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Polymerization of sodium 4-styrenesulfonate via atom transfer radical polymerization in protic media

P.D. Iddon, K.L. Robinson, S.P. Armes*

Department of Chemistry, School of Life Sciences, University of Sussex, Falmer, Brighton BN1 9QJ, UK

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Abstract

The homopolymerization of sodium 4-styrenesulfonate (NaStS) in both aqueous and water/methanol solutions at 20 °C using atom transfer radical polymerization (ATRP) is described. Syntheses conducted using a sodium 4-bromomethylbenzoate initiator were poorly controlled in water but reasonably well-controlled in 1:1 water/methanol mixtures, with 3:1 water/methanol mixtures exhibiting intermediate behavior. In 1:1 water/methanol mixtures aqueous GPC analyses indicated polydispersities as low as 1.26 and conversions reached 80–90% within 18–20 h at 20 °C. Self-blocking experiments were conducted in 1:1 water/methanol mixtures, with the chain-extended NaStS polymers exhibiting unimodal GPC traces but relatively high polydispersities ($M_w/M_n = 1.61$). The use of poly(ethylene oxide)-based (PEO) macro-initiators yielded novel PEO–NaStS diblock copolymers of low polydispersity. Diblock copolymer syntheses via sequential monomer addition were less satisfactory, although one example of a polydisperse pH-responsive diblock copolymer was obtained.

Keywords: ATRP; Sodium 4-styrenesulfonate; Water-soluble polymer

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1. Introduction

Sodium 4-styrenesulfonate (NaStS) is a commercially important anionic monomer. Poly(NaStS) and NaStS-based copolymers are used in a wide range of applications, such as proton exchange membranes for fuel cell applications [1], polymeric stabilizers for emulsion polymerization [2], polymeric dispersants for inorganic materials [3], ion exchange resins [4], additives for use during oil drilling [5] and oil recovery [6], water softening [7], dye improving agents for cotton [8], and humidity sensors [9]. Biomedical applications of NaStS homopolymers include their use in multilayer polyelectrolyte membranes for controlled release of pharmaceutical compounds [10–12], treatments for abnormally high blood levels of potassium (hyperkalemia) [13], lithium poisoning [14], and viral inhibitors [15,16]. Poly(NaStS) may also be used as a polymeric dopant/steric stabilizer for conducting polymers such as polypyrrole [17,18], poly(3,4-ethylenedioxythiophene) [19] and polyaniline [20].

The synthesis of near-monodisperse poly(NaStS)-based copolymers was first achieved by chemical modification: in 1979 Varoqui et al. [21] prepared poly(2-vinylpyridine-*block*-sodium 4-styrenesulfonate) zwitterionic copolymers by selective sulfonation of a poly(2-vinylpyridine-*block*-styrene) precursor that had been previously prepared using anionic polymerization. Producing narrow molecular weight distribution samples by direct polymerization of NaStS has only been possible within the last 10 years, since this requires the use of living radical polymerization chemistry. The first example was based on nitroxide-mediated polymerization (NMP) and was reported by Keoshkerian et al. [22] These workers homopolymerized NaStS at 125 °C using a 3:1 v/v% ethylene glycol/water mixture using a potassium persulfate initiator in combination with 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO). Number-average molecular weights ranged from 7200 to 762,000, polydispersities varied from 1.12 to 1.33 and conversions were as high as 97%. Bouix et al. [2] also utilized NMP to prepare poly(NaStS-*block*-styrene) diblocks, which were subsequently employed as efficient steric stabilizers for the emulsion polymerization of styrene. Gabaston et al. [23] reported the synthesis of diblock copolymers comprising NaStS and sodium 4-vinylbenzoate

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* Corresponding author. Tel.: +44-1273-678650; fax: +44-1273-677196.

E-mail address: s.p.armes@sussex.ac.uk (S.P. Armes).

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(NaVBA) at 120 °C using NMP in 3:1 w/w% ethylene glycol/water mixtures. Well-defined TEMPO-capped poly(NaStS) macro-initiators with relatively low polydispersities were prepared first, followed by a second-stage NaVBA polymerization. However, NaVBA conversions were relatively low at around 28%. Nevertheless, these acidic diblock copolymers underwent reversible pH-induced aggregation in aqueous solution to produce NaVBA-core micelles at low pH.

Chiefari et al. [24] demonstrated the utility of reversible addition–fragmentation chain transfer polymerization (RAFT) for the synthesis of poly(NaStS) with a polydispersity of 1.13 and a number-average molecular weight of 8000. This RAFT synthesis was carried out in water at 70 °C and involved a 4,4′-azobis(4-cyanopentanoic acid) initiator in combination with 4-cyanopentanoic acid dithiobenzoate as chain transfer agent; a conversion of 73% was achieved after 4 h. Mitsukami et al. [25] also reported the RAFT synthesis of poly(NaStS) with a number-average molecular weight of 25,300 and a polydispersity of 1.25, achieving 86% conversion within 8 h under similar conditions to those described by Chiefari et al.

