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Well-defined polyelectrolytes and polyzwitterions via aqueous Cu(0)-mediated living radical polymerisation

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The scope of aqueous single electron transfer living radical polymerisation has been expanded for the preparation of a range of polyelectrolyes and polyzwitterions. Manipulation of the reaction conditions furnishes well-defined polymers, capable of undergoing chain extension and the synthesis of block copolymers at 0 °C.

Polyelectrolytes are key ingredients that have been employed as rheology modifiers, absorbents, coatings, hydrogel swelling agents, stabilisers and key components of biological devices and membranes. They are macromolecules that contain ionisable groups capable of undergoing dissociation in aqueous solution resulting in the accumulation of charge which occurs with concomitant release of counter-ions into solution.[1] This build-up of charge engenders distinguishing surface and solution properties into polyelectrolytes which differentiates them from neutral polymers.[2] At the simplest, non-quantitative level, accumulated charge results in intra chain repulsive interactions that impose a more extended and less coil-like, conformation as compared to neutral polymers. The effect of repulsion can be dissipated by the addition of electrolyte solutes which can shield the prevailing polymer charge leading to adoption of a more common coiled conformation.[3, 4]

The opposite, or 'anti-polyelectrolyte effect,' is true for polyzwitterions,[5] which incorporate monomers, such as sulfobetaine, carboxybetaine and phosphorylcholine, into the polymer. In aqueous solution opposing charges promote intra chain charge shielding leading to a coil-like conformation which can be swollen, and expanded, upon addition of electrolytes. Furthermore, betaine monomers give additional properties including variable wettability (super hydrophilicity of phosphorylcholine vs UCST phenomenon of sulfobetaines), bio- and heamocompatibility and universal low-fouling potential.[6-10]

Thus, the properties of polyelectrolytes and polyzwitterions in aqueous solution make them attractive targets for controlled radical polymerisation, however, they also make handling and characterising the monomers and ensuing polymers challenging. Nevertheless, a number of groups have been successful in the polymerisation of some common electrolytic monomers. For example, 2-acrylamido-2-methylpropane sulfonic acid (AMPS) and its sodium salt (NaAMPS) have been employed in atom transfer radical polymerisation (ATRP) and reversible addition fragmentation chain transfer polymerisation (RAFT).[11-16] Likewise, both ATRP and RAFT have been exploited for the controlled polymerisation of betaine monomers.[17-22] The resulting polymers have found use in protein/peptide conjugation[23] and surface modification technologies[24, 25] as well as in the fabrication of polymer nanoparticles[26-30] decorated in, and possessing the desirable properties of polyzwitterionic constituents.

The solubility of electrolytes and zwitterions[31] dictates that the polymerisation is limited to aqueous solution or binary mixtures with complimentary, highly polar organic solvents (*e.g.* MeOH). In 2013, an aqueous based variation of Cu-mediated living radical polymerisation (Cu(0)-mediated LRP) was introduced.[32] Relying on the rapid disproportionation of Cu(I)Br/*N*-aliphatic ligand complexes in water, this technique facilitates the rapid polymerisation of (meth)acrylates and acrylamides at ambient temperature and below and is most commonly carried out at 0 °C so as to reduce any increase in reaction temperature from the reaction exotherm.

Since the introduction of aqueous Cu(0)-mediated LRP, a number of investigations have been carried out to ascertain the scope and limitations of this reaction. Primarily, the polymerisation has been shown to be tolerant of complex aqueous mixtures,[33, 34] whilst ongoing work includes investigations into monomer compatibility as well as the degree of functionality present in the initiating species.

