

Unusual Aggregation Behavior of a Novel Tertiary Amine Methacrylate-Based Diblock Copolymer: Formation of Micelles and Reverse Micelles in Aqueous Solution

V. Büttin, N. C. Billingham, and S. P. Armes*

School of Chemistry
Physics and Environmental Science
University of Sussex
Falmer, Brighton, BN1 9QJ, UK

Received July 1, 1998

It is well-known that AB diblock copolymers aggregate to form micelles in solvents which are selective for either the A block or the B block.^{1–5} Provided that the block ratio is not too asymmetric, it is also possible to obtain micelles or reverse (inverted) micelles from the *same* block copolymer by choosing appropriate selective solvents. For example, Oranli and co-workers reported⁶ that styrene–butadiene diblock copolymers can form micelles with either polystyrene cores (in *n*-alkanes) or polybutadiene cores (in DMF or MEK, respectively). Similarly, it is well-known that small molecule surfactants can form micelles or reverse micelles in aqueous and nonaqueous media, respectively. However, as far as we are aware, there are no literature examples of block copolymers or surfactants which are capable of forming both micelles (A block in core) and reverse micelles (B block in core) *solely in aqueous media*. At first sight this might appear impossible, but in this paper we describe a novel water-soluble AB diblock copolymer which exhibits this highly unusual behavior at room temperature at around neutral pH (see Figure 1). The critical parameters which affect the solvency and, hence, govern the formation of micelles or reverse micelles are the solution pH, electrolyte concentration, temperature, and block symmetry.

Recently we reported⁷ the synthesis of a range of new diblock copolymers based on 2-(dimethylamino)ethyl methacrylate (DMAEMA) via group transfer polymerization (GTP).^{8,9} DMAEMA was block-copolymerized in turn with three other tertiary methacrylates, 2-(diethylamino)ethyl methacrylate (DEAEMA), 2-(diisopropylamino)ethyl methacrylate (DPAEMA), and 2-(*N*-morpholino)ethyl methacrylate (MEMA). In the present work GTP was used to synthesize a novel MEMA–DEAEMA diblock copolymer (see Figure 2) in THF at room temperature using 1-methoxy-1-(trimethylsilyloxy)-2-methylpropene (MTS) as initiator and *n*-tetrabutylammonium bibenzoate as catalyst. The DEAEMA monomer was polymerized first, and quantitative conversion was obtained for both monomers. Precipitation of the block copolymer into *n*-hexane proved effective in removing traces of DEAEMA homopolymer since this impurity is soluble in this solvent. Gel permeation chromatography (GPC) analysis [poly(methyl meth-

acrylate) standards, PL mixed “E” column, refractive index detector, THF eluent, 1.0 mL min⁻¹ flow rate] confirmed that the MEMA–DEAEMA diblock copolymer had a narrow, unimodal molecular weight distribution, with an M_n of ca. 22 000 and a polydispersity index (M_w/M_n) of 1.05. Proton NMR spectroscopy (in CDCl₃, which is a good solvent for both parts of the block; see Figure 3a) indicated a MEMA content of around 60 mol % (the signal at δ 3.7 due to the four –H₂C–O–CH₂– protons of the MEMA residues were compared to the signal due to the –OCH₂ groups of both residues at δ 4.1).

Recently we have studied the aqueous solution behavior of MEMA and DEAEMA homopolymers.^{7,10} Salient details are briefly summarized here. MEMA homopolymer exhibits inverse temperature solubility behavior; its cloud point lies between 34 and 45 °C at pH 7, depending on molecular weight. In acidic solution the weakly basic MEMA residues become protonated and hence more hydrophilic, and there is no cloud point. Compared to most other water-soluble polymers, MEMA homopolymer can be precipitated (salted out) relatively easily from aqueous solution on addition of electrolytes such as Na₂SO₄. DEAEMA homopolymer is insoluble in aqueous media at around pH 7–8, but it can be dissolved molecularly in acidic media as a weak cationic polyelectrolyte. It is reprecipitated on addition of base. Under the latter conditions, MEMA homopolymer remains water-soluble at room temperature. In view of these differences in the aqueous solution properties of the respective homopolymers, we felt that a MEMA–DEAEMA diblock copolymer might form either micelles or reverse micelles, depending on subtle variations in solution pH and/or electrolyte concentration. This proved to be the case.

Micelles with DEAEMA cores were obtained by careful adjustment of the solution pH. The MEMA–DEAEMA diblock copolymer dissolved molecularly in dilute HCl at pH 4 to give a 1.0 w/v % copolymer solution. Careful addition of KOH to this acidic solution at 20 °C produced a final pH of 8.5. Under these conditions, the DEAEMA block is substantially deprotonated and therefore hydrophobic,¹⁰ whereas the MEMA block remains solvated. Thus, micelles comprising DEAEMA cores and MEMA corona are expected. Proton NMR studies confirm this to be the case. Comparing Figure 3b and c, it is clear that the signals due to the DEAEMA residues at δ 1.3 and 3.3 are suppressed (indicating lower mobility and decreased solvation), whereas those signals due to the MEMA block at δ 2.6 and δ 3.7 are still prominent, albeit somewhat broadened. Dynamic light-scattering studies (80 mW argon ion laser; Malvern 4700 instrument; scattered light detected at 90°) indicated near-monodisperse micelles, with an intensity-average micelle diameter of 32 nm at 20 °C and pH 8.5. Addition of acid led to reprotonation of the DEAEMA residues and unimers were again produced at pH 6.7 or lower.