Atom transfer radical polymerization (ATRP) is a form of living radical polymerization developed independently by Matyjaszewski's group [26–29] and Sawamoto and co-workers [30]. Tsarevsky et al. [31] investigated the ATRP of NaStS in a 1:1 v/v% water/pyridine mixture at 30 °C and obtained a conversion of 70%, a number-average molecular weight of 10,900 and a polydispersity of 1.26. Polymerization of NaStS in pure water under the same conditions produced poly(NaStS) with a much higher polydispersity of 2.06, and a conversion of only 32% was achieved. The ATRP of NaVBA (an anionic styrenic monomer closely related to NaStS) in alkaline aqueous solution was reported by Wang et al. [32]. A final polydispersity of around 1.32 was obtained, with a conversion of 95% being achieved within 30 min at 20 °C. However, more recent work in our laboratory suggests that ATRP in aqueous media usually has less than ideal living character [33–36]. For many hydrophilic methacrylates better control is achieved by carrying out ATRP syntheses either in water/methanol mixtures or, more preferably, methanol [33–35]. Under these conditions the rate of polymerization is considerably slower, which allows more efficient halogen-capping of the propagating polymer radicals by the ATRP catalyst. Nevertheless, it is clear that for many ionic monomers such as NaStS, the presence of water is a prerequisite for solution polymerization. Herein we describe our studies of the homopolymerization and block copolymerization of NaStS via ATRP in both water and water/methanol mixtures at 20 °C, see Fig. 1. We were prompted to report our results after the recent publication of a closely related preliminary report by Choi and Kim [37].

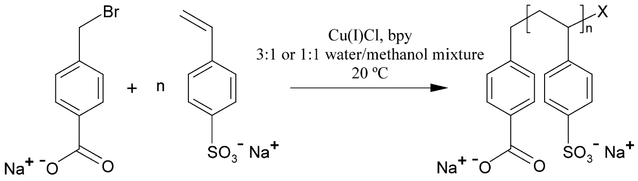

Fig. 1. Reaction scheme for the homopolymerization of NaStS using the NaBMB initiator in aqueous methanol solution at 20 °C.

2. Experimental

2.1. Materials

The following reagents were purchased from Aldrich, and used as supplied: sodium 4-styrenesulfonate (NaStS); copper(I) chloride (98%; ACS) (Cu(I)Cl); copper(I) bromide (98%) (Cu(I)Br); 2,2′-bipyridine (99%) (bpy); 4-(bromomethyl)benzoic acid (97%) (BMB); methanol (99.9%, HPLC grade). Deuterated methanol (CD_3OD), and NaOH pellets were purchased from Acros and were used as supplied. Silica gel 60 (60–200 μm particle size) was purchased from Merck and used as supplied. Three monomethoxy-capped poly(ethylene oxide)s (PEO; mean degrees of polymerization, D_p, of 22, 45 and 113) and a monomethoxy-capped oligo(ethylene oxide) (OEO; mean $D_p = 8$) were either purchased from Aldrich or donated by Cognis Performance Chemicals (Hythe, UK) and were used as supplied. Polydispersities were less than 1.10 in each case, as judged by aqueous GPC analysis using near-monodisperse PEO calibration standards. Deuterium oxide (D_2O) was purchased from Goss Scientific Instruments and was used as supplied. The water used in these experiments was initially de-ionized and then doubly distilled using a Fistream Cyclon double distillation apparatus. 4-Vinylbenzoic acid (VBA) was synthesized as described previously by Liu and Armes [38].

2.2. Initiator syntheses

An oligo(ethylene oxide)-based macro-initiator (OEO-Br) with a mean degree of polymerisation of 8 and poly(ethylene oxide)-based ATRP macro-initiators (PEO-Br) of three different chain lengths were synthesized by reacting the OEO and PEO monohydroxy precursors with excess 2-bromoisobutyryl bromide as described by Robinson and co-workers [36]. 4-(2-Hydroxyethyl)morpholine was reacted with 2-bromoisobutyryl bromide to give 2-(4-morpholino)ethyl 2-bromoisobutyrate (ME-Br), as described previously [36].

2.3. Homopolymer syntheses

The NaStS monomer was estimated to contain approximately 8–10% water by both elemental microanalyses and thermogravimetric analysis. This water content was taken into account when calculating monomer concentrations and target D_p values. Typical polymerizations were conducted at 20 °C in either a 3:1 or 1:1 v/v% water/methanol solution. The NaStS monomer (4.89 g; 21.3 mmol; target $D_p = 45$) was first dissolved in water (20.8 ml) in a round-bottomed flask. The BMB initiator (102 mg; 0.47 mmol) was added to this solution and the pH was adjusted to pH 9–10 using 1 M NaOH solution so as to just dissolve the initiator in its sodium salt form (NaBMB). This alkaline aqueous solution was then purged with nitrogen gas for 30 min. During this time, an excess of methanol was also purged with nitrogen gas. After 30 min, methanol (6.9 ml) was added to the monomer/initiator solution using a nitrogen-purged syringe. The solution was then purged for an additional 5 min. The copper catalyst (Cu(I)Cl; 47 mg; 0.47 mmol; 1 equiv.) and bpy ligand (148 mg; 0.95 mmol; 2 equiv.) were added together as solids, while maintaining a slow nitrogen purge. The reaction mixture turned dark brown and the resulting exotherm (typically 1–3 °C) was monitored using a thermocouple fixed to the bottom of the reactor flask. The reaction mixture was stirred overnight (18–48 h, depending on the solvent composition) using a magnetic stirrer.

2.4. Diblock copolymer synthesis

All diblock copolymer syntheses were carried out at 20 °C. The PEO–NaStS diblock copolymer synthesis protocol is essentially the same as that used for the NaStS homopolymer syntheses. For a typical polymerization conducted in a 3:1 v/v% water/methanol solution, the NaStS monomer (4.02 g; 17.6 mmol; target $D_p = 36$) and PEO-based macro-initiator (PEO_{45}-Br; 0.98 g; 0.49 mmol) were first dissolved in water (17.1 ml) in a round-bottomed flask. This aqueous solution was then purged with nitrogen gas for 30 min. During this time, an excess of methanol was also purged with nitrogen gas. After 30 min, methanol (5.7 ml) was added to the monomer/initiator solution using a nitrogen-purged syringe. The solution was then purged for an additional 5 min. The copper catalyst (Cu(I)Cl; 48 mg; 0.48 mmol; 1 equiv.) and bpy ligand (152 mg; 0.97 mmol; 2 equiv.) were added together as solids, while maintaining a slow nitrogen purge. The reaction mixture turned dark brown and was stirred overnight (24 h) using a magnetic stirrer.

