copolymer amphiphiles have previously been reported. A PMPS–poly(ethylene oxide) multi-block copolymer (diameter: 100–180 nm) has been observed to form vesicles and cylindrical micelles.[15a] In some elegant work, Sakurai and co-workers[30] have also described the aggregates formed by amphiphilic poly(methyl(n-hexyl)silane) (PHMS) di-block copolymers. Micelles of 50–60 nm diameter (determined by AFM) were formed from methanol solutions of a di-block copolymer of PHMS and PHEMA. Certain of the polysilane micelles were subsequently utilised in the synthesis of hollow
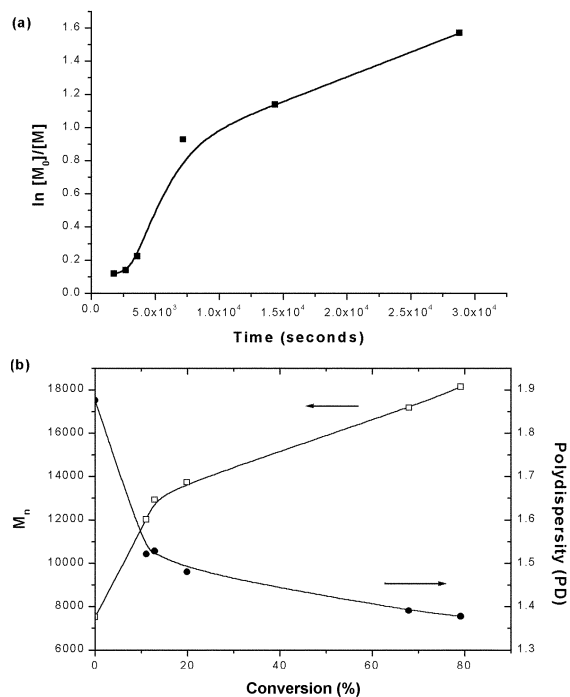

Fig. 3 (a) Monomer conversion with time and (b) number average molecular weight and polydispersity index change with conversion.

polymer nanoparticles.[31] The tri-block copolymers synthesised in this study are an extension of our previous work on polysilane amphiphiles. As ABA tri-block amphiphiles, these copolymers were expected to form micelles and it was hoped 'higher order' structures (such as cylindrical micelles and/or vesicles) would be observed.

TEM was used to study the size and types of aggregates formed by the various copolymers after dialysis, and representative micrographs are shown in Fig. 4. Three predominant aggregate structures were observed; small spherical aggregates (often existing as micelles), large spherical aggregates and sheet-like ('crystalline') layers (Table 4). Small spherical aggregates were formed for all of the samples studied with the exception of copolymer **8**. In most cases they appeared to be the majority of structures present, as measured by TEM, and dynamic light scattering (DLS) subsequently confirmed this. DLS indicated all of the small aggregate sizes fall between 15 and 30 nm. The lengths of individual, fully extended copolymer chains were calculated to be from 8–16 nm. This broad agreement between the TEM and DLS observations indicates that solvent induced self-assembly of copolymer chains occurs resulting in the formation of standard micellar structures (with

Table 4 Analysis of the dialysed copolymer aqueous solutions

Copolymer	Weight ratio[a]	TEM	Appearance[b]	Particle diameter[c]/nm
PMPS–(PHEMA)$_2$ **2**		Micelles, aggregated clusters, ~10–20 nm	—	—
PMPS–(PHEMA)$_2$ **6**		Micelles, 10–20 nm	—	—
PMPS–(POEGMA)$_2$ **8**	3.6	Large spherical aggregates Plate-like structures	Milky, opaque	540
PMPS–(POEGMA)$_2$ **9**	2.4	Micelles Sheet-like ('crystalline') structures	Transparent	15
PMPS–(POEGMA) **7**	2.2	Micelles Large spherical aggregates Some sheet-like structures	Transparent, blue tinge	16
PMPS–(POEGMA)$_2$ **12**	1.8	Micelles Some large spherical aggregates	Transparent, blue tinge	27