Using this unimer solution, reverse micelles containing MEMA residues in the cores were obtained by selectively salting out the MEMA block using 1.0 M Na₂SO₄. Careful control of the solution acidity was essential here. If the solution pH was too low, both the MEMA and DEAEMA blocks would become soluble as weak cationic polyelectrolytes. Conversely, if the solution pH was too high, the DEAEMA block would become de-solvated in addition to the MEMA block, and macroscopic precipitation would occur. A solution pH of 6.0 to 6.7 was found to be a suitable compromise. Under these conditions, dynamic light-scattering studies indicated the formation of stable, near-monodisperse micelles with an intensity-average diameter of around 26 nm. Proton NMR studies at 20 °C in D₂O at pH 6.7 with 1.0 M Na₂SO₄ again confirmed that the DEAEMA block

(10) Büttin, V.; Billingham, N. C.; Armes, S. P. *Chem. Commun.* 1997, 671–672.

* To whom correspondence should be addressed. E-mail: S.P.Armes@sussex.ac.uk.

(1) Moffit, M.; Khougaz, K.; Eisenberg, A. *Acc. Chem. Res.* 1996, 29, 95–102.

(2) Gast, A. P. *Curr. Opin. Colloid Interface Sci.* 1997, 2, 258–263.

(3) Prochazka, K.; Martin, T. J.; Munk, P.; Webber, S. E. *Macromolecules* 1996, 29, 6518–6525.

(4) Yu, G. E.; Yang, Z.; Ameri, M.; Attwood, D.; Collett, J. H.; Price, C.; Booth, C. *J. Phys. Chem. B* 1997, 101, 4394–4401.

(5) Baines, F. L.; Armes, S. P.; Billingham, N. C.; Tuzar, Z. *Macromolecules* 1996, 29, 8151–8159.

(6) Oranli, L.; Bahadur, P.; Riess, G. *Can. J. Chem.* 1985, 63, 2691–2696.

(7) Büttin, V.; Bennett, C. E.; Vamvakaki, M.; Lowe, A. B.; Billingham, N. C.; Armes, S. P. *J. Mater. Chem.* 1997, 7, 1693–1695.

(8) Webster, O. W.; Hertler, W. R.; Sogah, D. Y.; Farnham, W. B.; RanjanBabu, T. V. *J. Am. Chem. Soc.* 1983, 105, 5706.

(9) Dicker, I. B.; Cohen, G. M.; Farnham, W. B.; Hertler, W. R.; Langanis, E. D.; Sogah, D. Y. *Macromolecules* 1990, 23, 4034–4041.

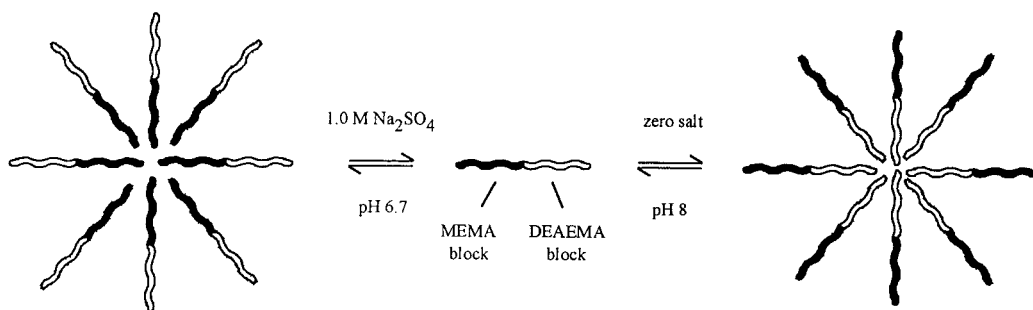


Figure 1. Schematic representation of the formation of micelles and reverse micelles for an AB diblock copolymer.