Synthesis of the NaStS–NaVBA diblock copolymer involved following the above NaStS homopolymerization protocol in the same 3:1 water/methanol mixture. The NaStS conversion was approximately 92% after 2 h (confirmed by ^1H NMR analysis of an extracted aliquot). VBA in its sodium salt form (NaVBA) was then added via syringe as a degassed solution (with a solution composition and concentration identical to that of the NaStS). The second-stage polymerization was allowed to continue for an additional 22 h at 20 °C. ^1H NMR analysis of the final copolymer solution indicated that the total monomer conversion was more than 90%.

2.5. Homopolymer purification

The reaction solution was quenched by dilution with aerated methanol, followed by aerated water, with stirring. The reaction solution turned from brown to blue, indicating aerial oxidation of the Cu(I) to Cu(II); this solution was then passed through a silica gel column. The resulting solution was either pale yellow or colourless. The reaction products were dried using a rotary evaporator at 40 °C, and a ^1H NMR spectrum was recorded in D_2O to determine the monomer conversion. The dried reaction products were then dissolved in water and precipitated into THF (this precipitation clean-up was repeated up to three times) to remove any unreacted initiator, monomer, and ligand. The purified aqueous polymer solution was then freeze-dried, and another ^1H NMR spectrum was recorded in D_2O to assess the polymer purity.

2.6. Diblock copolymer purification

The PEO–NaStS and NaStS–NaVBA diblock copolymers were purified using the same method as for the homopolymers, although the PEO_{22}–NaStS and PEO_{45}–NaStS were purified by an additional precipitation into excess methanol just prior to freeze-drying.

2.7. Kinetic sampling

Kinetic data were obtained by removing aliquots at regular intervals. Approximately, 3 ml of the reaction solution was transferred under nitrogen by double-tipped needle into an aerated water/methanol mixture to terminate the reaction. The diluted reaction solution was then freeze-dried. ^1H NMR spectra were recorded in D_2O to determine the conversion at the time of sampling.

2.8. Characterization

^1H NMR spectra in D_2O and/or CD_3OD were obtained using a Bruker AC-P 300 MHz spectrometer. ^{13}C NMR spectra in water/D_2O were obtained using a Bruker AMX500 spectrometer operating at 125.76 MHz. As the aromatic carbon signals of interest are broad and well separated from the other ^{13}C signals, all spectra (for both homopolymers and diblock copolymers) were run without proton decoupling to avoid the nuclear Overhauser effect with a single pulse of 30° and a recycle delay of 7.5 s. Preliminary experiments using variable delay times confirmed that 7.5 s was sufficiently long to give reliable, quantitative results. Typically, between 3600 and 6400 scans were accumulated for each sample. Molecular weights were determined by aqueous gel permeation chromatography (GPC) using two Polymer Laboratories Aquagel-OH 8 μm columns (Type 40 first, followed by Type 30) in series with a Polymer Laboratories ERC-7515A refractive index detector with a mobile phase of 70% 0.2 M $NaNO_3$ and

0.1 M NaH_2PO_4 (adjusted to pH 7) and 30% methanol co-solvent at 1.0 ml min^{-1}. The GPC columns were calibrated using 10 NaStS homopolymer standards ($M_p = 1100$ to 208,000 g mol^{-1}). Thermogravimetric analyses (TGA) were performed in air at a heating rate of 20 °C min^{-1} using a Perkin–Elmer TGA-7 thermogravimetric analyzer. Dynamic light scattering (DLS) studies were performed using a Brookhaven Instruments Corp. BI-200SM goniometer equipped with a BI-9000AT digital correlator using a solid-state laser (125 mW, $\lambda = 532$ nm) at a fixed scattering angle of 90°. The intensity-average hydrodynamic diameter, $\langle D_h \rangle$, and polydispersity (μ_2/Γ^2) were calculated by cumulants analysis of the experimental correlation function.

2.9. Determination of the residual ATRP catalyst level

After silica treatment to remove the ATRP catalyst, aqueous solutions of selected, purified NaStS homopolymers were analyzed for their Cu contents using a Perkin–Elmer Plasma 400 Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES) using the following protocol. Approximately 50 mg of polymer was accurately weighed, dissolved in distilled water containing 5.0 v/v% ‘trace analysis’ grade nitric acid and made up to 5.00 ml. The unknown aqueous polymer solution was introduced into the argon plasma and the Cu emission at 327.396 nm was measured and compared to that found for stock solutions containing 0.100, 0.050 and 0.020 ppm Cu; a blank solution containing 5.0 v/v% nitric acid in distilled water was used as a fourth calibration solution. For sample solutions that exceeded 0.100 ppm Cu, a second analysis was performed using calibration solutions containing 1.000 and 0.100 ppm, together with the blank solution. The manufacturer’s estimated detection limit is around 0.0097 ppm Cu for the above emission wavelength.

