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Use of oxyanion-initiated polymerization for the synthesis of amine methacrylate-based homopolymers and block copolymers

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Abstract

A series of amine methacrylate homopolymers, diblock copolymers and triblock copolymers has been synthesized using oxyanion-initiated polymerization. The amine methacrylate monomers of interest were 2-(dimethylamino)ethyl methacrylate (DMA), 2-(diethylamino)ethyl methacrylate (DEA), 2-(*N*-morpholino)ethyl methacrylate (MEMA) and *t*-(butylamino)ethyl methacrylate (BAE). In most experiments potassium benzyl alcoholate was utilized as an initiator since this facilitated both UV GPC studies and end group analysis using ^{1}H NMR spectroscopy. For the homopolymerization of DMA, molecular weights increased linearly with conversion and polydispersities were reasonably narrow. Together with successful block copolymer formation, this constitutes good evidence for the “living” character of oxyanion-initiated polymerization. Most of the diblocks are novel copolymers and selected copolymers undergo reversible temperature-induced micellization in aqueous media. NMR studies confirmed that the DMA residues of a DMA–BAE diblock copolymer could be selectively quaternized using a stoichiometric amount of methyl iodide under mild conditions. Finally, shell cross-linked micelles could be prepared from ABC triblock copolymers. The C block formed the core, the B block contained cross-linkable residues and the A block acted as a steric stabilizer and prevented inter-micelle aggregation even when the cross-linking chemistry was carried out at high copolymer concentrations. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Oxyanion-initiated polymerization; Amine methacrylates; Shell cross-linked micelles

1. Introduction

In 1997, Nagasaki and co-workers reported [1] the homopolymerization of 2-(diethylamino)ethyl methacrylate (DEA) using potassium ethoxide in THF at or above ambient temperature. Such oxyanionic initiators do not normally polymerize methacrylate monomers: the Japanese group attributed their unexpected success to complexation of the potassium counter-ion with the nitrogen heteroatom of the DEA. However, this explanation remains speculative; the precise mechanism for this polymerization has not yet been established. It was also shown that a potassium 4-vinylbenzyl alcoholate initiator led to formation of well-defined, styrene-capped DEA macromonomers $M_w/M_n < 1.30$). Recently we extended [2] these macromonomer syntheses to include other tertiary amine methacrylates, via 2-(dimethylamino)ethyl methacrylate (DMA), 2-(*N*-morpholino)ethyl methacrylate (MEMA) and 2-(di-*iso*-propylamino)ethyl methacrylate (DPA). It was shown that these macromonomers can act as reactive polymeric stabilizers for polystyrene latex syntheses under both aqueous emulsion and alcoholic dispersion polymerization conditions. In a separate study, a poly(ethylene oxide)-based macro-initiator (PEO) was used to polymerize either DMA or DEA and hence obtain novel water-soluble poly (ethylene oxide-*block*-tertiary amine methacrylates) [3]. These hydrophilic–hydrophilic diblock copolymers undergo reversible self-assembly in aqueous solution to form micelles, with the tertiary amine block forming the micelle core. ^{1}H NMR studies indicated that pH-induced micellization of the PEO–DEA diblock led to micelles with dehydrated cores, whereas temperature-induced micellization of the PEO–DMA diblock led to micelles with relatively hydrated cores.

In the present work we further assess the scope and limitation of the oxyanion-initiated polymerization of amine methacrylates. In particular the livingness of this chemistry was examined by synthesizing diblock copolymers

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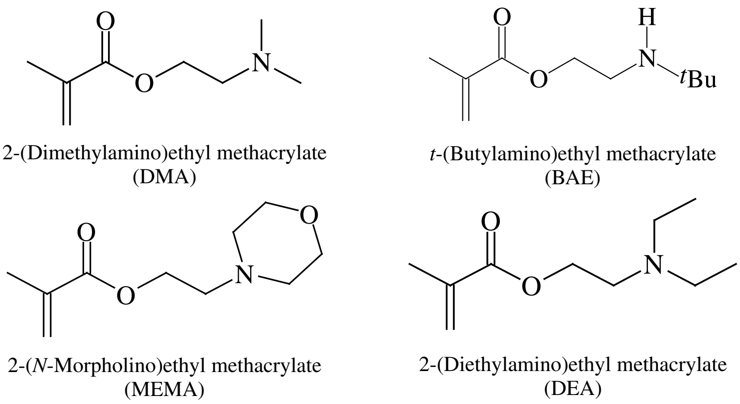

Fig. 1. Chemical structures of the four amine methacrylate monomers examined in this study.

and triblock copolymers by sequential monomer addition. Three tertiary amine methacrylates (DMA, DEA and MEMA) and a secondary amine methacrylate [*t*-(butylamino)ethylmethacrylate (BAE)] were used in this study, see Fig. 1. The resulting diblock and triblock copolymers were characterized in terms of their micellization behaviour in aqueous solution. Finally, the aqueous solution properties of selected copolymers were assessed using surface tensiometry and dynamic light scattering.