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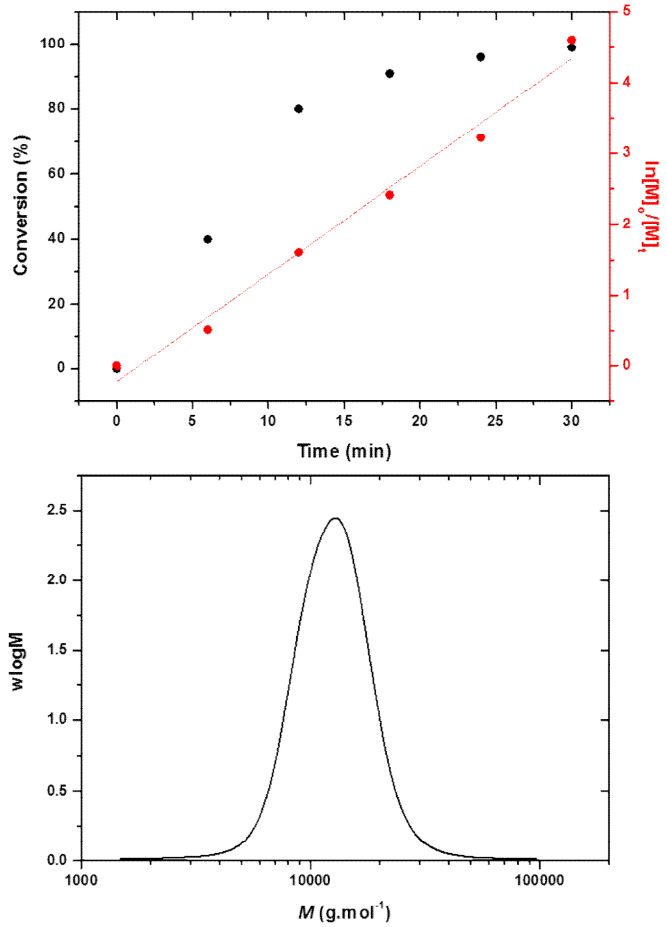
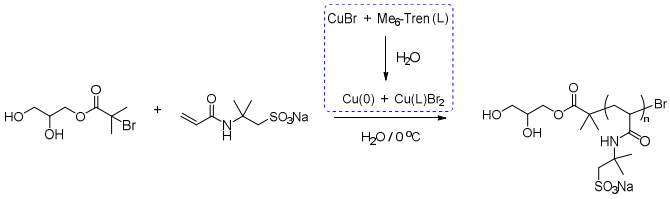


Fig. 1 Kinetic data for the polymerisation of AMPS (top) and the aqueous SEC of PNaAMPS using [NaAMPS] : [I] : [CuBr] : [Me_6-Tren] = [20] : [1] : [0.4] : [4], M_n= 11500 g.mol^{-1} $Đ$ = 1.16.

To this end, functional initiators have been employed for the preparation of α-functional and α,ω-telechelic linear polymers capable of undergoing further chemistry at their chain terminii, such as conjugation to peptides and the introduction of hydrophobic moieties.[35, 36] Furthermore, multifunctional initiating species, derived from proteins, have been prepared and aqueous Cu(0)-mediated LRP has been demonstrated in a 'grafting-from' process.[37] Herein, we report, the use of aqueous Cu(0)-mediated LRP for the synthesis of polyacrylate and polyacrylamide polyelectrolytes, containing a neutralised sulfonic acid group, as well as acrylic phosphorylcholine derived polyzwitterions.

A caveat of the aqueous system which needs to be noted is the frequent requirement to adjust the polymerisations conditions, particularly the [I] : [CuBr] : [Me_6-Tren], depending on the targeted degree of polymerisation (DP$_{n,th}$). In line with previous investigations, the initial polymerisation of NaAMPS (50 wt.% in H_2O) was carried out using [NaAMPS] : [I] : [CuBr] : [Me_6-Tren] = [20] : [1] : [0.4] : [4]; conditions which have proved to be almost universal for the polymerisation of a variety of acrylates and acrylamides

Table 1. Synthesis of PNaAMPS with various *DP via* aqueous Cu(0)-mediated LRP



DP	[Cu]:[L]	Time (min)	Conv. (%)	$M_{n,th}$ (g.mol^{-1})	*$M_{n,SEC}$ (g.mol^{-1})	*$Đ$
20	[0.4]:[0.4]	30	100	4800	11500 (4600)	1.16
40	[0.4]:[0.4]	30	100	9400	23500 (10500)	1.20
80	[0.8]:[0.4]	30	100	18600	29700 (19700)	1.30
160	[0.8]:[0.4]	30	100	36900	43000	2.00
160	[1.6]:[1]	30	100	36900	42000	1.70

* Determined by aqueous SEC (see ESI for conditions).
Number in parentheses are those obtained from ^{1}H NMR (not applicable for DP = 160).

with a target DP$_{n,th}$ = 20.[32] The polymerisation was monitored by ^{1}H NMR which showed full monomer conversion within 30 min, according to disappearance of the vinyl signals between 5.5 and 6.5 ppm (Figure S1). The controlled nature of the polymerisation was demonstrated by aqueous SEC, which showed a symmetrical, mono-modal molecular weight distribution ($M_{n,SEC}$ = 11500 g.mol^{-1}, $Đ$ = 1.16) with kinetic analysis revealing a relatively linear increase of ln([M]$_0$/[M]$_t$) *vs.* time (Figure 1).