[a]Calculated from ^{1}H NMR analysis of copolymers in CDCl$_3$–d_6-DMSO solution. [b]Visual appearance of the dialysed solution. [c]Peak value of volume measurement.
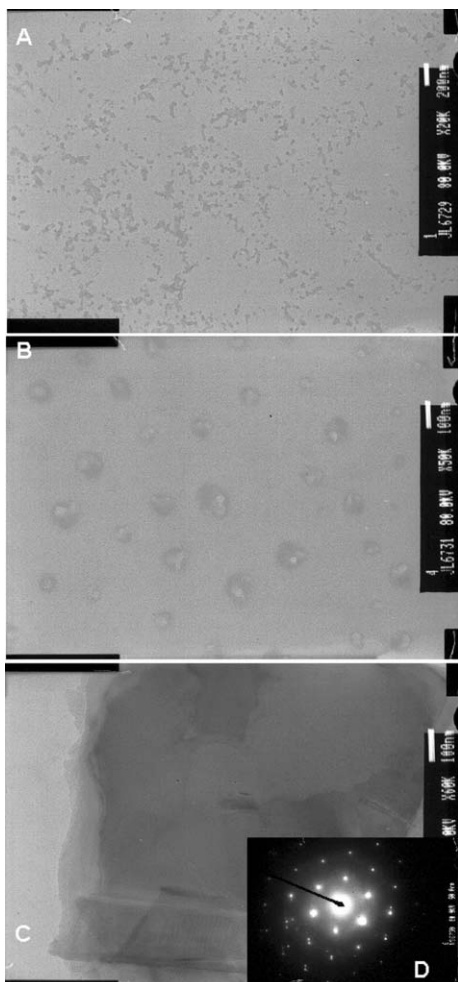
Fig. 4 TEM images of (A) copolymer **2**, micelles, (B) copolymer **8**, large spherical aggregates, (C) copolymer **9**, sheet structures with inset (D) a diffraction pattern demonstrating hexagonal packing.

the hydrophobic PMPS chains at the centre and a corona of POEGMA).

The POEGMA–PMPS–POEGMA copolymers (copolymers **7–9** and **12**) formed larger spherical aggregates in addition to micelles (Fig. 4B). The sizes of these aggregates varied from 300 nm to 1000 nm by TEM and by DLS. The internal structures of the aggregates remains unknown though the lighter areas in the centre of many of them (Figure 4B) indicates that the centres contain predominantly carbon chains or are hollow. The dark areas are expected to be Si containing regions (due to a higher electron capture cross-section of Si compared with C). Negative staining of the TEM grids was carried out to improve the visibility of aggregates but the improvement in contrast was negligible. Further work is in progress to further elucidate the structures of these large spherical aggregates.

Large sheet-like aggregates, were also observed for POEGMA–PMPS–POEGMA **9** (Fig. 4C), and electron diffraction patterns revealed a hexagonal close-packed internal structure (Fig. 4D). Although usually described as amorphous, PMPS has been shown to posses 10% crystallinity at room temperature, and to have diffraction patterns indicative of a lattice of near-hexagonal symmetry for a mesophase.[32] Hexagonal close-packed mesophases such as this are more commonly associated with dialkyl substituted polysilanes such as poly(di-*n*-hexylsilane).[33,34] The observation of these sheet-like structures with hexagonal structures strongly sug- gest a bilayer with smectic-like organisation of the PMPS chains. In many ways this is similar to recent observations of crystalline aggregates of amphiphilic polythiophenes in aqueous dispersions.[35]

SEM analysis generally agreed with the TEM data showing

the presence of micelles, large spherical aggregates and sheet-like 'crystalline' material.

Further analysis of the self-assembly of these block copolymers in aqueous solutions is necessary. They are not directly dispersible in water and the method of preparation could have a profound influence on the structures of aggregates.[36] This has been previously observed for polysilane systems and many others.[37] The molecular weight of the PMPS central block also differs substantially between some samples. A more systematic study of the effect of preparation, weight ratio and polysilane length on the resultant structures is in progress.

Photodegradation of the aggregates in water. Polysilanes are photolabile and undergo photodegradation reactions primarily *via* photoscission in the presence of UV light.[38] We have previously studied the photodegradation of a PMPS–PEO multi-block copolymer as a monolayer and the degradation products were observed to dissolve in the aqueous substrate.[39] It was expected that the degradation of the micellar solutions would result in photodegradation products (primarily oligo-silanes and siloxanes) that would dissolve into the body of the aqueous solution. Our interest in this stems from a desire to utilise films and aggregates of polysilane amphiphiles as photodegradable chemical delivery materials.