2. Experimental

2.1. Materials

THF was dried with sodium wire for three days and subsequently refluxed in the presence of potassium. It was distilled under nitrogen just prior to use. Common solvents and reagents were purchased from Aldrich and used as received. All monomers were passed through basic alumina columns, stirred over calcium hydride for 24 h, stored at −9°C, and distilled immediately prior to use. All polymerizations were carried out under dry nitrogen. All glassware was heated overnight at 200°C before use. Assembled glassware was then heated under vacuum to eliminate the surface moisture. Liquid reagents were handled using standard schlenk techniques.

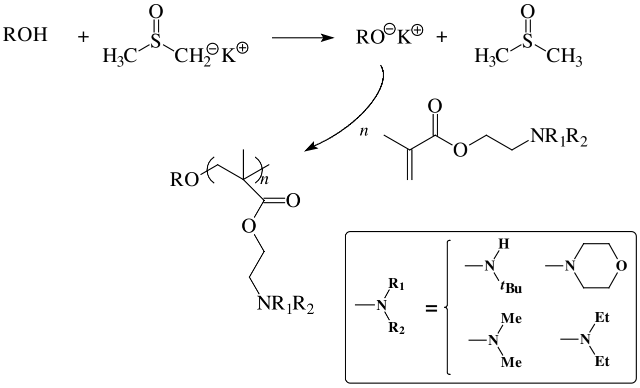

Fig. 2. Reaction scheme for the synthesis of amine methacrylate polymers via oxyanion-initiated polymerization.

2.2. Homopolymer and block copolymer synthesis

A suspension of potassium hydride (1–2 g) in mineral oil at 35% was introduced in a dry pre-weighed 100 ml schlenk tube. The mineral oil was removed by three extractions with *n*-pentane added via a cannula. Solvent was removed from the potassium hydride under vacuum. The resulting white solid was suspended in THF. The suspension was cooled to 0°C using an ice bath before addition of DMSO (2 molar excess). Hydrogen gas was evolved and the stirred suspension was allowed to warm up to room temperature. Stirring was continued until all the potassium hydride had reacted, leading to the formation of an homogeneous phase. The prepared solution was titrated against 2-naphthol in THF under an inert atmosphere, using triphenylmethane (~5 mg) as indicator. The end-point of the titration was easily observed by a bright red colour due to triphenylmethyl carbanion. This $DMSO^-K^+$ solution was then used to generate the potassium alcoholate initiator.

In a typical polymerization, as shown in Fig. 2, either benzyl alcohol or the poly(ethylene oxide)-based macroinitiator (synthesized as described previously [4]) was dissolved in dry THF or toluene (0.01 M) along with triphenylmethane indicator. The THF solution of $DMSO^-K^+$ was added until the reaction mixture turned slightly pink due to the formation of triphenylmethyl carbanion. More $DMSO^-K^+$ solution was added until the characteristic pink colour was evident for at least 30 min to ensure complete alcoholate formation. Freshly distilled monomer was added to the initiator solution at the desired polymerization temperature. The reaction was stirred for 2 h before quenching with degassed methanol. For the synthesis of diblock and triblock copolymers, an aliquot of this reaction mixture was taken immediately prior to the addition of the second monomer. This aliquot was analysed by GPC and ^1H NMR in order to obtain the degree of polymerization of the first block. This process was repeated when addition of a

