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Novel α,α-Bischolesteryl Functional (Co)Polymers: RAFT Radical Polymerization Synthesis and Preliminary Solution Characterization

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Abstract

Well-defined poly[pentafluorophenyl (meth)acrylate] (PPFP(M)A) homopolymers are prepared by RAFT radical polymerisation mediated by a novel chain transfer agent containing two cholesteryl groups in the R-group fragment. Subsequent reaction with a series of small molecule amines in the presence of an appropriate Michael acceptor for ω-group end-capping yielded a library of novel bis cholesteryl functional hydrophilic homopolymers. Two examples of statistical copolymers were also prepared including a biologically relevant sugar derivative. Specific examples of these homopolymers were examined with respect to their ability to self assemble in aqueous media – a process driven entirely by the cholesteryl end groups. In all instances evaluated, and under the preparation conditions examined, the *homopolymers* aggregated clearly forming polymersomes spanning an impressive size range.

1. Introduction

The self-directed assembly of amphiphilic surfactants and copolymers in a selective solvent at, or above, a critical temperature and concentration is well documented and results in the formation of nano-sized particles with an impressive range of solution morphologies including micelles, cylinders and vesicles.[1] In the case of polymers this has involved, by necessity, the synthesis of suitable amphiphilic block copolymers that may have AB, ABA or ABC-type topologies with suitable molar compositions. As a consequence of the required block architecture, an appropriate polymerization technique must be employed that allows for the control of copolymer molecular weight, composition (hydrophilic-hydrophobic balance) and dispersity, since each of these features is known to play a role in the self-assembly process and on the final solution morphology formed.[2] Fortunately, the discovery and development of the suite of reversible deactivation radical polymerisations (RDRPs) now allows for the direct synthesis of almost any conceivable type of block copolymer with respect to functionality, composition, topology and overall architecture.

In homopolymers, or copolymers, of sufficiently low molecular weight the nature of the end-groups becomes an important consideration with respect to the bulk and solution properties since these groups can represent an overall significant weight/molar fraction of the polymeric material.[3] For example, Furyk et al.[4] have evaluated the effect of end groups on the lower critical solution temperature (LCST) of poly(*N*-isopropylacrylamide) (PNIPAM), and in a similar vein, Li and co-workers[5] homopolymerised *N,N*-diethylacrylamide (DEA) via 1-cyano-1-methylethyldithiobenzoate-mediated RAFT to give a homopolymer with a calculated average degree of polymerisation ($\bar{X}_n$) of 30 ($\bar{M}_n$ = 3,800 and $Đ_M = \bar{M}_w/\bar{M}_n$ = 1.10) and a corresponding cloud point (CP, 1 wt% aqueous solution) of 23°C. Cleavage of the ω-thiocarbonylthio end groups to the corresponding macromolecular thiol followed by base

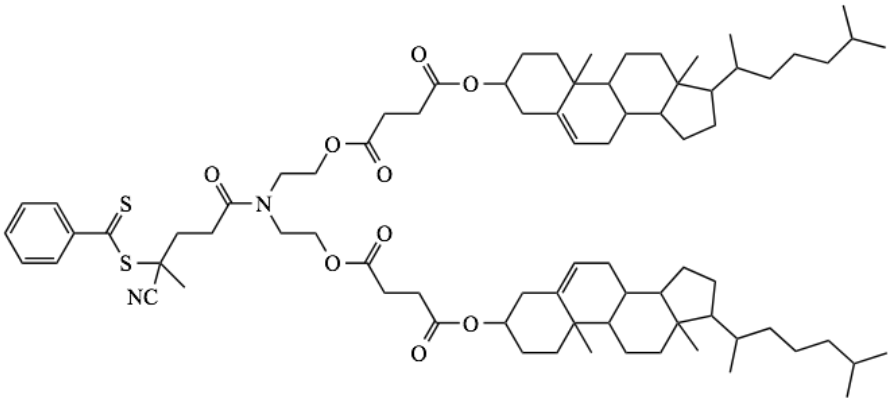
catalysed reaction with a series of small hydrophobic isocyanates yielded a family of thiocarbamate functional poly(DEA)s (PDEAs). The measured CPs of these functional, hydrophilic homopolymer derivatives were found to range from 23-34 °C with the only structural variable being the chemical nature of the thiocarbamate end group. While these two examples highlight the effect of end groups on inverse temperature dependent solubility characteristics of two common thermoresponsive polymers, end groups can also affect other properties. Qui et al.[6] reported the effect of introducing cholesterol (Chol) groups at one and both ends of a low molecular weight poly(ethylene glycol) (PEG, $\bar{M}_n$ = 2,000) and noted that the Chol groups retarded the crystallization process and decreased the overall degree of crystallinity.

