

Direct synthesis and aqueous solution properties of Y-shaped, stimulus-responsive block copolymer surfactants†

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We report the direct synthesis of a wide range of well-defined, Y-shaped stimulus-responsive block copolymers under mild conditions; the aqueous solution behaviour of these new polymeric surfactants has been investigated.

There is increasing interest in the synthesis of well-defined water-soluble block copolymers and exploiting their surfactant-like properties (e.g. micellar self-assembly in aqueous solution, interfacial adsorption). Recent research has confirmed that non-linear (AB₂ or AB₃ type) block copolymers exhibit fundamentally different behaviour to that of the corresponding linear AB diblocks.^{1–5} Y-Shaped (i.e. AB₂ type) block copolymers have been typically synthesized *via* living anionic or cationic polymerization.^{1–4} However, Gnanou and co-workers recently synthesized polystyrene-block-[poly(*tert*-butyl acrylate)]₂ (PS-*b*-PtBA₂) copolymers by Atom Transfer Radical Polymerisation (ATRP) using a multi-step route involving protecting group chemistry.⁶ Hydrolysis resulted in the removal of the *tert*-butyl groups and the formation of amphiphilic PS-*b*-PAA₂ copolymers. In a recent review article Haddleton and co-workers also briefly mentioned the synthesis of an ABA₂-type block copolymer, again using ATRP in combination with protecting group chemistry.⁷

Stimulus-responsive linear diblock copolymers have been extensively studied both in our research group and also by others.⁸ However, to the best of our knowledge, stimulus-responsive block copolymers with *non-linear* architectures have not yet been studied. Herein we describe the first direct synthesis of a wide range of well-defined, stimulus-responsive, Y-shaped block copolymers under mild conditions, as shown in Fig. 1.

Firstly, Jeffamine JM1000, a monoamine-capped statistical copolymer of ethylene oxide (EO) and propylene oxide (PO) (EO/PO molar ratio = 19/3) with $M_n = 1000 \text{ g mol}^{-1}$ and $M_w/M_n =$

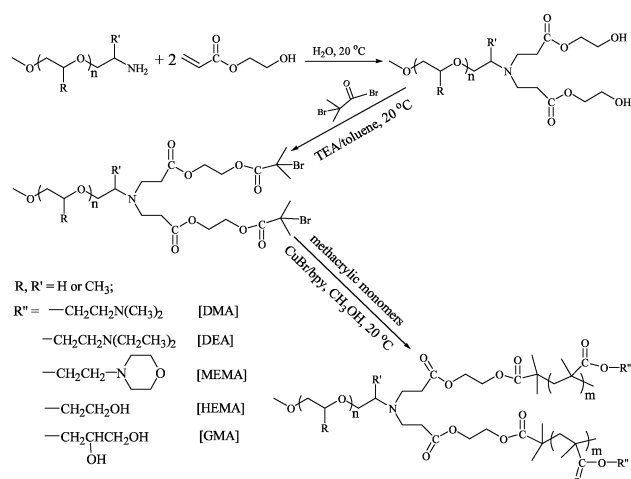


Fig. 1 Direct synthesis of poly(alkylene oxide)-based Y-shaped block copolymers from a primary amine-functional polymeric Jeffamine precursor using ATRP.

† Electronic Supplementary Information (ESI) available: synthesis and characterisation of diblock copolymers. See <http://www.rsc.org/suppdata/cc/b4/b400161c/>

1.10, a gift from Huntsman Chemicals (UK), was used as a precursor for the bifunctional ATRP macro-initiator synthesis. The terminal primary amine group on the JM1000 was reacted with excess 2-hydroxyethyl acrylate (HEA; HEA/R-NH₂ molar ratio = 6.0) *via* Michael addition, affording a macro-initiator precursor with two hydroxy groups at one end. Water (5 wt.% relative to JM1000) was added to accelerate this reaction.⁹ After stirring for five days at 20 °C, ¹H NMR analysis indicated complete reaction. The bifunctional ATRP macro-initiator (JM1000-Br₂) was obtained by esterification of this dihydroxy-functionalised JM1000 with excess 2-bromoisobutryl bromide (see Fig. 1). THF GPC analyses (vs. PMMA standards) of this macro-initiator indicated an M_n of 2100 and an M_w/M_n of 1.10.