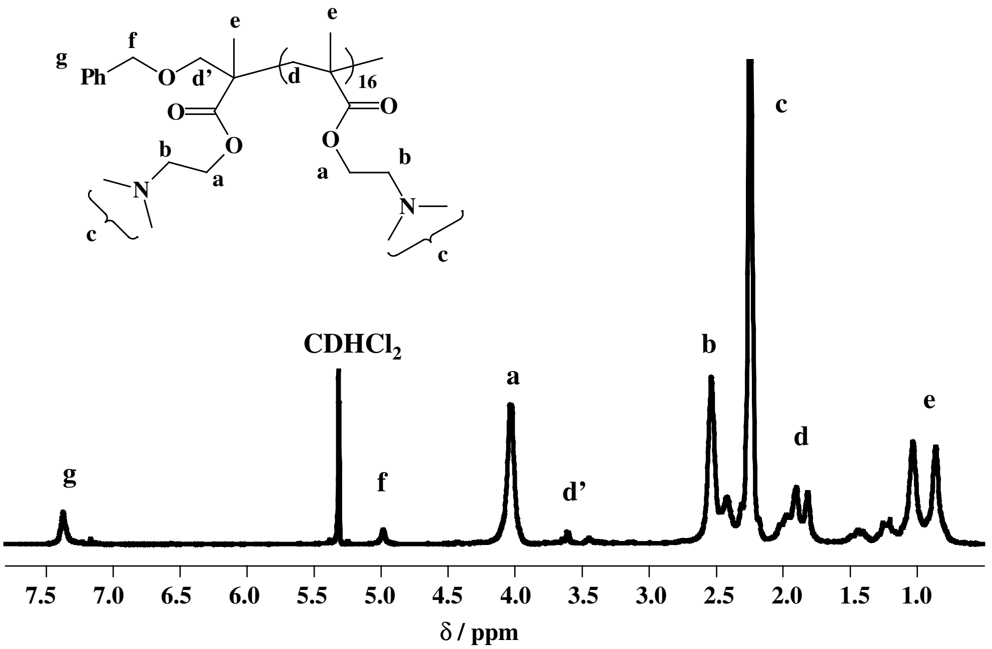

Fig. 3. ^1H NMR spectrum of a BzO–DMA homopolymer. Note the initiator signals at δ 7.40 and at δ 5.00 which were used to determine the number-average degree of polymerization.

third monomer was necessary. In cases where a second or third monomer was used, the polymerization was allowed to proceed for a further 2 and 4 h, respectively.

The reaction mixture was filtered and the solvents were evaporated to leave a yellow residue. Purification was achieved by dissolving the (co)polymers in dilute acid and extracting with *n*-hexane to remove the indicator. The (co)polymers were recovered from the aqueous solution by neutralizing the solution with KOH and subsequently “salting out” with NaCl. The purified (co)polymers were dissolved in CH_2Cl_2, dried with $MgSO_4$ and the solvent removed under vacuum. The overall yields were in excess of 90%.

2.3. Characterization

Copolymers were characterized by GPC and ^1H NMR spectroscopy. The GPC set-up comprised a Polymer Laboratories PL gel 3 μm Mixed ‘E’ column with THF eluent at a flow rate of 1 ml/min. A Knauer UV detector ($\lambda = 254$ nm) was used in series with a Knauer refractive index detector. A series of near-monodisperse PMMA homopolymers were used as calibration standards. ^1H NMR spectra were recorded using a 300 MHz Bruker AC-P spectrometer. Copolymers were dissolved at approximately 6 wt% in either $CDCl_3$, D_2O, DCl/D_2O or $NaOD/D_2O$.

Dynamic light scattering measurements were carried out using a Malvern PCS 4700 instrument equipped with a 80 mV argon laser operating at 632.8 nm and a 7032 Multi-8 correlator. All measurements were carried out using 1.0 %w/v solutions and the scattered light was detected at 90° to the incident beam. The data were fitted using both monomodal cumulants analysis and the NNLS algorithm. TEM studies were carried out using a Hitachi 7100 instrument operating at 75 kV.

3. Results and discussion

3.1. Homopolymerizations

In our preliminary experiments the potassium benzyl alcoholate initiator generally gave narrower polydispersities than either potassium *t*-butoxide or potassium ethoxide under the same conditions. Thus potassium benzyl alcoholate was selected as a model initiator in this study. If the (co)polymer molecular weight is not too high, this initiator has the added advantage that its aromatic protons are a very useful label for determining reliable M_n’s by end-group analysis using NMR spectroscopy. In addition, the aromatic group is a strong UV chromophore, which allows further information to be gained from dual detector (UV and refractive index) GPC analysis. In an earlier study, Lascelles et al. found that DMA macromonomers prepared by oxyanion-initiated polymerization were contaminated with significant quantities of the potassium 4-vinylbenzyl alcoholate initiator [2]. This problem, which was associated with the in situ preparation of the initiator, was clearly identified by GPC analysis, since two peaks were observed in the UV chromatogram. The major high molecular weight peak was due to the UV chromophore-labelled polymer and the minor peak

Table 1
Molecular weight data for the various amine methacrylate homopolymers synthesized using the potassium benzyl alcoholate initiator

Polymer ID	Composition	Temp. (°C)	Theoretical		NMR		GPC M_w/M_n
			M_n (g mol^{-1})	D_p	M_n (g mol^{-1})	D_p	
KV12	BzO–(BAE)	22.0	3800	20	3600	19	1.24
KV13	BzO–(BAE)	50.0	3800	20	4200	22	1.15
KV14	BzO–(MEMA)	50.0	4500	22	5900	29	1.27
KV15	BzO–(MEMA)	25.0	4500	22	4500	22	1.25
KV16	BzO–(DMA)	26.2	4000	25	4500	28	1.29
KV17	BzO–(DMA)	50.0	4000	25	2900	18	1.23
KV102	BzO–(DMA)	25.0	10,500	66	9500	60	1.14

