

# Synthesis and aqueous solution properties of novel hydrophilic–hydrophobic block copolymers based on tertiary amine methacrylates

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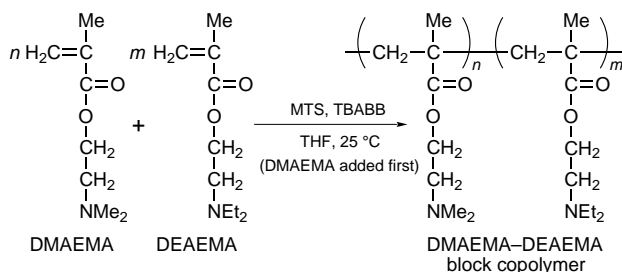
**A series of near-monodisperse novel diblock copolymers based on tertiary amine methacrylates has been synthesised using group transfer polymerisation chemistry; subtle differences in basicity between the two blocks lead to interesting aqueous solution behaviour, including pH-induced micellisation and very high surface activity.**

Over the last decade or so group transfer polymerisation<sup>1,2</sup> has become recognised as an excellent method for the synthesis of methacrylate (co)polymers of controlled structure and narrow molecular weight distribution. Recently we have used this technique to prepare well-defined homopolymers and block copolymers based on 2-(dimethylamino)ethyl methacrylate (DMAEMA).<sup>3,4</sup> DMAEMA homopolymer is a weak polybase which is soluble at neutral pH or in acidic media due to protonation of the tertiary amine groups. Functionalisation of the DMAEMA residues is possible: for example, quantitative derivatisation under mild conditions has been recently achieved using propane-1,3-sultone to yield near-monodisperse polysulfopropylbetaines.<sup>5</sup> Here we describe the block copolymerisation of DMAEMA with a related tertiary amine methacrylate, 2-(diethylamino)ethyl methacrylate (DEAEMA) (Scheme 1). Although structurally very similar to DMAEMA, the DEAEMA monomer is immiscible in water and DEAEMA

homopolymers are completely insoluble at neutral pH. On the other hand, DEAEMA homopolymers readily dissolve in acidic aqueous solution (*ca.* pH 2) due to protonation of the tertiary amine residues. Here it is demonstrated that the subtle difference in chemical structure between these two tertiary methacrylate comonomers has profound implications for the aqueous solution behaviour of DMAEMA–DEAEMA block copolymers.

A series of DMAEMA–DEAEMA block copolymers was prepared using group transfer polymerisation under similar conditions to those previously described.<sup>4</sup> All copolymerisations were carried out using 1-methoxy-1-trimethylsilyloxy-2-methylprop-1-ene (MTS) as initiator and tetrabutylammonium bibenzoate (TBABB) catalyst at 25 °C in dry THF using Schlenk techniques. The DMAEMA monomer was polymerised first and quantitative yields were obtained in all syntheses. The molecular weights, polydispersities and copolymer compositions of the resulting block copolymers are summarised in Table 1. Narrow molecular weight distributions were obtained in all cases ( $M_w/M_n \leq 1.15$ ) as judged by gel permeation chromatography (THF eluent, PMMA standards, RI detector). The actual copolymer compositions as determined by <sup>1</sup>H NMR spectroscopy corresponded closely (within experimental error) to those expected from the comonomer feeds. As far as we are aware, these are the first reported examples of diblock copolymers in which both block components are polybases.