3. Results and discussion

3.1. Background

As stated earlier, a preliminary account of the homopolymerization of NaStS in protic media at 20 °C has recently been reported by Choi and Kim [37]. They obtained relatively poor control in purely aqueous solution, with a polydispersity of 1.56 being reported for a target D_p of 60. However, addition of Cu(II) to this formulation led to a slower polymerization and a final polydispersity of 1.20, indicating significantly improved living character. Similar effects were reported for the addition of methanol, which also leads to a reduced rate of polymerization. However, no detailed kinetic data were presented, no chain extension experiments were performed and no new diblock copolymers were synthesized. In the present study, which was largely complete before the paper by Choi and Kim was published, we have studied the effect of adding methanol to the homopolymerization of NaStS in some detail and these reaction conditions were subsequently used to prepare several new examples of anionic diblock copolymers. Although there are many similarities, there are also several subtle differences between the work reported by Choi and Kim [37] and the present study. The Korean team used a Cu(I)Br catalyst in combination with a previously reported water-soluble oligo(ethylene oxide)-based ATRP initiator [36,39,40]. In contrast, we preferred Cu(I)Cl and a sodium 4-bromomethylbenzoate initiator, since our initial exploratory experiments suggested that these reagents gave improved control (lower polydispersities) compared to Cu(I)Br and the oligo(ethylene oxide)-based ATRP initiator (OEO-Br). This is consistent with the halogen exchange effect reported by Matyjaszewski et al. [41], in which greater control is achieved during the polymerization as the bromine end groups of the polymer chain are replaced with chlorine atoms derived from the Cu(I) catalyst. Initially, the weaker C–Br bond allows for faster initiation, whereas the stronger C–Cl bond formed during ATRP retards activation of the dormant halogen-capped polymer chains to give a more controlled polymerization.

3.2. Homopolymerizations

Data for the homopolymer syntheses are shown in Table 1. Conversion vs. time curves obtained from ^{1}H NMR studies for the homopolymerization of NaStS via ATRP at 20 °C are depicted in Fig. 2. The rates of polymerization in pure water and 3:1 water/methanol are quite similar, but the rate of polymerization in 1:1 water/methanol under the same conditions is significantly slower. The corresponding semi-logarithmic plots of monomer conversion vs. time show pronounced curvature in all three cases, see Fig. 3. According to Matyjaszewski and co-workers [42], this suggests that the polymer radical concentration does not remain constant during the polymerization, which implies less than ideal living character. The evolution of M_n with

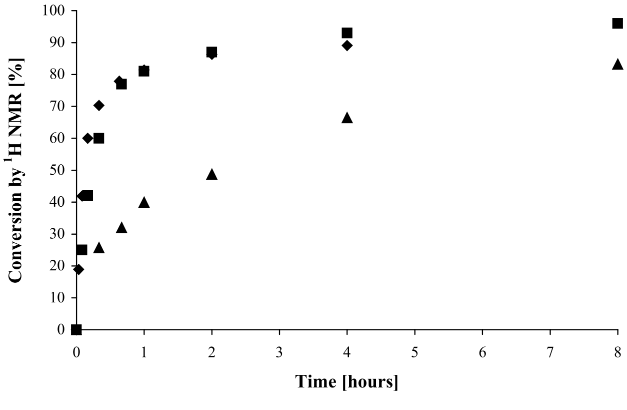

Fig. 2. Conversion versus time plots for the homopolymerization of NaStS at 20 °C using the NaBMB initiator and Cu(I)Cl catalyst, in 1:1 water/methanol (▲), 3:1 water/methanol (■), and 100% water (◆).

Table 1
Summary of molecular weight and conversion data for NaStS homopolymers prepared in either water or aqueous methanol at 20 °C using the NaBMB initiator

Sample ID	Target D_p for NaStS homopolymers	Water:methanol ratio (v/v%)	Reaction time (h)	Conversion by ^{1}H NMR (%)	Target M_n[a]	GPC data			Residual Cu (ppm)[b]
						Exp. M_n	Exp. D_p	M_w/M_n	
1	45	[c]	21	94	8900	13,700	65	2.03[d]	54
2	18	3:1	18	94	3700	5200	24	1.38	2.0
3	32	3:1	19	98	6700	9300	44	1.48	1.0
4	45	3:1	26	98	9300	12,500	60	1.63	29
5	90	3:1	19	98	18,420	23,800	114	1.66	75
6	18	1:1	18	78	3100	4000	18	1.30	0.9
7	32	1:1	18	81	5500	6900	32	1.26	10
8	45	1:1	20	80	7600	11,000	50	1.30	6.7
9	68	1:1	18	92	13,100	16,800	80	1.55	64
10	90	1:1	19	90	16,900	24,000	115	1.47	63
11[e]	54	[c]	1	45	5200	5900	26	1.36	1.2
12[f]	54	3:2	$1\frac{1}{3}$	55	6400	7500	34	1.44	1.8

The relative molar ratios of NaBMB:Cu(I)Cl:bpy were 1:1:2 for all entries (except for entries 11 and 12). All reactions were carried out at 20 °C for 18–26 h. Aqueous GPC data was calibrated using a series of near-monodisperse poly(NaStS) standards.

[a] Target M_n was calculated as follows: (Initiator M_n + (Target $D_p \times$ Monomer M_n)) $\times$ Conversion.

[b] Calculated by ICP-AES.

[c] Conducted in purely aqueous solution.

[d] This GPC peak also had a lower molecular weight shoulder.

[e] Used OEO-Br initiator and Cu(I)Br/Cu(II)Br_2 catalyst mixture, the relative molar ratios of OEO-Br:Cu(I)Br:Cu(II)Br_2:bpy was 1:0.5:0.5:2.