at low molecular weight was due to residual inactive initiator. Although this initiator impurity could be removed from the macromonomers by selective precipitation, incomplete initiation meant that the experimental polymer molecular weights were always higher than the target molecular weights calculated from monomer/initiator ratios. In contrast, in the present work only a single high molecular weight peak was observed in the UV chromatogram of the reaction solution, indicating a very high initiator efficiency. Fig. 3 depicts a typical ^{1}H NMR spectrum (CD_2Cl_2) of a BzO–DMA homopolymer. The aromatic and benzyl protons of the benzyl alcohol initiator fragment are clearly visible at δ 7.40 and δ 5.00, respectively. In addition, an extra $-OCH_2$ peak at δ 3.60 due to the first DMA unit in the polymer chain is also observed. Comparing the aromatic peak integral to that due to the dimethylamino proton signal at δ 2.35 enables the degree of polymerization of the DMA chain to be calculated. If this polymer solution is deliberately contaminated with benzyl alcohol, *additional* aromatic and benzyl signals appear in the NMR spectrum at δ 7.45 and 4.60, respectively. Thus NMR can distinguish between benzyl alcohol and the benzyl initiator fragment on the DMA polymer chain. In summary, residual benzyl alcohol initiator cannot be detected in these (co)polymers by either UV GPC or NMR spectroscopy.

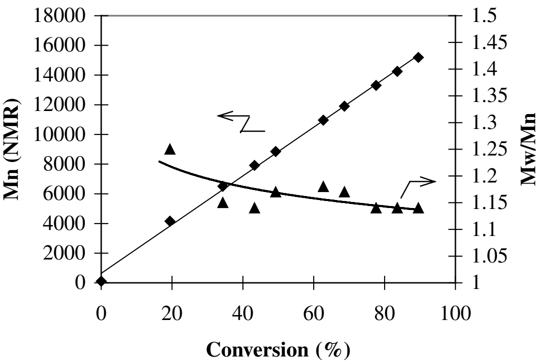

Fig. 4. M_n conversion and polydispersity vs conversion data for the oxyanionic polymerization of DMA monomer initiated by potassium benzyl alcoholate in THF at room temperature. ((DMA)$_0$ = 0.7 mol dm^{-3}; (Initiator)$_0$ = 0.01 mol dm^{-3}]. The solid line for the M_n vs conversion data is calculated from the monomer/initiator molar ratio. The solid line for the polydispersity data is guide for the eye and has no theoretical basis.

In general, much better molecular weight control was achieved than that reported by Lascelles et al. (see Table 1). These improvements bear testimony to the success of the DMSO carbanion titration method. GPC analyses also confirmed little or no residual monomer, which is consistent with the high polymer yields obtained. Homopolymer polydispersities ranged from 1.14 to 1.29, indicating reasonably narrow molecular weight distributions.

It is generally accepted that the most important characteristics of a ‘living’ polymerization are: (1) the linear evolution of molecular weight with conversion; and (2) block copolymer formation. In addition, provided that the rate of initiation is fast relative to the rate of propagation, narrow polydispersities should be obtained. The oxyanion-initiated homopolymerization of DMA at ambient temperature was studied in detail in order to examine the ‘livingness’ of this chemistry. The reaction solution was sampled periodically and the aliquots were analysed both gravimetrically and by NMR spectroscopy in order to obtain conversion and molecular weight data. The results are depicted in Fig. 4. The number-average molecular weight increases linearly with conversion and the polydispersity remains low throughout the polymerization. Furthermore, diblock and triblock copolymers can be readily obtained (see below), thus this oxyanionic polymerization chemistry appears to have reasonable ‘living’ character. In addition, a semi-logarithm plot of monomer concentration vs time (not shown) was linear over the conversion range studied, indicating first-order kinetics with respect to DMA monomer. A kinetic study of the oxyanion-initiated polymerization of MEMA was also carried out under the same conditions. In this case polymerization was much more rapid, with over 90% conversion being obtained within 3 min at 25°C. This difference is perhaps surprising: since the tertiary amine group in MEMA is significantly less basic than that in DMA, [5] weaker co-ordination to the potassium counter-ion and hence slower polymerization might have been expected. [1]

It is worth comparing oxyanion-initiated polymerization with so-called group transfer polymerization (GTP). GTP was developed by workers at Du Pont in the early 1980s [6] and is an excellent method for preparing methacrylate

Table 2
Molecular weight data for the amine methacrylate diblock copolymers prepared by oxyanion-initiated polymerization using sequential monomer addition. For copolymer entries, the D_p and M_n values are for the overall diblock copolymer