A series of hydrophilic methacrylic monomers were polymerized *via* ATRP to obtain a range of Y-shaped copolymers, including stimulus-responsive examples (see Table 1). Since the poly(alkylene oxide) block is relatively short, it was considered important to restrict the degrees of polymerisation (DP_n) targeted during ATRP. However, high catalyst concentrations can lead to a high concentration of radicals being generated in the early stages of the polymerisation, which can lead to unwanted termination and reduced control. For example, for the ATRP of DMA in 50% methanol at a [DMA] : [JM1000-Br₂] : [CuBr] : [bpy] relative molar ratio of 20 : 1 : 1 : 2 (i.e. a mean DP_n of 10 for each DMA block), GPC analysis at 90% conversion (achieved within 1 h at 20 °C) indicated an M_n of 4200 and an M_w/M_n of 1.37, with a pronounced low molecular weight tail. This suggested that significant radical coupling occurred in the early stages of this polymerisation. In contrast, at a [DMA] : [JM1000-Br₂] : [CuBr] : [bpy] relative molar ratio of 20 : 1 : 0.5 : 1 under the same conditions, the DMA conversion reached 98% after 5 h and a significantly lower polydispersity of 1.19 was obtained (see ESI, Fig. S1†). The relatively high M_n value of 7200 obtained by THF GPC analysis is due in part to the calibration error incurred using poly(methyl methacrylate) standards. Thus ATRP can be reasonably well controlled even at relatively low target degrees of polymerisation provided that lower catalyst concentrations are employed.

Linear PEO₂₃-*b*-DEA₁₀ and PEO₂₃-*b*-DEA₂₀ diblock copolymers were also synthesized using conventional monofunctional PEO-based macro-initiators (see ESI†) and their aqueous solution

Table 1 Synthesis parameters and molecular weight data obtained for copolymers synthesized by ATRP using the JM1000-Br₂ macro-initiator at a [monomer] : [JM1000-Br₂] : [CuBr] : [bpy] relative molar ratio of 20 : 1 : 0.5 : 1 in 50% methanol at 20 °C

Target Y-shaped diblock copolymers	Conv. ^a t/h (%)	$M_{n,NMR}$ g mol ⁻¹	$M_{n,GPC}$ g mol ⁻¹	M_w/M_n
JM1000- <i>b</i> -(DEA ₁₀) ₂	5.0 98	5200	8400 ^b	1.23
JM1000- <i>b</i> -(DMA ₁₀) ₂	5.0 98	4650	7200 ^b	1.19
JM1000- <i>b</i> -(MEMA ₁₀) ₂	5.0 96	5000	7400 ^b	1.16
JM1000- <i>b</i> -(HEMA ₁₀) ₂	4.5 99	4650	13100 ^c	1.18
JM1000- <i>b</i> -(GMA ₁₀) ₂	4.0 100	5900	12800 ^c	1.20

^a Conversions as determined from ¹H NMR studies. ^b Determined using THF GPC (vs. PMMA standards). ^c Determined using DMF GPC (vs. PMMA standards).

properties were compared with those of the non-linear Y-shaped JM1000-b-(DEA₁₀)₂ copolymer.

The pH-responsive micellar self-assembly of the JM1000-b-(DEA₁₀)₂ copolymer was investigated by ¹H NMR spectroscopy, dynamic light scattering (DLS) and surface tensiometry. In acidic solution, both blocks were molecularly dissolved into water. Thus all the expected signals for the JM1000 block and the protonated DEA residues are detected by ¹H NMR (see Fig. 2), and no colloidal aggregates were detected by DLS. The light scattering intensity increases dramatically at around pH 7.3, which corresponds to the approximate pK_a of the DEA residues.¹¹ This indicates that micellar self-assembly occurs and indeed near-monodisperse micelles with a hydrodynamic diameter (*D*_h) of 45 nm and polydispersity index μ_2/I^2 of 0.054–0.077 were detected from pH 7.4 to pH 11.3. Under these conditions, only the ¹H NMR signals due to the JM1000 block are detected (see Fig. 2), which indicates that the non-solvated DEA blocks form the micelle cores. The copolymer surface activity also depends on the solution pH (see ESI, Fig. S2†). Above pH 7, the DEA block is relatively hydrophobic and hence strongly adsorbed at the air–water interface; thus high surface activity (low surface tension) is observed. Below pH 7, the DEA residues become protonated and copolymer desorption from the interface occurred, resulting in much lower surface activity (higher surface tension).