[f] Used OEO-Br initiator and Cu(I)Br catalyst, the relative molar ratios of OEO-Br:Cu(I)Br:bpy was 1:1:2.

conversion and M_w/M_n with conversion is shown in Fig. 4. The M_n is almost independent of conversion for the homopolymerization conducted in pure water, while the evolution of M_n with conversion for the 1:1 water/methanol synthesis is approximately linear and the 3:1 water/methanol synthesis is intermediate in behavior. The polydispersity data also allow clear differentiation between the three syntheses, see Fig. 4. In pure water the polydispersity is almost constant at around 2 throughout the polymerization, whereas for the 1:1 water/methanol synthesis the polydispersity starts high but decreases monotonically throughout the polymerization, reaching a final value of less than 1.4. The 3:1 water/methanol synthesis again exhibits intermediate behavior. Finally, typical GPC curves for the NaStS homopolymers obtained at high conversion ($>80\%$) are overlaid in Fig. 5. The molecular weight distribution curves become progressively narrower as the methanol content of the reaction mixture is systematically increased, indicating improved control. Addition of methanol reduces the solvent polarity of the reaction solution, which is expected to lead to lower rates of polymerization [33–35]. Recently Bories–Azeau and Armes have reported that non-negligible degrees of transesterification occur during ATRP syntheses of certain monomers conducted in the presence of methanol [43]. However, this unwanted side reaction is characteristic of (meth)acrylic monomers and does not occur with NaStS. Rannard and MacDonald have advocated the use of alcohol-rich iso-propanol/water mixtures for improved control in ATRP syntheses [44]. The general utility of this approach has been confirmed in our laboratory [33], but unfortunately it is not easily applicable to NaStS due to the poor solubility of this ionic monomer in such solvent mixtures. Methanol was also used as a co-solvent in our aqueous GPC analyses. The use of methanol (or acetonitrile) co-solvent is part of the standard protocol for NaStS homopolymers, since it is believed to reduce hydrophobic interactions between the polymer backbone and the column [45]. In contrast, Choi and Kim preferred a purely aqueous eluent containing 0.1 M $NaNO_3$ [37].

In all syntheses the spent ATRP catalyst was removed by passing the NaStS homopolymer reaction solution (regardless of its composition) through a silica column. According to thermogravimetric analyses this protocol did not lead to any significant silica contamination of the polymers, presumably because there was little or no affinity between the anionic polyelectrolyte and the anionic silica gel. Subsequent ICP-AES analysis indicated residual copper levels of around 1–75 ppm for the purified NaStS homopolymers and diblock copolymers.

Unfortunately the alkylbenzoate end-group derived from the initiator cannot be differentiated from the NaStS residues by ^{1}H NMR spectroscopy. Thus this technique cannot be used to estimate mean degrees of polymerization. However, ^{13}C NMR spectroscopy provides the necessary discrimination, although this technique is rather less sensitive and more difficult to quantify. Nevertheless, provided that sufficient care is taken to ensure that complete relaxation occurs between pulses, reasonably good quality spectra can be obtained for quantification purposes, albeit at the expense of long accumulation times (typically more than 24 h for 6400 scans). A typical spectrum is shown in Fig. 6. The *para* aromatic carbon due to the alkylbenzoate end-group is well separated from the equivalent *para* aromatic

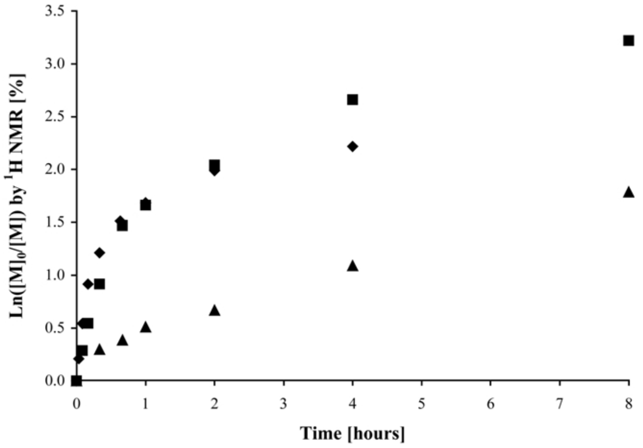

Fig. 3. Semi-logarithmic kinetic plots for the homopolymerization of NaStS at 20 °C using the NaBMB initiator and Cu(I)Cl catalyst in 1:1 water/methanol (▲), 3:1 water/methanol (■), and 100% water (◆).

carbon atom on the sodium 4-styrenesulfonate residues: direct comparison of these peak integrals allows the degree of polymerization to be estimated. Selected NaStS homopolymers were analyzed by this method and reasonably good agreement was obtained with the degrees of polymerization calculated from the GPC data. In most cases the degrees of polymerization were somewhat higher than the target degrees of polymerization calculated from the monomer/initiator molar ratios. This suggests that some initiator hydrolysis may occur prior to polymerization. Partial hydrolysis of halogen-capped chain ends may also account for the non-constant polymer radical concentration indicated by the kinetic data (see above).

The results of our so-called ‘self-blocking’ chain extension experiments are shown in Fig. 7. In these experiments a further charge of NaStS monomer dissolved in the appropriate solution was added to the reaction solution after the first-stage NaStS homopolymerization. In all three cases the chain-extended polymer gave a unimodal GPC trace, indicating little evidence of homopolymer contamination. On the other hand, the final polydispersities were above 1.5 in all cases, which suggests imperfect living character under these conditions. In summary, the ATRP of NaStS is much more controlled in water/methanol mixtures than in purely aqueous solution under the stated conditions. However, even under the best conditions reported in this study, the living character of this polymerization is not as good as that reported for other monomers [34,46], nor is it comparable to that reported by Choi and Kim [37].