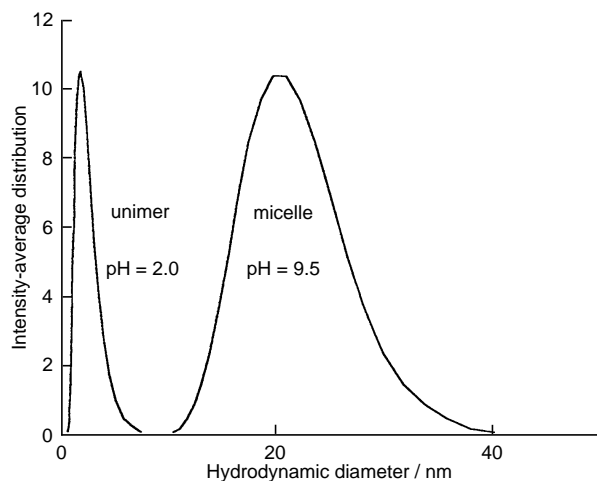
For reasons outlined above, these DMAEMA–DEAEMA copolymers behave as hydrophilic–hydrophobic blocks in aqueous solution at neutral pH. One of the problems in studying the micellisation behaviour of such copolymers is that water-miscible co-solvents (THF, alcohols, DMF *etc.*) are normally required for efficient dissolution in aqueous solution. Even then, the hydrophobic component usually ensures that the majority of the copolymer chains exist as micellar aggregates, rather than as molecularly dissolved chains. Thus there is little opportunity to study the kinetics of micellisation under true equilibrium conditions. Recently there have been several reports<sup>6–8</sup> of the



**Table 1** A summary of the molecular weights, polydispersities and copolymer compositions of the tertiary amine methacrylate block copolymers determined using gel permeation chromatography and <sup>1</sup>H NMR spectroscopy, respectively

Polymer	Theoretical DMAEMA content (mol%)	Actual DMAEMA content <sup>a</sup> (mol%)	Theoretical $M_n/g\ mol^{-1}$	Actual <sup>b</sup> $M_n/g\ mol^{-1}$	$M_w/M_n$
PDMAEMA	100	100.0	10 100	12 400	1.07
PDEAEMA	—	—	9 700	11 000	1.06
DMAEMA-b-DEAEMA	80	77.8	10 400	12 400	1.10
DMAEMA-b-DEAEMA	74	72.0	9 000	11 400	1.10
DMAEMA-b-DEAEMA	66	63.9	9 900	9 700	1.12
DMAEMA-b-DEAEMA	49	48.7	10 600	9 600	1.15
DMAEMA-b-DEAEMA	35	36.0	9 900	11 900	1.09
DMAEMA-b-DEAEMA	22	24.0	9 900	9 500	1.10
DMAEMA-b-DEAEMA	68	66.9	18 900	21 600	1.09

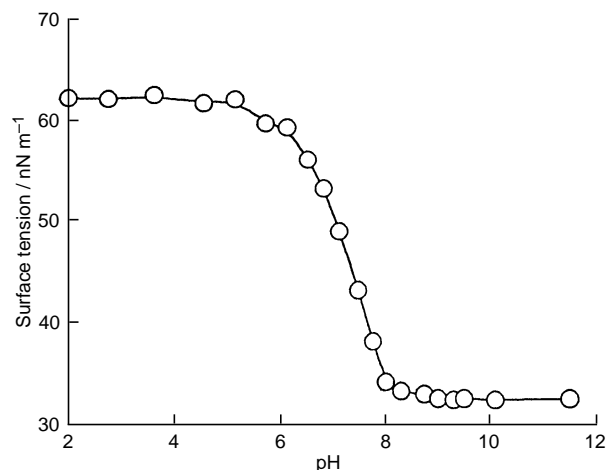
<sup>a</sup> As determined by <sup>1</sup>H NMR spectroscopy in CDCl<sub>3</sub>. <sup>b</sup> As determined by GPC in THF [RI detector; calibrated with poly(methyl methacrylate) standards].