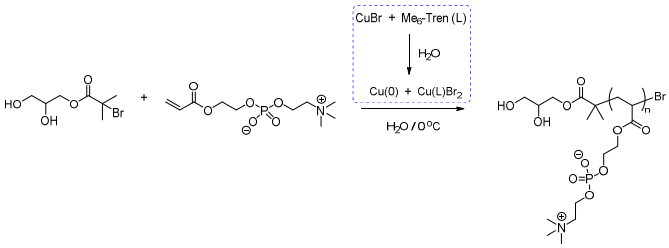
Under identical conditions, the full polymerisation of NaAMPS (DP$_{n,th}$ = 40) was also complete within 30 mins, with comparable control retained throughout the reaction ($M_{n,SEC}$ = 23500 g.mol^{-1}, $Đ$ = 1.20, Table 1, Figure S2). When targeting DP$_{n,th}$ ≥ 80, optimised conditions of [I] : [CuBr] : [Me_6-Tren] = [1] : [0.8] : [0.4] have been established. Under these conditions the amount of deactivating species [Cu(Me_6-Tren)Br_2] formed during the disproportionation step is maximised which enhances the control over the polymerisation without compromising the rate of reaction. Thus, the polymerisation of NaAMPS was realised using [NaAMPS] : [I] : [CuBr] : [Me_6-Tren] = [80] : [1] : [0.8] : [0.4] ($M_{n,SEC}$ = 29700 g.mol^{-1}, $Đ$ = 1.30, Table 1, Figure S3). Attempts to prepare higher molecular weight PNaAMPS (DP$_{n,th}$ = 160) were unsuccessful (Table 1, Figure S4-S5).

A similar trend was observed with sulfopropyl acrylate potassium salt (KSPA) monomer. Short chain PKSPA (DP$_{n,th}$ ≤ 40) was synthesised using [I] : [CuBr] : [Me_6-Tren] = [1] : [0.4] : [0.4] ($Đ$ ≈ 1.20), whereas longer chain PKSPA (DP$_{n,th}$ = 80) again required an increased amount of deactivating species to be formed in the disproportionation step. In this case [I] : [CuBr] : [Me_6-Tren] = [1] : [0.6] : [0.4] was sufficient to regain control over the polymerisation ($Đ$ ≈ 1.31, Table S1, Figure S6). Under the same conditions the dispersity was found to increase when

higher molecular weight polymers were targeted ($DP_{n,th}$ = 160, 320, $Đ \approx$ 1.47-1.84).

The polymerisation of the zwitterionic biocompatible monomer 2-methacryloyloxyethyl phosphorylcholine (MPC) has been studied and the ensuing properties of the polymers in solution and on surfaces have been characterised.[19, 20, 38] However,

Table 2. Synthesis of PAPC *via* aqueous Cu(0)-mediated LRP



DP	[Cu]:[L]	Time (min)	Conv. (%)	$M_{n,th}$ (g.mol^{-1})	*$M_{n,SEC}$ (g.mol^{-1})	*$Đ$
10	[0.4]:[0.4]	30	100	3100	2800 (3100)	1.16
20	[0.6]:[0.8]	30	100	5900	4300 (5600)	1.20
50	[0.8]:[1.0]	120	93	14300	6900 (14900)	1.30
100	[1.0]:[1.2]	1140	45	28400	7100 (34200)	2.00

* Determined by aqueous SEC (see ESI for conditions).
Number in parentheses are those obtained from ^{1}H NMR.

the controlled polymerisation of the acrylate analogue, 2-acryloyloxyethyl phosphorylcholine (APC) has not yet been reported. Using aqueous Cu(0)-mediated LRP, low molecular weight ($DP_{n,th}$ = 10) PAPC was synthesised using [I] : [CuBr] : [Me_6-Tren] = [1] : [0.4] : [0.4] ($Đ \approx$ 1.07). Furthermore, manipulation of the [I] : [CuBr] : [Me_6-Tren] providing access to PAPC up to $DP_{n,th}$ = 50 ($M_{n,NMR}$ = 3100-14900 g.mol^{-1}, $Đ$ = 1.07-1.22, Table 2, Figure S7), which proved to be the limit in this investigation as when higher molecular weights were targeted ($DP_{n,th}$ = 100) conversion was limited to < 50%.