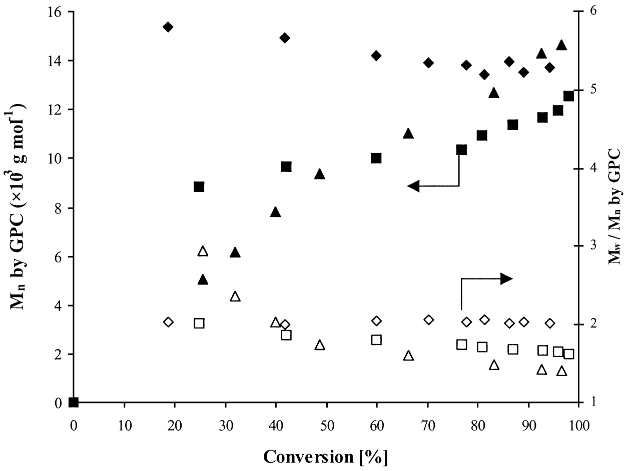

Fig. 4. Evolution of M_n with conversion for the homopolymerization of NaStS at 20 °C using the NaBMB initiator and Cu(I)Cl catalyst in 1:1 water/methanol (▲), 3:1 water/methanol (■), and 100% water (◆), and corresponding variation in M_w/M_n with conversion in 1:1 water/methanol (△), 3:1 water/methanol (□), and 100% water (◇).

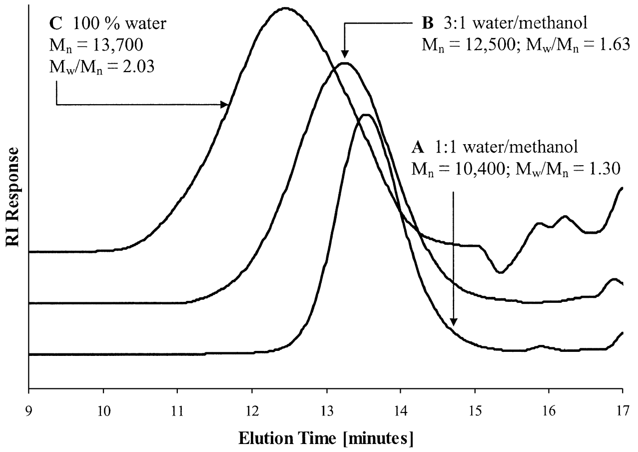

Fig. 5. Final GPC traces for NaStS homopolymers synthesized using the NaBMB initiator and Cu(I)Cl catalyst (target $D_p = 45$), in 1:1 water/-methanol (A), 3:1 water/methanol (B), and 100% water (C).

3.3. Attempted replication of previously reported syntheses

Our attempts to reproduce some of the data reported by Choi and Kim [37] using the same OEO-Br initiator, Cu(I)Br or Cu(I)Br/Cu(II)Br$_2$ catalyst system, and solvent(s) were unsuccessful (see entries 11 and 12 in Table 1). Choi and Kim did not mention the solution pH in their syntheses but we assume that this is similar to that of our own syntheses, i.e. around pH 6.5. Entry 11 in Table 1 concerns the homopolymerization of NaStS in purely aqueous solution in the presence of added Cu(II)Br$_2$ such that the relative molar ratio of NaStS:OEO-Br:Cu(I)Br:Cu(II)Br$_2$:bipy was 54:1:0.5:0.5:2 (as Choi and Kim did not report the water content of the NaStS monomer used in their experiments, we can only assume that this was not taken into account; hence we believe that our target D_p of 54 is actually equivalent to their target D_p of 60). Using the above conditions, Choi and Kim reported a conversion of 92% within 60 min., yielding an M_n of 14,500 and an M_w/M_n of 1.20, as calculated by aqueous GPC. In contrast, in our hands the conversion was only 45% after 60 min, the M_n was 5900 and the M_w/M_n was 1.36. Moreover, after 54% conversion the M_w/M_n had increased to 1.64. Entry 12 in Table 1 concerns the homopolymerization of NaStS in a 3:2 water/methanol solution using Cu(I)Br catalyst using an NaStS:OEO-Br:Cu(I)Br:bipy relative molar ratio of

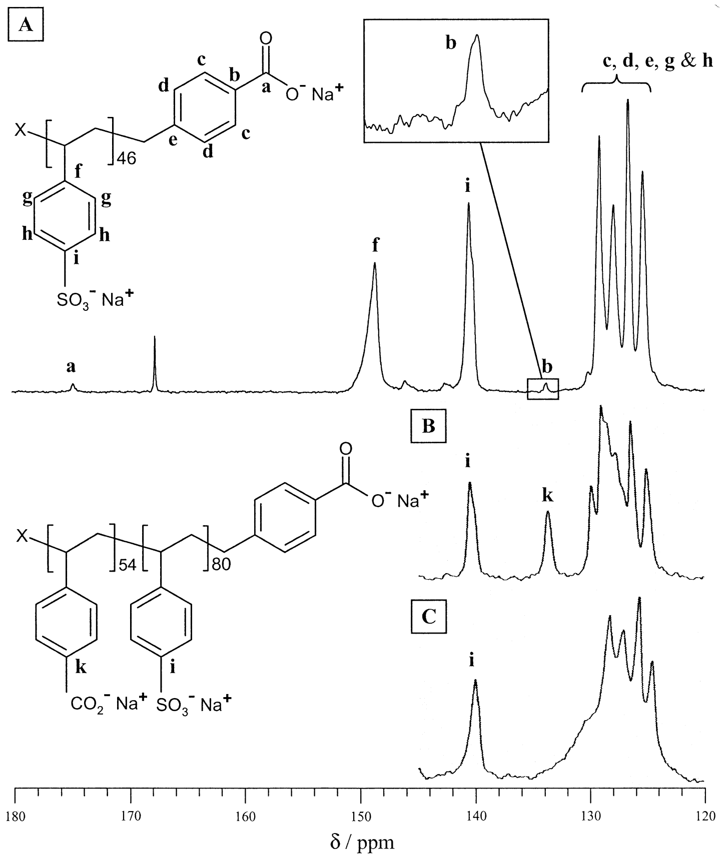

Fig. 6. ^{13}C NMR spectra (recorded in D_2O/H_2O mixtures) for: (A) an NaStS homopolymer, (B) the $NaStS_{80}–NaVBA_{54}$ diblock copolymer at pH 10 and (C) the same diblock copolymer at pH 2.