**Fig. 1** Hydrodynamic size of a 72:28 DMAEMA-DEAEMA block copolymer (dissolved in dilute HCl as a 1.0% w/v solution at 25 °C and then titrated to pH 9.5 using KOH)

synthesis of hydrophilic-hydrophilic block copolymers which can be dissolved as unimers in aqueous solution and then aggregated into micelles. One way of inducing micellisation is by raising the solution temperature to the cloud point of the least hydrophilic block component. Alternatively, Martin *et al.*<sup>8</sup> have shown that poly(2-vinylpyridine-block-ethylene oxide) copolymers can be molecularly dissolved in acidic media (hydrophilic protonated 2-vinylpyridine residues) and then aggregated into micelles by adding base (hydrophobic deprotonated 2-vinylpyridine residues). The DMAEMA-DEAEMA blocks described here exhibit similar behaviour but their synthesis is much more controlled, with only minimal levels (< 5%) of DMAEMA homopolymer contamination indicated by GPC analyses. In contrast, Martin *et al.* reported that the single block copolymer example synthesised in their laboratory contained 30% poly(2-vinylpyridine) homopolymer. In this latter case the homopolymer contaminant is the less hydrophilic block, which profoundly affects the micellisation behaviour of the block copolymer.

Examination of a 1.0% w/v solution of the 72:28 DMAEMA-DEAEMA block in dilute HCl (pH 2) by dynamic light scattering confirmed very weak light scattering and unimer sizes (see Fig. 1). However, adjusting this solution to pH 9.5 with KOH produced much more intense light scattering due to the formation of micelles of around 20 nm diameter with a narrow size distribution. We believe that the DEAEMA block becomes hydrophobic and forms the micelle core, with the still-solvated DMAEMA chains forming the micellar corona. This micellisation proved to be completely reversible: the subsequent addition of acid resulted in complete dissolution of the micelles. Preliminary surface tension vs. pH data for the same 72:28 copolymer obtained using a Kruss K10ST surface tensiometer (very similar results were obtained using both plate and ring methods) are shown in Fig. 2. As the solution pH is increased the block copolymer becomes significantly more surface active. Presumably the deprotonated hydrophobic DEAEMA block becomes adsorbed strongly at the air-water interface, thus lowering the surface tension of the solution. Above pH 8 the limiting surface tension of this solution is approximately 32–33 mN m<sup>-1</sup> (gentle agitation produces a large volume of long-lasting foam), which is similar to that obtained with small molecule surfactants but relatively low compared to most other synthetic water-soluble block copolymers. For example, Baines *et al.*<sup>3</sup> reported that the limiting surface tension obtained for a 1.0% w/v aqueous solution of an 80:20 DMAEMA-methyl methacrylate block copolymer of comparable molecular weight was only 46 mN m<sup>-1</sup>. Similarly, a surface tension plateau of ca. 42 mN m<sup>-1</sup> was observed by Teyssie and co-workers<sup>9</sup> for a sulfonated glycidyl methacry-



**Fig. 2** Variation of surface tension with solution pH for a 1.0% w/v aqueous solution of a 72:28 DMAEMA-DEAEMA block copolymer. The block copolymer was first dissolved in dilute HCl and the solution pH was then adjusted by addition of KOH.

late-methyl methacrylate block copolymer with a similar hydrophilic-hydrophobic balance.

Provided that the DMAEMA content of the copolymer is greater than approximately 50 mol% these DMAEMA-DEAEMA block copolymers can be dispersed directly into water at around neutral pH to form micelles of around 15 nm diameter. However, DEAEMA-rich block copolymers are insoluble under these conditions. In this context it is noteworthy that the limiting surface tension obtained with the 72:28 DMAEMA-DEAEMA block dissolved directly into water is ca. 33 mN m<sup>-1</sup> at a copolymer concentration of 0.15% w/v. These surface tension data suggest that such hydrophilic-hydrophilic block copolymers may have interesting applications as novel surfactants or emulsifiers.

In summary, a series of new polybase block copolymers have been synthesised using GTP chemistry. These copolymers can be molecularly dissolved in aqueous solution without the use of co-solvents. They exhibit reversible pH-induced micellisation and are remarkably surface active at around neutral pH.

We wish to thank the Turkish government for funding a studentship for V. B. and Sussex University for project consumables support. An EPSRC ROPA grant (GR/K86855) was used to purchase the argon ion laser for the dynamic light scattering studies.

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Received in Bath, 22nd January 1997; Com. 7/00772H