Selective betainisation of tertiary amine methacrylate block copolymers

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2-(Dimethylamino)ethyl methacrylate (DMAEMA) was block copolymerised in turn with three other tertiary amine methacrylate comonomers using group transfer polymerisation; the DMAEMA residues of each of these diblock copolymers were *selectively* betainised using propane-1,3-sultone under mild conditions to yield a series of novel water-soluble sulfobetaine block copolymers which exhibit reversible pH- and temperature-induced micellisation.

Recently, several groups have described the polymerisation of 2-(dimethylamino)ethyl methacrylate (DMAEMA) *via* anionic[1,2] or group transfer polymerisation (GTP).[3,4] DMAEMA homopolymer is a weak polybase which is water soluble at neutral pH or in acidic media due to protonation of the tertiary amine groups. In 1996 we reported that near-monodisperse DMAEMA homopolymers and DMAEMA–alkyl methacrylate block copolymers can be quantitatively betainised under remarkably mild conditions using propane-1,3-sultone.[5]

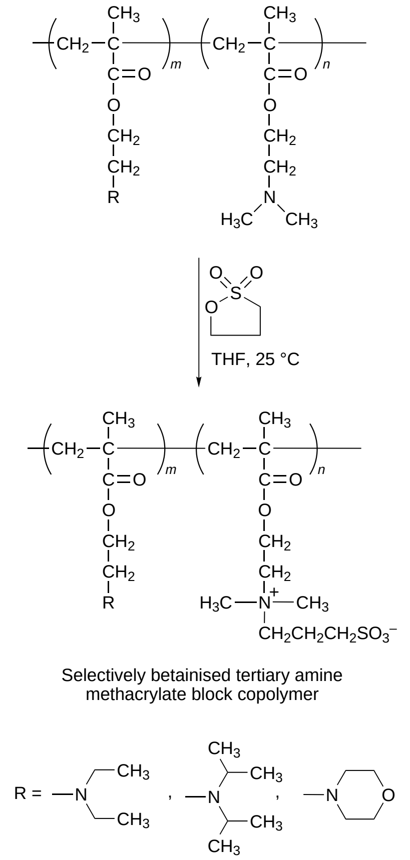
In the present work DMAEMA was block copolymerised with three related tertiary amine methacrylate monomers, 2-(diethylamino)ethyl methacrylate (DMAEMA), 2-(diisopropylamino)ethyl methacrylate (DPAEMA) and 2-(*N*-morpholino)ethyl methacrylate (MEMA) (see Scheme 1). Homopolymers of each of these four tertiary amine methacrylates were also synthesised. All (co)polymers were prepared *via* GTP techniques using a 1-methoxy-1-trimethylsilyloxy-2-methyl prop-1-ene (MTS) initiator and tetrabutylammonium bibenzoate (TBABB) [$Bu_4N^+(PhCO_2^-)_2H^+$] catalyst at 25 °C in dry THF as previously described.[3–5] Narrow molecular weight distributions (M_w/M_ns $\leqslant 1.15$) were obtained in all cases as judged by gel permeation chromatography [THF eluent, poly(methyl methacrylate) standards, RI detector]. The molecular weights of the four homopolymers ranged from 4 800 to 12 400. The DMAEMA and MEMA homopolymers were water soluble at room temperature and neutral pH but precipitated from aqueous solution at 32–47 °C, depending on their molecular weight.[6] In contrast, the DMAEMA and DPAEMA homopolymers were both completely insoluble in aqueous media at neutral pH. However, these latter homopolymers both dissolved readily in acidic aqueous solution (*ca.* pH 3–4) due to protonation of the tertiary amine residues. In the block copolymer syntheses the DMAEMA monomer was always polymerised first and quantitative yields were obtained in all cases; molecular weights and polydispersities of the copolymers are summarised in Table 1. Copolymer compositions were determined by ^1H NMR spectroscopy and corresponded closely (within experimental error) to those expected from the comonomer feeds. For example, Fig. 1(*a*) shows the NMR spectrum of a 61 : 39 DMAEMA–DPAEMA block copolymer dissolved in DCl–D_2O. The signal at δ 3.0 is due to the six dimethylamino protons in the DMAEMA residues[5] and the signal at δ 1.4–1.5 corresponds to the twelve equivalent methyl protons of the two isopropyl groups in the DPAEMA residues. Ratioing the peak integrals of these signals gives the block copolymer composition.