Polymer ID	Composition	Theoretical		NMR		GPC
		M_n (g mol^{-1})	D_p	M_n (g mol^{-1})	D_p	M_w/M_n
KV34	BzO–(BAE)	4900	26	4400	23	1.32
	BzO–(BAE)–(MEMA)	10,300	53	10,100	52	1.35
KV75	BzO–(BAE)	6600	35	6000	32	1.21
	BzO–(BAE)–(DMA)	16,800	100	16,100	96	1.30
KV106[a]	BzO–(BAE)	9400	50	9400	50	–
	BzO–(BAE)–(DMA)	15800	91	12,800	72	1.10
KV76	BzO–(MEMA)	8100	40	8900	44	1.19
	BzO–(MEMA)–(BAE)	19,200	100	20,300	106	1.32
KV107[a]	BzO–(BAE)	11,200	60	11,000	59	–
	BzO–(BAE)–(MEMA)	17,200	90	18,000	94	1.17
KV77	BzO –(DEA)	9400	50	9600	51	1.38
	BzO –(DEA)–(DMA)	17,200	100	18,400	107	1.45
KV108[a]	BzO –(DEA)	9400	50	8300	44	–
	BzO –(DEA)–(DMA)	15,800	91	15,200	88	1.22

[a] All polymerizations were carried out at 25°C except for these, which were carried out at 50°C.

polymers with controlled architectures and low polydispersities (typical M_w/M_n's range from 1.05 to 1.15) in THF at room temperature. However, one drawback of GTP is the relatively high cost of the silyl ketene acetal initiator. Oxyanion-initiated polymerization also works well at ambient temperature in THF and, unlike GTP, requires no nucleophilic catalyst, but this approach appears to be restricted to a rather small subset of heteroatom-containing methacrylate monomers [1]. Potassium alcoholates are cheaper initiators than silyl ketene acetals but polydispersities tend to be somewhat broader with oxyanion-initiated polymerization, typically around 1.20 to 1.35. Remarkably, syntheses at 50°C often produce polymers with narrower molecular weight distributions than those conducted at 20°C, [1,2] which suggests that the initiation is relatively slow for oxyanion-initiated polymerizations at ambient temperature. It is noteworthy that there is some evidence for narrower polydispersities at higher temperatures in Tables 1 and 2.

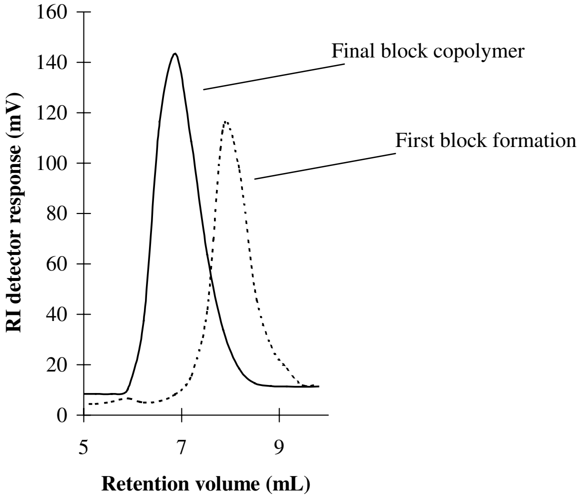

Fig. 5. Typical GPC traces for a BzO–DMA homopolymer and the final BzO–DMA–BAE (BAE = 90 mol%) diblock copolymer indicating little or no evidence of homopolymer contamination.

Recently Creutz et al. described [7] the homopolymerization of a secondary amine methacrylate, *t*-(butylamino)ethyl methacrylate (BAE), using a diphenylmethylithium initiator at −78°C in THF. GPC analyses indicated polydispersities of around 1.25. In the presence of added LiCl, polydispersities as low as 1.10 were obtained under the same conditions. Usually such classical anionic polymerization conditions are intolerant of monomer functionality; the authors attributed their success to the reduced basicity of the growing methacrylic chain-ends and the sterically hindered nature of the secondary amine groups. In the present work we examined the (co)polymerization of BAE using the potassium benzyl alcoholate initiator. As anticipated, good control over molecular weight and reasonably low polydispersities were achieved for the homopolymerization of BAE at *ambient* temperature (see Table 1). Furthermore, block copolymerization of BAE with various tertiary amine methacrylates resulted in the formation of well-defined diblock and triblock copolymers (see below). These observations suggest that the oxyanion-initiated polymerization of BAE has reasonably good living character.

3.2. Block copolymerizations

A series of novel diblock copolymers were prepared by sequential monomer addition using a potassium benzyl alcoholate initiator (see Table 2). In general, slightly higher polydispersities were obtained for the final diblocks, but molecular weight control for both blocks was excellent. Conversions of monomer to polymer were generally very high. As expected for methacrylate monomers, blocking efficiencies were not affected by the order of monomer addition (compare entries KV76 and KV107). GPC analyses of the homopolymer precursors and the final diblock copolymers indicated efficient chain extension, with little or no evidence of homopolymer contamination (see Fig. 5; overlay of two representative GPC traces). With the exception of the DEA–DMA diblock copolymers, which have been previously synthesized by GTP [5,8,9], all these diblock copolymers are novel materials. Fig. 6 depicts the assigned ^{1}H NMR spectra ($CDCl_3$) for a BzO–DEA–DMA and a BzO–BAE–MEMA diblock copolymer, respectively.