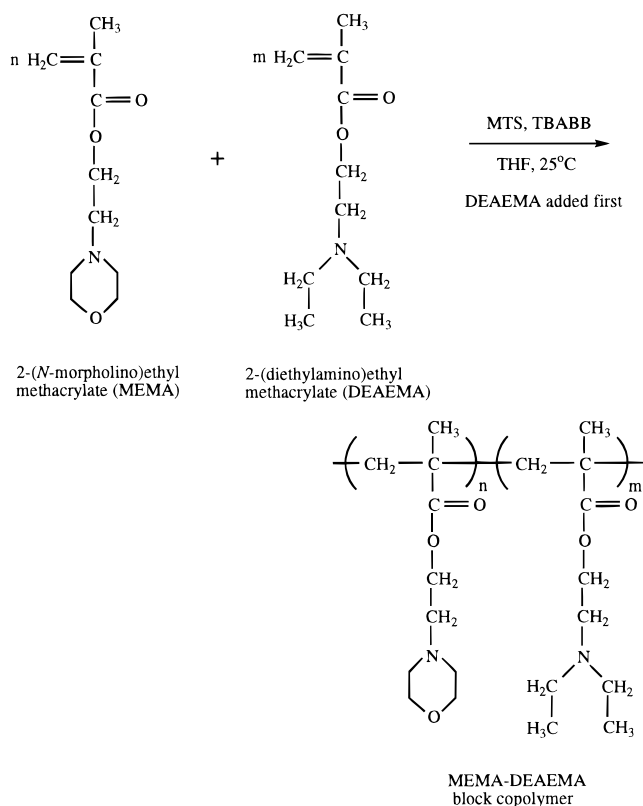


Figure 2. Synthesis and chemical structure of the 2-(*N*-morpholino)-ethyl methacrylate-2-(diethylamino)ethyl methacrylate (MEMA-DEAEMA) diblock copolymer used in this study.

remains solvated under these conditions (prominent signals at δ 1.3, 3.3, 3.5 and 4.4), whereas the signals due to the MEMA block at δ 2.6, 3.7 and 4.1 are suppressed (compare Figure 3b and d). This is consistent with the MEMA block forming the nonsolvated micellar core, which is entirely expected, given its low tolerance to added electrolyte.⁷

As expected, block symmetry is important for the formation of stable micelles and reverse micelles. Our preliminary studies with a more asymmetric 73:27 MEMA-DEAEMA diblock copolymer were only partially successful; since the DEAEMA block was relatively short, the long-term stability of the "MEMA-core" micelles was poor. Careful control of the solution temperature is also critical; more polydisperse micelles and/or macroscopic precipitation were obtained at 25 °C or higher.

In summary, we have demonstrated for the first time that an AB diblock copolymer can form micelles with nonsolvated cores comprising either the A block or the B block in aqueous media. It is worth emphasizing that, in both cases, micellization is fully reversible. It is remarkable that this highly unusual behavior can be observed at room temperature merely by judicious control of the solution pH and the electrolyte concentration.

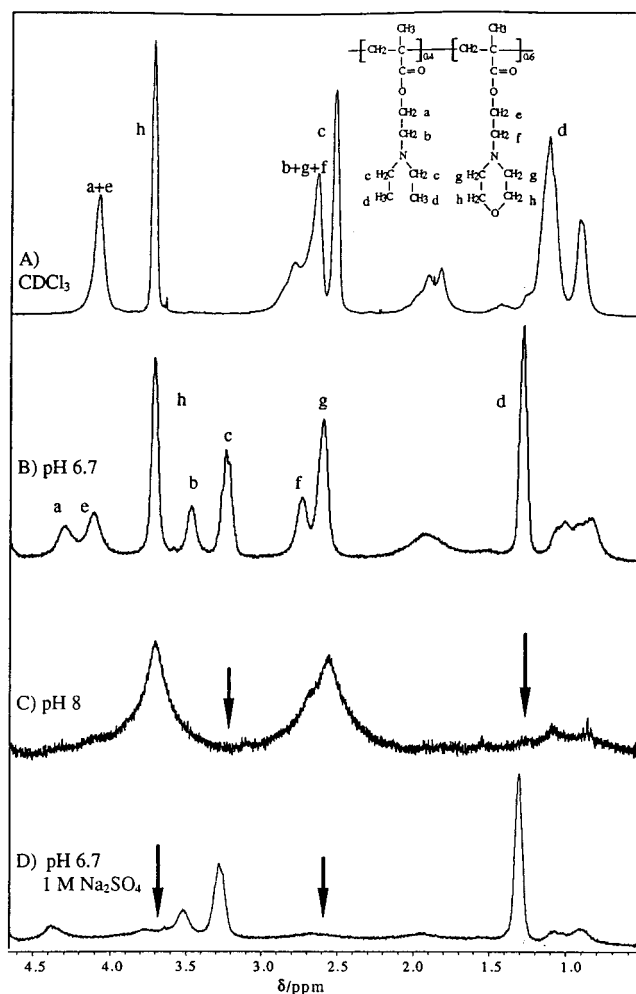


Figure 3. Proton NMR spectra of the 60:40 MEMA-DEAEMA diblock copolymer obtained under the following conditions: (a) in CDCl_3 (a nonselective solvent; thus, both blocks are solvated, and there is no micelle formation); (b) in D_2O at 20 °C and pH 6.7 (both MEMA and DEAEMA blocks are solvated, and the DEAEMA block is partially protonated); (c) in D_2O at 20 °C and pH 8.0 (micelle formation with DEAEMA residues forming the nonsolvated micelle core; note suppression of the signals at δ 1.3 and 3.3); (d) in D_2O at 20 °C and pH 6.7 in the presence of 1.0 M Na_2SO_4 (reverse micelle formation with MEMA residues forming the nonsolvated micelle core; note suppression of the signals at δ 2.6 and 3.7).

Acknowledgment. We wish to thank Ozmangazi University, Turkey, 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.