Experimental conditions for the betainisation reaction have been described previously.[5] A 10 mol% excess of propane-1,3-sultone based on DMAEMA residues was used. Preliminary betainisation experiments on the DMAEMA, DEAEMA, DPAEMA and MEMA homopolymers confirmed that only the DMAEMA homopolymer was quantitatively betainised at room temperature in THF within 16–24 h. The DEAEMA and MEMA homopolymers both required significantly longer reaction times (48–96 h) and/or refluxing THF for any significant degree of betainisation to be observed, as judged by the onset of gelation. The DPAEMA homopolymer remained completely unbetainised even after four days in refluxing THF. Presumably this much reduced reactivity is due to steric crowding of the tertiary amine residues. These observations suggested that the DMAEMA residues in the DMAEMA–DEAEMA, DMAEMA–MEMA and DMAEMA–DPAEMA block copolymers could be selectively betainised at room temperature by restricting the reaction time to 24 h (see Scheme 1). This proved to be the case. The degrees of betainisation of the DMAEMA block sequences were determined by elemental microanalyses (see Table 1) and confirmed by ^1H NMR spectroscopy. Fig. 1(*b*) shows the NMR spectrum of a betainised 61 : 39 DMAEMA–DPAEMA block copolymer dissolved in DCl–D_2O, which is a good solvent for both block sequences. The signal at δ 3.2–3.3 is due to the six dimethylamino protons of the

Table 1 A summary of the molecular weights, polydispersities, copolymer compositions and degrees of betainisation of the four tertiary amine methacrylate diblock copolymers

block copolymer	M_n[a]/g mol^{-1}	M_w/M_n[a]	DMAEMA content[b] (mol%)	degree of betainisation[c]	calc. M_n for betainised copolymers[d]
DMAEMA–DEAEMA	9500	1.15	49	88 ± 5	12 400
DMAEMA–DEAEMA	12 100	1.10	78	89 ± 5	18 500
DMAEMA–DPAEMA	15 700	1.11	61	80 ± 5	21 100
DMAEMA–DPAEMA	11 500	1.10	80	93 ± 5	17 900
DMAEMA–MEMA	5200	1.11	36	92 ± 5	7400

[a] As determined by GPC using PMMA standards for the precursor blocks prior to betainisation. [b] As determined for the precursor blocks using ^1H NMR spectroscopy. [c] Calculated from the S/N ratio taking into account the DMAEMA content of the precursor block obtained from ^1H NMR spectroscopy. [d] Calculated using a combination of GPC, ^1H NMR and microanalytical data.



Scheme 1 Selective betainisation of 2-(dimethylamino)ethyl methacrylate residues in tertiary amine methacrylate block copolymers using propane-1,3-sultone under mild conditions

betainised DMAEMA residues,[5] whereas the signal at δ 1.4–1.5 corresponds to the twelve protons of the four equivalent methyl groups in each of the non-betainised DPAEMA residues. Ratioing the peak integrals of these two signals gives the same 61 : 39 copolymer composition as that determined for the original DMAEMA–DPAEMA precursor block prior to betainisation. Thus betainisation of the DMAEMA residues is both selective and near-quantitative. Similar results were obtained with DMAEMA–MEMA and DMAEMA–DEAEMA block copolymers.

In an earlier communication[4] we reported that DMAEMA–DEAEMA block copolymers exhibited highly pH-dependent surface activity and micellisation. It was suggested that the more hydrophobic DEAEMA block adsorbed at the air–water interface and also formed the interior of the copolymer micelles. Our NMR studies of the betainised 61 : 39 DMAEMA–DPAEMA block copolymer now support this hypothesis. Initially, this copolymer was molecularly dissolved in DCl–D_2O [see Fig. 1(*b*)]. On addition of excess NaOD, the strong signal at δ 1.4–1.5 observed in Fig. 1(*b*) due to the twelve equivalent methyl protons of the DPAEMA residues completely disappears [see Fig. 1(*c*)], indicating that this deprotonated block sequence is no longer solvated. This is strong evidence for the DPAEMA block forming a hydrophobic micellar core, as expected. Similar, though less striking, spectral changes are observed in the NMR spectrum of the betainised DMAEMA–DEAEMA block under similar conditions. It is noteworthy that the surface activity and micellisation behaviour previously reported[4] for the DMAEMA–DEAEMA precursor blocks only occur over a rather narrow pH range, since precipitation occurs above pH 8–9 due to deprotonation of the more hydrophilic DMAEMA residues. In contrast, since the betainised DMAEMA residues are soluble in alkaline media the betainised blocks remain in solution as micelles up to pH 12. However, betainisation significantly reduces the surface activities of the copolymers.[7] For example, the limiting surface tension for a selectively betainised 78 : 22 DMAEMA–DEAEMA block is only *ca.* 51 mN m^{-1}, whereas the precursor block is much more surface active, exhibiting a limiting surface tension as low as 34 mN m^{-1}.