We have previously reported [8,9] that DEA–DMA diblock copolymers can act as polymeric surfactants whose properties depend markedly on the solution pH. Thus at low pH these copolymers are molecularly dissolved as cationic polyelectrolytes due to extensive protonation of both types of tertiary amine residues and they exhibit very low surface activity. However, at around neutral pH the DEA block becomes hydrophobic while the DMA block remains hydrophilic and surface activity increases markedly [8]. In addition, well-defined micelles are formed in aqueous solution [9], with the DEA blocks forming the dehydrated micelle cores. In the course of the present work we have found that similar reversible micellization can be induced simply by varying the solution temperature. Two NMR spectra of a BzO–DEA–DMA diblock copolymer (KV 77) dissolved in D_2O at pH 8 are depicted in Fig. 7. The lower spectrum was recorded at 5°C and the correct block composition can be calculated by comparing the peak integral of the dimethylamino protons of the DMA residues at δ 2.4 with that due to the oxymethylene protons due to both

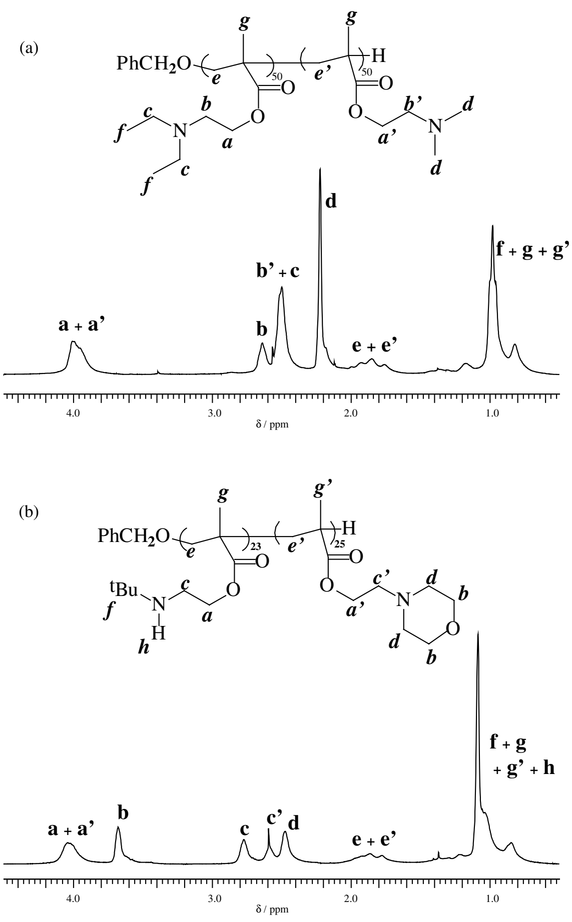

Fig. 6. ^{1}H NMR spectra and signal assignments for: (a) a BzO–DEA–DMA diblock copolymer; and (b) a BzO–BAE–MEMA diblock copolymer.

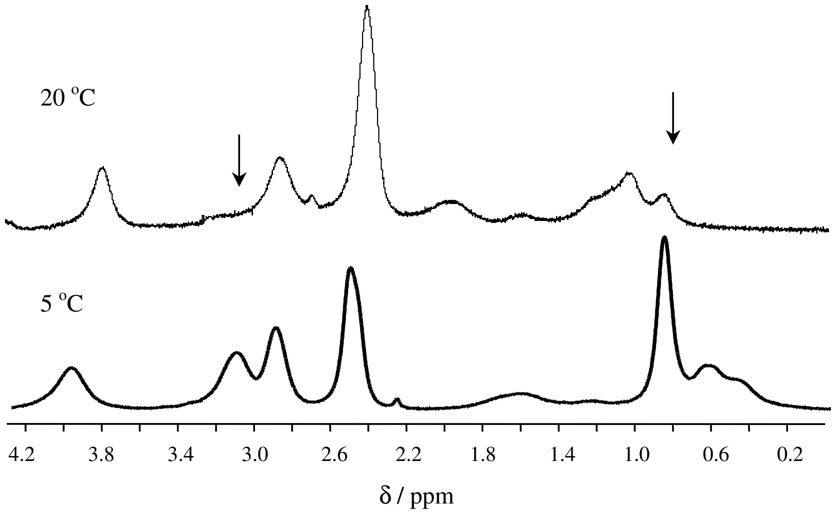

Fig. 7. NMR spectra of a BzO–DEA–DMA diblock copolymer (KV 77) dissolved in D_2O at pH 8. The lower spectrum was recorded at 5°C and the upper spectrum at 20°C.