Similar pH-dependent micellisation and surface activity behaviour were observed for the linear PEO₂₃-b-DEA₁₀ and PEO₂₃-b-DEA₂₀ diblock copolymers. However, the PEO₂₃-b-DEA₂₀ copolymer had a larger *D*_h of 53 nm and the PEO₂₃-b-DEA₁₀ copolymer had a smaller *D*_h of 33 nm. Thus the non-linear JM1000-b-(DEA₁₀)₂ copolymer forms micelles of intermediate diameter (45 nm). The surface activity of JM1000-b-(DEA₁₀)₂ is the lowest of these three copolymers (see ESI, Fig. S2†). Presumably this is due to the less efficient self-assembly of this Y-shaped copolymer at the aqueous/air surface.

Acidic Y-shaped copolymers were also readily obtained by esterification of the JM1000-b-(HEMA₁₀)₂ and JM1000-b-(GMA₁₀)₂ Y-shaped copolymers using succinic anhydride in

anhydrous pyridine at 20 °C.¹⁰ As shown in ESI Fig. S3,† the ¹H NMR signal assigned to the HEMA residues at δ 3.9 disappeared and a new signal assigned to the 2-succinyloxyethyl methacrylate (SEMA) residues at δ 2.8 was observed. ¹H NMR analysis confirmed that very high degrees of esterification were achieved (>95%). The micellar self-assembly behaviour of these new carboxylic acid-based Y-shaped copolymers was complementary to that of the JM1000-b-(DEA₁₀)₂ copolymer: molecular dissolution occurred at neutral or alkaline pH but SEMA-core micelles were formed at low pH, since the SEMA blocks are hydrophobic in their free acid (neutral) form.

The same synthetic route to Y-shaped AB₂ copolymers was also employed using a second Jeffamine precursor, JM2005 (*M*_n = 2000, *M*_w/*M*_n = 1.08). This is also a primary amine-functionalised statistical copolymer but it contains 29 PO and 6 EO units, in contrast to the EO-rich JM1000 precursor. Michael addition with HEA (HEA/R-NH₂ molar ratio = 5.0) proceeded more slowly with JM2005 but was complete within four days at 50 °C in the presence of added water. Esterification of this bishydroxy precursor was essentially complete after 72 h at 20 °C. This ATRP macro-initiator was used to polymerise GMA in methanol at 20 °C. This produced the target Y-shaped JM2005-b-(GMA₂₀)₂ copolymer, which exhibited thermo-responsive micellisation (see ESI, Fig. S4†) due to the inverse temperature solubility behaviour of the JM2005 component (the GMA blocks remain permanently hydrophilic regardless of the pH and solution temperature).

In summary, a wide range of new stimulus-responsive Y-shaped copolymers have been prepared *via* ATRP under mild conditions. Our synthetic route is a significant improvement on literature syntheses, since it avoids protecting group chemistry and also allows access to several types of stimulus-responsive block copolymers. Polymerisation of tertiary amine- or hydroxy-functional methacrylates is straightforward and high-yielding: moreover, acidic Y-shaped copolymers can be easily obtained by reacting the hydroxy-functional copolymers with succinic anhydride under mild conditions. Finally, it is shown that the non-linear copolymer architecture can lead to subtle differences in both the micellar self-assembly and the surface activity of these Y-shaped copolymers in aqueous solution.

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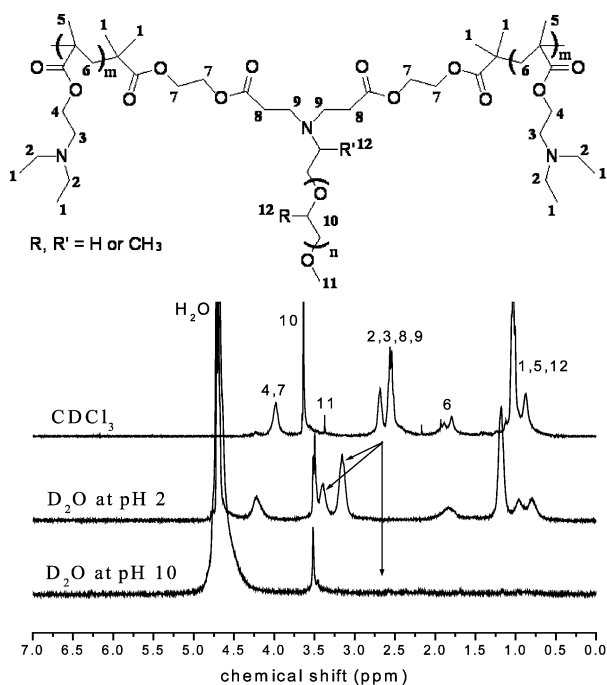


Fig. 2 ¹H NMR spectra obtained for the JM1000-b-(DEA₁₀)₂ copolymer in CDCl₃ and D₂O (at pH 2 and 10 respectively).