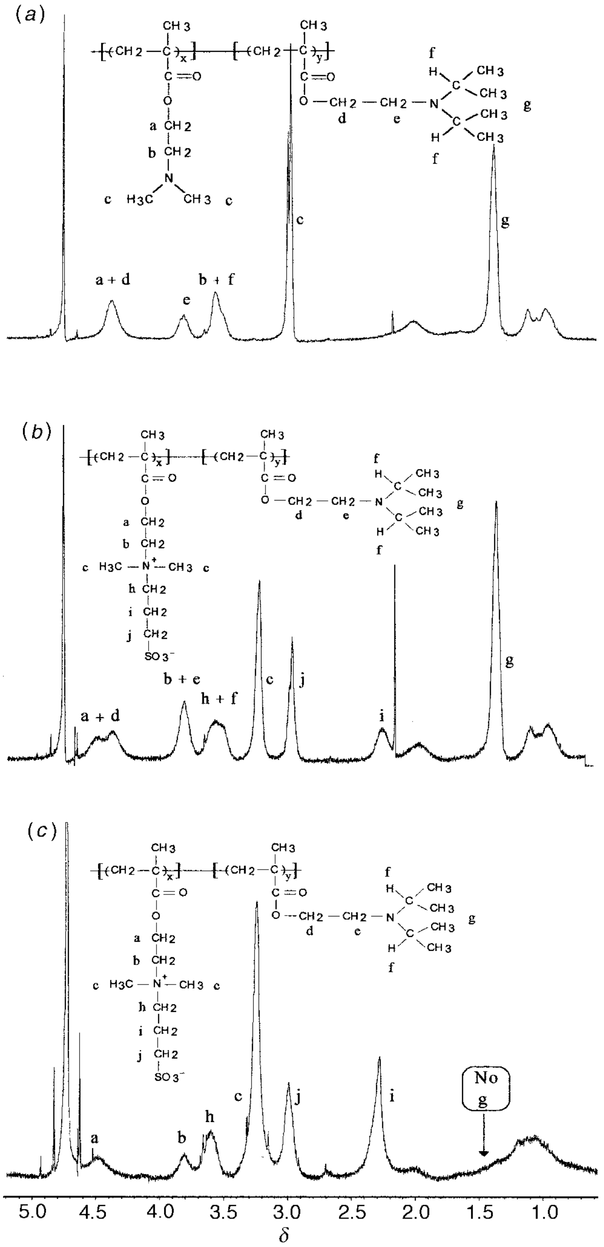


Fig. 1 ^{1}H NMR spectra of (*a*) a 61 : 39 DMAEMA–DPAEMA precursor block synthesised by GTP; (*b*) the same 61 : 39 DMAEMA–DPAEMA block dissolved in DCl–D_2O after selective betainisation of the DMAEMA residues using propane-1,3-sultone; (*c*) a micellar solution of the same betaine block copolymer achieved by adjusting the solution pH with excess NaOD (the disappearance of the signal at δ 1.4–1.5 due to the DPAEMA residues indicates that this non-solvated block forms the interior of the micelle)

Dynamic light scattering studies of pH- and temperature-induced micellisation were carried out on dilute aqueous solutions of the betainised block copolymers. The betainised DMAEMA–DEAEMA and DMAEMA–DPAEMA blocks each formed micelles of *ca.* 20 nm with reasonably narrow size distributions. A betainised 36:64 DMAEMA–MEMA block exhibited temperature-induced micellisation behaviour at around 70 °C, forming micelles of around 100 nm diameter with a narrow size distribution. Micellisation was completely reversible in both cases. Addition of acid caused complete dissolution of the betainised DMAEMA–DEAEMA micelles. Similarly, micellar solutions of the betainised DMAEMA–MEMA dissociated on cooling to form the original unimers.

In summary, the unexpectedly selective betainisation of DMAEMA residues in DMAEMA-based block copolymers provides a facile route to new hydrophilic–hydrophilic betaine block copolymers. Preliminary studies confirm that these materials exhibit interesting aqueous solution properties.

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