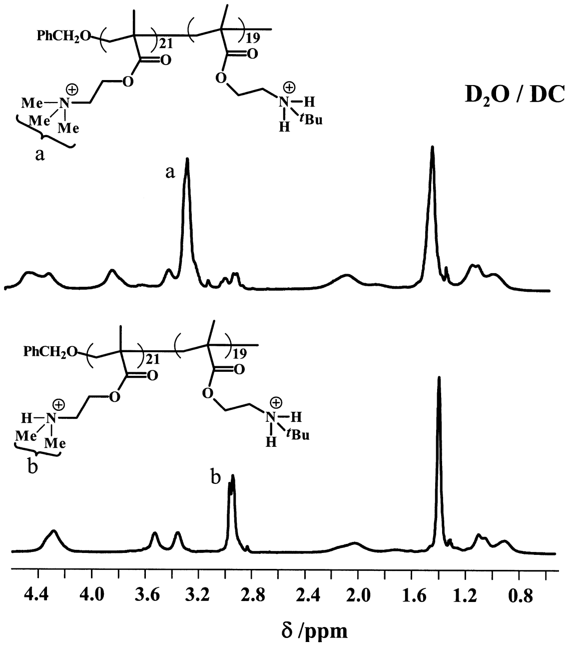

Fig. 8. ^{1}H NMR spectra before and after the selective quaternization of DMA residues of the DMA–BAE diblock copolymer using methyl iodide in THF at 20°C (MeI/DMA = 1.0).

DEA and DMA residues at δ 4.0. This composition indicates that both blocks are fully solvated at this temperature. However, the spectral features due to the DEA residues are clearly suppressed at 20°C (see upper spectrum). Temperature cycling confirms that these spectral changes are fully reversible. Dynamic light scattering studies on KV 77 at 20°C indicate an intensity-average micelle diameter of around 80 nm. It is well known that DMA homopolymer exhibits inverse temperature solubility behaviour at neutral pH: it is soluble in water at 20°C but becomes insoluble at elevated temperatures (its precise cloud point varies between 33 and 47°C, depending on the molecular weight of the DMA chains [5]). Based on our NMR observations, we conclude that the DEA block also exhibits inverse temperature solubility behaviour, except that in this case its cloud point is *below* room temperature (somewhere between 5 and 20°C).

We have previously reported the remarkably selective reactivity of DMA residues towards quaternization with 1,3-propanesultone for both DMA–DEA and DMA–MEMA diblocks prepared by GTP [10]. ^{1}H NMR studies indicated that, for a 1,3-propanesultone/DMA molar ratio of unity, quaternization is essentially exclusive for the DMA residues under mild conditions. Similarly, in the present study we found that the DMA residues of a BzO–BAE–DMA diblock copolymer can be selectively quaternized within 4 h using methyl iodide in THF at 20°C, providing that a stoichiometric amount of the methyl iodide is utilized relative to the DMA residues. Fig. 8 depicts NMR spectra for both the precursor diblock and the quaternized diblock in DCl/D_2O (this solvent mixture was chosen in preference to D_2O since the BAE residues are soluble in acid but not in D_2O). The six dimethylamino protons associated with the DMA residues give rise to a signal at δ 3.00 in the diblock precursor. This signal shifts to δ 3.30 and becomes more intense relative to the signal due to the nine methyl protons of the BAE residues at δ 1.45 in the quaternized diblock. Peak integration confirms that almost all (>90%) of the DMA residues have reacted with the methyl iodide. These observations are consistent with a control experiment utilizing BAE homopolymer in which no discernible reaction with methyl iodide was detected even after 12 h at 20°C.

It is perhaps surprising that the tertiary amine groups of the DMA residues are much more susceptible to quaternization than the secondary amine groups of the BAE residues; presumably this is due to the steric congestion imposed by the *t*-butyl substituent of the secondary amine. This unexpected selectivity has some synthetic utility, as is demonstrated in the synthesis of the shell cross-linked micelles discussed below.