54:1:1:2. After 80 min, Choi and Kim obtained a conversion of more than 95%, an M_n of 13,800 and an M_w/M_n of 1.21. Again, markedly different results were obtained in our laboratory: a conversion of only 55% was obtained within the same time period and aqueous GPC analysis gave an M_n of 7500 and a M_w/M_n of 1.44. The reason(s) for these apparent discrepancies remain unclear, since the only discernable differences between our experimental protocols were an apparently small difference in reaction temperature (20 vs. 25 °C) and the use of different inert gases (nitrogen instead of argon) during degassing. We do not believe that these minor differences are responsible for the discrepancies between our results and those of Choi and Kim.

3.4. Block copolymerizations

PEO-based macro-initiators were used to synthesize PEO–NaStS diblock copolymers with well-defined block junctions and relatively low polydispersities. Data from these reactions are shown in Table 2. Three different macro-initiators ($D_p = 22$, 45 or 113) were used in the preparation of these diblock copolymers. Although 1:1 water/methanol mixtures gave reasonably good results for the homopolymerization of NaStS using the NaBMB initiator, this solvent composition gave very poor conversions (less than 20%) when used with the PEO-based macro-initiators. Thus all

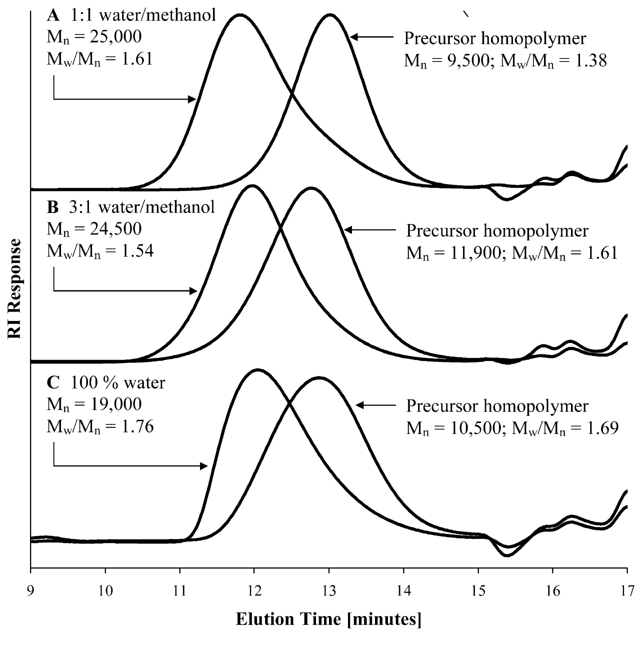

Fig. 7. GPC traces for the chain-extended NaStS homopolymers (target $D_p = 90$) and corresponding NaStS homopolymer precursors (target $D_p = 45$), synthesized using the NaBMB initiator and Cu(I)Cl catalyst in (A) 1:1 water/methanol, (B) 3:1 water/methanol, and (C) 100% water.

Table 2
Summary of molecular weight and conversion data for NaStS-based diblock copolymers prepared in 3:1 water/methanol at 20 °C

Sample ID	Target composition	Reaction time (h)		Conversion by ^{1}H NMR (%)		Target M_n[a]		Exp. M_n (GPC)		M_w/M_n (GPC)		Residual Cu (ppm)[b]
		Homo	Diblock	Homo	Diblock	Homo	Diblock	Homo	Diblock	Homo	Diblock	
1	PEO$_{22}$-*b*-NaStS$_{36}$	–	24	–	84	–	7100	1000[c]	11,100[d]	<1.1[c]	1.21[d]	3.4
2	PEO$_{45}$-*b*-NaStS$_{36}$	–	24	–	86	–	8100	2000[c]	19,100[d]	<1.1[c]	1.31[d]	55
3	PEO$_{113}$-*b*-NaStS$_{27}$	–	24	–	46	–	4900	5000[c]	12,000[d]	<1.1[c]	1.24[d]	3.0
4	NaStS$_{45}$-*b*-NaVBA$_{30}$[e]	2	24	92	90	8800	13,200	16,700[d]	23,600[d]	1.71[d]	1.66[d]	2.6

The relative molar ratios of initiator:Cu(I)Cl:bpy were 1:1:2 for all entries. All reactions carried out at 20 °C for 18–48 h.

[a] Target M_n was calculated as follows: (Initiator M_n + (Target D_p × Monomer M_n)) × Conversion.

[b] Calculated by ICP-AES.

[c] Calculated by aqueous GPC calibrated using a series of near-monodisperse PEO standards.

[d] Calculated by aqueous GPC calibrated using a series of near-monodisperse poly(NaStS) standards.

[e] Actual composition was NaStS$_{80}$-*b*-NaVBA$_{54}$ as calculated by ^{13}C NMR spectroscopy.

three PEO–NaStS diblock copolymers were synthesised using a 3:1 water/methanol solution. This led to moderate to good conversions being obtained with relatively low polydispersities of around 1.3.