The dialysed aqueous solutions of POEGMA–PMPS–POEGMA and PHEMA–PMPS–PHEMA were irradiated using a diode UV lamp (wavelength range of 180 nm to 450 nm). The effect of irradiation on the PMPS block copolymers was followed by measuring their UV absorptions at five minute intervals over a two hour period. PMPS typically absorbs at 335–341 nm and this absorption is due to the σ–σ* transition of the Si backbone of the polymer. The wavelength of the σ–σ*$_{Si–Si}$ is dependent on the chain length[40] and thus degradation of PMPS was readily followed. An example of a copolymer degradation followed by UV-Vis spectroscopic analysis is shown in Fig. 5a. After 2 hours, the broad
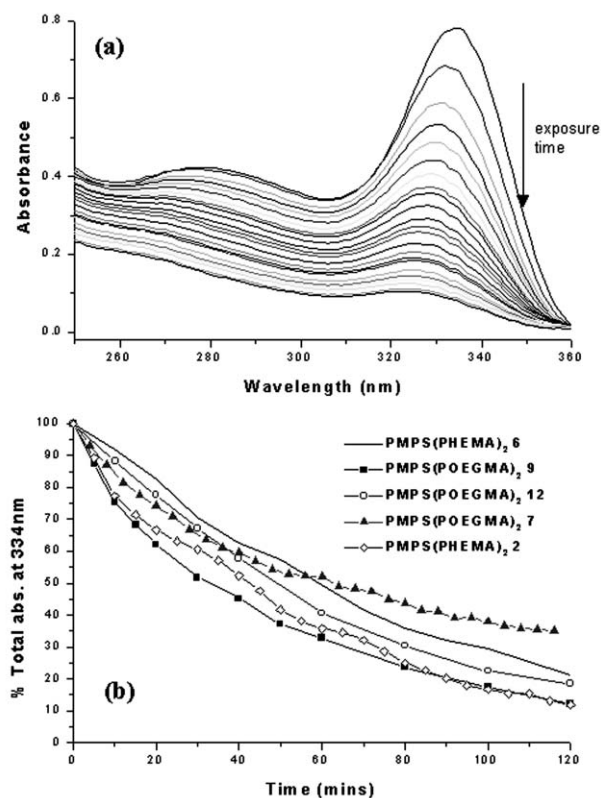

Fig. 5 Irradiation from 180–600 nm: (a) UV-Vis spectra recorded at 60 min intervals for the degradation of copolymer **5**; (b) a plot of $A/A_0 \times 100\%$ at λ_{max} *versus* irradiation time for various copolymers.

absorption with a λ_{max} of 335 nm had decreased to 20% of its initial absorbance value. The σ–π* peak at 275 nm has also disappeared as the interaction between the backbone and the phenyl ring decreased. Fig. 5b shows the plots of absorption *vs.* time for the σ–σ* peak for some of the aggregates. Very similar plots were observed for each block copolymer sample. It was expected that the type of aggregate might affect the rate of degradation, however there is no immediate evidence for this.

After the samples were degraded, the water was removed under reduced pressure and the remaining sample dissolved in THF and the samples were then analysed by SEC. The molecular weight of the copolymers had decreased considerably and the polydispersity had increased as would be expected for the proposed methods of photolytic degradation.[41]