Following a seminal paper by Wooley and co-workers [11] in 1996, there has been a considerable interest in shell cross-linked micelles derived from the self-assembly

Table 3
Block compositions and polydispersities for the ABC triblock copolymers prepared by oxyanion-initiated polymerization

Polymer ID	Block compositions		GPC M_w/M_n
	Theoretical	NMR	
KV36[a]	PEO–$(DMA)_{42}$	PEO–$(DMA)_{49}$	1.32
	PEO–$(DMA)_{42}$–$(MEMA)_{79}$	PEO–$(DMA)_{49}$–$(MEMA)_{71}$	1.32
KV37[a]	PEO–$(DMA)_{42}$	PEO–$(DMA)_{50}$	1.32
	PEO–$(DMA)_{42}$–$(BAE)_{74}$	PEO–$(DMA)_{50}$–$(BAE)_{79}$	1.32
KV78	BzO –$(MEMA)_{25}$	BzO –$(MEMA)_{24}$	1.16
	BzO –$(MEMA)_{25}$–$(DMA)_{65}$	BzO –$(MEMA)_{24}$–$(DMA)_{65}$	1.30
	BzO –$(MEMA)_{25}$–$(DMA)_{65}$–$(DEA)_{81}$	BzO –$(MEMA)_{24}$–$(DMA)_{65}$–$(DEA)_{87}$	1.32

[a] Toluene was used as the solvent in place of THF and monomethoxy-capped poly(ethylene oxide), [PEO] was used to form the macroinitiator.

of block copolymers [12–16]. However, one significant problem associated with these fascinating new nanoparticles is that syntheses must be carried out at high dilution ($<0.5\%$) in order to avoid unwanted inter-micelle cross-linking. In a preliminary communication we have recently shown [4] that the use of ABC triblock copolymers leads to three-layer onion micelle structures in aqueous solution, which in turn allows 'inner-shell' cross-linking to be carried out at much higher copolymer concentrations ($>10\%$). This is a potentially significant discovery if these nanoparticles are to become commercially viable.

In the present study, a series of novel ABC triblock copolymers were prepared via sequential monomer addition using either potassium benzyl alcoholate or a poly(ethylene oxide)-based macro-initiator (see Table 3). Again, high yields, predictable molecular weights and relatively low polydispersities were usually obtained. One of these triblocks was selected for closer examination. ^{1}H NMR studies confirmed that the PEO–DMA–BAE triblock copolymer undergoes self-assembly in aqueous solution to form three-layer onion micelles, with the relatively hydrophobic BAE block forming the non-solvated micelle core (the NMR signals due to these residues disappear), the hydrophilic DMA block forming the inner shell and the highly hydrophilic PEO block forming the outer shell. Shell cross-linked micelles could be prepared at high solids (10 or 25%) by adding a *bifunctional* quaternizing agent, 1,2-bis-(2-iodoethoxy) ethane (BIEE), to this micellar solution. As demonstrated earlier, quaternization of the DMA residues in the inner shell of the three-layer micelles occurs exclusively, with the BAE residues left unreacted. On shell cross-linking, the mobility of the DMA residues is dramatically reduced and the NMR signals due to these residues broaden and are substantially attenuated. The PEO block in the outer shell acts as a steric stabilizer and minimizes chain overlap between adjacent micelles via a steric stabilization mechanism, thus preventing inter-micelle cross-linking. If shell cross-linking had been unsuccessful, the micelles would be expected to dissociate on dilution in acidic solution (pH 2), which is a good solvent for the BAE residues. However, dynamic light scattering studies indicated the existence of micelles with a mean diameter of 67 nm under these conditions, thus confirming that shell cross- linking had occurred. Transmission electron microscopy studies of the diluted shell cross-linked micelles confirm that the particle morphology is spherical but somewhat polydisperse; the mean number-average diameter is approximately 40–60 nm. Allowing for polydispersity and dehydration effects, this particle size is in reasonably good agreement with that obtained from dynamic light scattering. Finally, NMR studies confirmed that on cooling these shell cross-linked micelles to 5°C (i.e. below the cloud point of the BAE block), partial rehydration of the micelle cores could be achieved.

4. Conclusions

The oxyanion-initiated polymerization of various amine methacrylates has been examined in detail. Molecular weight increases linearly with conversion and efficient block copolymer formation has been demonstrated, which are indicative of good living characteristics. In addition, reasonably narrow polydispersities are obtained. Potassium benzyl alcoholate proved to be a useful model initiator in this study since it allowed polymer molecular weights to be calculated by NMR spectroscopy. Moreover, UV GPC confirmed that much higher initiator efficiencies can be achieved if a titration method is used for the in situ preparation of this initiator. A secondary amine methacrylate, *t*-(butylamino)ethyl methacrylate, proved amenable to oxyanion-initiated polymerization, in addition to the four tertiary amine methacrylates previously reported. Novel diblock and triblock copolymers were synthesized and selected copolymers undergo reversible temperature-induced micellization in aqueous solution. In particular, an ethylene oxide-2-(dimethylamino)ethyl methacrylate–*t*-butylaminoethyl methacrylate ABC triblock copolymer undergoes self-assembly to form three-layer micelles. The inner shell comprises 2-(dimethylamino)ethyl methacrylate residues, which can be selectively cross-linked using a bifunctional alkyl iodide reagent. The poly(ethylene oxide) block prevents inter-micelle cross-linking, thus allowing the efficient synthesis of shell cross-linked micelles at high solids.

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