These results are in contrast to initial experiments using the small molecule ME-Br initiator, which gave homopolymers with broad polydispersities and bimodal aqueous GPC traces. This initiator has an identical end-group structure to the PEO-Br and OEO-Br initiators, so its poor efficiency as an ATRP initiator for NaStS was unexpected. This observation is particularly surprising given that the ME-Br initiator has been used successfully in our laboratory to polymerize other hydrophilic monomers such as 2-hydroxyethyl methacrylate.

In collaboration with Meldrum's group we have recently described the homopolymerization of ammonium 2-sulfatoethyl methacrylate (SEM) using PEO-based macro-initiators. The resulting PEO-SEM diblock copolymers are relatively polydisperse but show considerable promise as crystal habit modifiers for the in situ precipitation of barium sulfate [36]. The PEO–NaStS diblock copolymers and NaStS homopolymers described in the present study are now also being evaluated for their effect on the morphology of barium sulfate and these results will be reported elsewhere.

The PEO$_{113}$–NaStS$_{43}$ diblock copolymer (entry 3 in Table 2) has been successfully used as a cross-linker for the preparation of shell cross-linked micelles [47]. Micelles formed by a cationic ABC triblock copolymer were *ionically* cross-linked on addition of the PEO$_{113}$–NaStS$_{43}$ diblock to form shell cross-linked micelles with surprisingly good tolerance to added electrolyte. Compared to conventional chemical cross-linking, this ionic cross-linking strategy requires only a non-toxic, non-volatile polymeric reagent and produces no small molecule by-products. It is noteworthy that a *diblock copolymer* architecture is essential in this regard; our control experiments using a NaStS homopolymer did not lead to the formation of robust shell cross-linked micelles.

The NaStS–NaVBA diblock copolymer in Table 2 has been previously reported by Gabaston and co-workers [23], who noted its interesting pH-responsive behavior in aqueous solution. This diblock copolymer was originally prepared by TEMPO-mediated polymerization in 3:1 w/w% ethylene glycol/water at elevated temperature. This protocol works very well for the NaStS monomer, but only low conversions (28%) were obtained for the second-stage polymerization of the NaVBA. In contrast, high conversions were obtained for both monomers under the ATRP conditions described in the present study. However, due to poor (macro)-initiator efficiencies, the actual block composition of NaStS$_{80}$-*b*-NaVBA$_{54}$ calculated from ^{13}C NMR spectroscopy (and supported by sulfur microanalyses) was somewhat different to the target block composition of NaStS$_{45}$-*b*-NaVBA$_{30}$.

3.5. Aqueous solution behavior of the NaStS$_{80}$–NaVBA$_{54}$ diblock copolymer

Returning to Fig. 6, two ^{13}C NMR spectra of a NaStS$_{80}$–NaVBA$_{54}$ diblock copolymer recorded at pH 10 (D$_2$O/NaOD) and pH 2 (D$_2$O/DCl) are shown. As expected, the *para* aromatic carbon signal that is assigned to both the initiator fragment and also the NaVBA residues is prominent at pH 10, since the NaVBA block is well solvated in alkaline solution. However, this signal is substantially attenuated at pH 2 since the NaVBA block is hydrophobic under these conditions and the diblock copolymer undergoes micellar self-assembly [23]. Dynamic light scattering studies conducted at pH 2 indicated an intensity-average micelle diameter of 13 nm. This pH-induced self-assembly was reversible: dissociation of the micelles occurs on raising the solution pH to above pH 7.

The surface activity of this pH-responsive diblock copolymer was also examined, see Fig. 8. Even for a relatively high copolymer concentration of 5.0 w/v% only very weak surface activity was observed at low pH, where the VBA residues are protonated and therefore hydrophobic. This disappointing result is consistent with a recent paper by

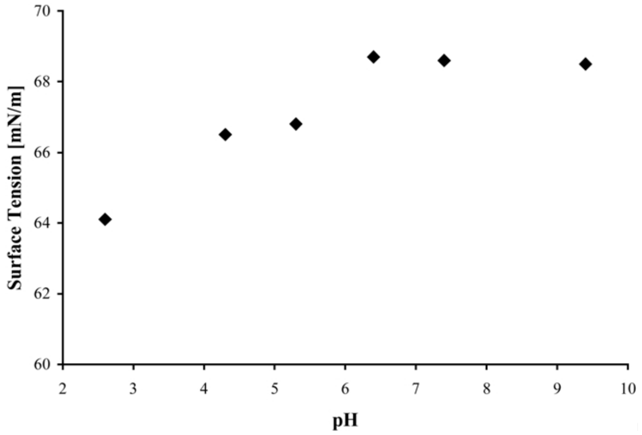

Fig. 8. Surface tension vs. pH curve for a 5.0 w/v% aqueous solution of the $NaStS_{80}-NaVBA_{54}$ diblock copolymer at 20 °C.

Matsuoka and co-workers [48], who have shown that if the solvated block is highly anionic (as is the case here for the NaStS block) then very little adsorption at the air/water interface occurs, even if micelles are formed in bulk solution.

4. Conclusions

In our hands, the homopolymerization of NaStS in purely aqueous solution at 20 °C under conventional ATRP conditions is rather poorly controlled and only high polydispersity polymers are produced. Slower polymerizations and improved living character are obtained in water/methanol mixtures, as reported for a number of other vinyl monomers. The use of poly(ethylene oxide)-based macro-initiators allow reasonably well-defined diblock copolymers to be prepared and interesting applications for these copolymers have been identified and continue to be explored. In contrast, chain extension experiments indicate that diblock copolymers prepared via sequential monomer addition have relatively high polydispersities, although one example of a weakly surface-active pH-responsive diblock copolymer was obtained.

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