3.3 Thermal analysis

The POEGMA–PMPS–POEGMA polymers have previously been demonstrated to display unusual properties when spin-coated onto glass surfaces with gold electrodes. Upon exposure to water these copolymer films were found to selectively desorb from the glass areas but remain attached to the gold surfaces.[42] AFM studies indicated that the block copolymer films underwent microphase separation, though the relative degree of separation was uncertain. Thermal analysis of these samples (Fig. 6) confirms a degree of microphase separation between the PMPS and POEGMA blocks exists as observed by AFM. Generally the T_gs were difficult to discern, particularly those associated with PMPS, and appeared in the majority of cases as broad changes in slope associated with changes in heat capacity. The exact temperatures in Table 5 may therefore be subject to a significant degree of error and consequently the existence and general occurrence within certain temperature ranges for the thermal events becomes the most important factor for consideration. Two apparent glass transitions were observed for the copolymers. The lower transition (T_{g1}) is associated with POEGMA (the T_g for POEGMA has previously been reported as −51 °C)[43] and appears largely constant for three of the samples though decreasing in 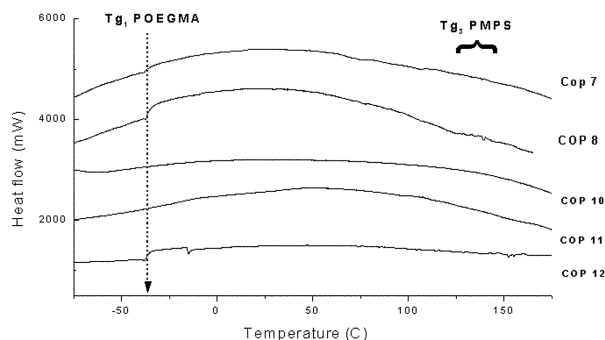size with reduced POEGMA content. The upper glass transition temperatures (T_{g3}) are most likely associated with PMPS which typically has T_gs of around 110–130 °C.[20] All samples display a broad thermal event characterised by a change in the slope between T_{g1} and T_{g3}. This is associated with an intermediate range of glass transitions associated with regions where microphase separation is incomplete and POEGMA and PMPS coexist. Given the relatively low degrees of polymerisation (particularly the POEGMA) and the relatively high polydispersities of both segments, coexistence regions with incomplete or no microphase separation are not unexpected. Whether or not this has any bearing on the thin film behaviour in terms of selective adhesion remains to be seen.

4. Summary

The ABA amphiphilic block copolymers, poly(hydroxyethyl methacrylate-*block*-methylphenylsilane-*block*-hydroxyethyl methacrylate) (PHEMA–PMPS–PHEMA) and poly[oligo(ethylene glycol) methyl ether methacrylate-*block*-methylphenylsilane-*block*-oligo(ethylene glycol) methyl ether methacrylate] (POEGMA–PMPS–POEGMA) were successfully synthesised *via* atom transfer radical polymerisation (ATRP). The copolymers were characterised using ^{1}H NMR and ^{13}C NMR spectroscopy and molecular weight characteristics were determined using size exclusion chromatography and ^{1}H NMR. The aggregation behaviour of some of the copolymers in water was studied using transmission and scanning electron microscopy and dynamic light scattering. These revealed the prevalent aggregate species to be micelles. Larger aggregates of 300–1000 nm were also observed whose structures remain to be elucidated. The UV induced degradation of the aggregates was studied by UV-Vis spectroscopy. Further work is now in progress to study the effect of preparation, weight ratio and polysilane length on the aggregate structures. Simultaneously they are being studied as both aqueous borne and solid-state photosensitive release materials.

The thermal behaviour of selected copolymers was studied by differential scanning calorimetry and a degree of microphase separation was observed. A large degree of mixing between the two block components was also evident. Current work on these thin films is concentrating on the origin of the selective adhesion and the nature of the surface structure of the POEGMA–PMPS–POEGMA copolymers, in particular, and ABA amphiphilic copolymers in general.

Fig. 6 DSC thermal traces for the second heat run (at 10 °C min⁻¹) of several block copolymers.

Table 5 Thermal analytical data from differential scanning calorimetry studies of the POEGMA–PMPS–POEGMA copolymers

Copolymer	Weight ratio[a]	T_{g1}[b]/°C	T_{g2}[c]/°C	T_{g3}[b]/°C
8	3.6	−35 (−38)	43 (55)	123 (77)
7	2.2	−39 (−39)	38 (38)	145 (145)
12	2.0	−35 (−37)	50 (50)	141 (111)
9	1.8	−31 (−29)	44 (47)	147 (107)
11	1.3	−37 (10)	65 (43)	138 (126)

[a]POEGMA : PMPS ratio from ^{1}H NMR. [b]2nd heat (1st heat). [c]Estimate of midway point for the broad transition between T_{g1} and T_{g3} (0–100 °C).

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