A defining characteristic of controlled radical polymerisation is the retention of active chain end(s) enabling the synthesis of well defined (multi)block copolymers via sequential monomer addition,[39-41]. Using aqueous Cu(0)-mediated LRP the *in-situ* chain extension and block copolymerisation of PNaAMPS (Table S2) and PAPC (Table S3) were investigated. Under optimised conditions ([NaAMPS] : [I] : [CuBr] : [Me_6-Tren] = [20] : [1] : [0.4] : [4]), the homopolymerisation of NaAMPS was complete within 30 mins at which point an aliquot of NaAMPS in water (50 wt%, N_2 purged, $DP_{n,th}$ = 20) was injected to the reaction medium. Within 30 mins (60 min total reaction time) chain extension was complete, according to ^{1}H NMR (>99 %, Figure S8) furnishing P[$(NaAMPS)_{20}$-*b*-$(AMPS)_{20}$]. SEC analysis indicated a controlled chain extension with a shift to higher molecular weight and retention of the low dispersity (M_n = 18000 g.mol^{-1}, $Đ$ = 1.21, Figure 2) exhibited by the homopolymer. Likewise, low molecular weight PAPC (DP_n = 10) was synthesised and successfully chain extended *in situ* upon addition of a second, followed by a third, aliquot of APC (50 wt%, N_2 purged, $DP_{n,th}$ = 10). The initial chain extension was complete (>99%) within 60 min whilst the second chain extension, yielding a pseudo triblock, was complete with 120 min (210 min total). Control was maintained throughout the polymerisation and each subsequent chain extension, exemplified by good agreement between $M_{n,th}$ and $M_{n,NMR}$ and the low dispersity of the final P[$(APC)_{10}$-*b*-$(APC)_{10}$-*b*-$(APC)_{10}$] polymer ($Đ$ = 1.23, Figure S9).

Double hydrophilic block copolymers containing NaAMPS were prepared from linear a poly(ethylene glycol) macroinitiator (Table S4) and P(polyethylene glycol methyl ether acrylate) (PPEGA) and P(2-hydroxyethyl acrylamide) (PHEAm) macroinitiator synthesised *in situ* using the aqueous conditions (Table S2). The linear PEG initiator was prepared according to previous literature[42] and employed for the polymerisation of NaAMPS using [NaAMPS] : [I] : [CuBr] : [Me_6-Tren] = [100]/[50]/[25] : [1] : [0.8] : [0.4]. Well controlled block copolymers were obtained when targeting low molecular weights (DP_n = 25/50) with good agreement $M_{n,th}$ and $M_{n,SEC}$ and low dispersities according to SEC ($Đ$ < 1.35, Figure S10). However, when targeting higher molecular weights (DP_n = 100), although good agreement $M_{n,th}$ and $M_{n,NMR}$ was obtained, the dispersity of the resulting polymer significantly increased ($Đ$ > 1.80).

Synthesis of PPEGA and PHEAm macroinitiators using [PEGA]/[HEAm] : [I] : [CuBr] : [Me_6-Tren] = [10]/[20] : [1] : [0.4] : [0.4] was complete within 30 mins at which point an aliquot of NaAMPS (50 wt%, N_2 purged, $DP_{n,th}$ = 20) was added to each reaction. Copolymerisation was complete within 30 min in both reactions (Figure S11-S12) and SEC analysis revealed shifts to higher molecular weight and low dispersity values for the P[$(PEGA)_{10}$-*b*-$(NaAMPS)_{20}$] ($Đ$ = 1.30) and P[$(HEAm)_{20}$-*b*-$(NaAMPS)_{20}$] ($Đ$ = 1.15) respectively (Figure 2 b,c). Block copolymerisation was also attempted from a PNaAMPS macroinitiator (Figure S13-S14) using *N*-Isopropylacrylamide (NIPAm) as the comonomer. Copolymerisation was complete within 30 min of the addition of an aliquot of NIPAm (50 wt%, N_2 purged, $DP_{n,th}$ = 20) to the PNaAMPS macroinitiator. Unfortunately, SEC analysis of the targeted P[$(NaAMPS)_{20}$-*b*-$(NIPAm)_{20}$] copolymer was not possible due to the insolubility to the copolymer in DMF and H_2O under the operating conditions of the SEC.

PAPC decorated polymer nanoparticles with high biocompatibility and low fouling potential were prepared from a P[(APC)-*b*-(NIPAm)] block copolymer (Table S5). The PAPC macroinitiator was synthesised ([APC] : [I] : [CuBr] : [Me_6-Tren] =

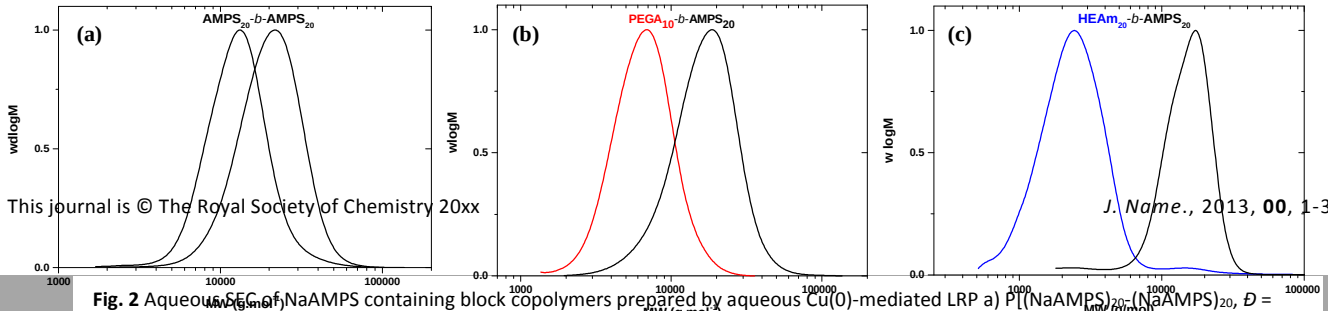


Fig. 2 Aqueous SEC of NaAMPS containing block copolymers prepared by aqueous Cu(0)-mediated LRP a) P[$(NaAMPS)_{20}$-$(NaAMPS)_{20}$, $Đ$ = 1.21; b) P[$(PEGA)_{10}$-$(NaAMPS)_{20}$, $Đ$ = 1.30; c) P[$(HEAm)_{20}$-$(NaAMPS)_{20}$, $Đ$ = 1.15.

[10] : [1] : [0.8] : [0.6]) within 60 min and chain extended, *in situ*, upon addition of an aliquot of NIPAm (50 wt%, N_2 purged, $DP_{n,th}$ = 80). A sample taken after 5 hours revealed high total monomer conversion (96 %). The presence of both APC and NIPAm monomers in the resulting block copolymer was confirmed by ^{1}H NMR (Figure S15) following purification by dialysis (3500 g.mol^{-1}, NMWCO) against water at ambient temperature. Molecular weight and dispersity analysis by SEC was again not possible due to the insolubility of the copolymer under the operating conditions of the SEC. Further support for the block copolymer structure was obtained from comparison of the LCST of the block copolymer (43 °C) with a PNIPAm homopolymer of comparable chain length (≈ 40 °C), also prepared by aqueous Cu(0)-mediated LRP. This thermal transition was exploited to assemble the P[$(APC)_{10}$-*b*-$(NIPAm)_{80}$] into low dispersity polymeric nanoparticles above the LCST (50 °C, Z_{av} = 29 nm, PDi = 0.086, Figure S16). When allowed to cool below the LCST the nanoparticles disassembled yielding unimers, as well as some higher ordered aggregates, which reorganised into nanoparticles upon reheating above the LCST for a second time with little hysteresis (50 °C, Z_{av} = 28 nm, PDi = 0.093, Figure S17). Although this provides minimal insight into the level of control exerted throughout the chain extension reaction, it does indicate that polymerisation occurred from the PAPC macroinitiator, and confirms the targeted block copolymer composition.

Conclusions

Aqueous Cu(0)-mediated LRP has been employed for the synthesis of polyelectrolytes and polyzwitterions. Controlled polymerisation of neutralised sulfonic acid containing monomers (AMPS, SPA) and a phosphorylcholine monomer (APC) was possible employing monomer-specific [I] : [CuBr] : [Me_6-Tren] ratios, which has proved to be a common feature of the aqueous system. The controlled nature of the polymerisations has been exemplified by the series of chain extensions and block polymerisations using PAMPS and PAPC macroinitiators prepared *in situ*. This has enabled the synthesis of thermoresponsive double hydrophilic diblock copolymers, P[$(AMPS)_{20}$-*b*-$(NIPAm)_{20}$] and P[$(APC)_{10}$-*b*-$(NIPAm)_{80}$], the latter of which was shown to reversibly assemble into narrowly dispersed polymeric nanoparticles above the LCST of the P[$(APC)_{10}$-*b*-$(NIPAm)_{80}$] diblock copolymer.

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