Given its high propensity towards self-association/organization, Chol has been widely employed as a hydrophobic end-group (either incorporated at one chain terminus or in dual α,ω-functional species (telechelics), and in the modification of naturally occurring sugars.[7] For example, Sugiyama, Shiraishi and Matsumoto[8] reported the synthesis of poly[2-(methacryloyloxy)ethyl phosphorylcholine] (PMPC) with Chol as one α-terminal group or two (α,ω-functionalisation) groups via the radical polymerization of MPC with the Chol functional azo initiator 4,4'-azobis[(3-cholesteryl)-4-cyanopentanoate] in the presence of 2-mercaptoethanol or thiocholesterol as chain transfer agents respectively. The self-assembly of these end functional hydrophilic polymers in aqueous media was confirmed using a combination of NMR spectroscopy and fluorescence measurements although no attempt was made at determining the morphology of the aggregates. More recently, Segui, Qiu and Winnik[9] reported the synthesis and self-assembly of PNIPAM, prepared by RAFT, functionalized at the α and ω termini with Chol or pyrenyl (Py) groups. The parent PNIPAM homopolymers ($\bar{M}_n$'s ranging from 7,800 - 44,500 as determined by multi angle laser light scattering (MALLS)) were prepared with a difunctional trithiocarbonate as the RAFT chain

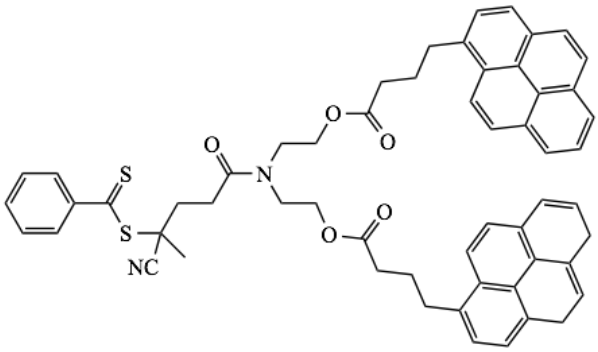
transfer agent yielding PNIPAMs with thiocarbonylthio groups at both chain ends. Aminolysis of these groups gave the corresponding dithiol PNIPAMs that were then reacted with iodo-derivatives of Chol and Py to give the novel telechelic species. Qualitative evidence for the self-association of these end-functional homopolymers was obtained by NMR spectroscopy, while fluorescence measurements were employed to determine the critical aggregation concentration and confirm the occurrence of inter and/or intra-chain associations. Again, no attempt was made in this initial report to determine the size or morphology of the self-associated species.

In the examples highlighted above the hydrophobic group is instilled as either a single species at one chain termini or in parent polymers containing two hydrophobic groups (these may or may not be the same) at the α and ω chain ends. There is also the possibility of installing two, or more, hydrophobic groups at a single chain end although examples of such species are less common. Xu and co-workers[10] recently reported the preparation of six novel RAFT phenyl dithioester-based chain transfer agents including examples containing two Chol or Py groups in the R fragment, Figure 1. RAFT homopolymerization of *N,N*-dimethylacrylamide (DMA) and *N*-(2-hydroxypropyl) methacrylamide (HPMA) with these two novel chain transfer agents (as well as others) gave a series of hydrophilic homopolymers with low-to-medium measured $\overline{M}_n$'s, and $Đ_M$'s ≤ 1.19. The ability of these α,α-bis functional homopolymers to self-assemble in aqueous media was then evaluated. As a representative example, a polyDMA (PDMA) with two Py groups (PDMA-diPy) and an $\overline{M}_n$ of ca. 6,000 and a polyHPMA (PHPMA) with two Chol groups (PHPMA-diChol) and $\overline{M}_n$ also of ca. 6,000 both self-assembled in aqueous media to form spherical polyniosomes (non-ionic polymersomes, ~200-600 nm in size) albeit with a fairly broad size distribution. Importantly though, these examples highlighted that in contrast to amphiphilic AB diblock copolymers that typically require ≥ 50 % (wt or mol fraction) hydrophobic species to form polymersomes, these homopolymers contained < 10%

by weight hydrophobic end groups yet still readily formed vesicular structures. It was postulated that the presence of the two, spatially close, cyclic-based end groups was one of the primary driving forces for this self-assembly and resulting morphology.



CTA1



CTA2

Figure 1. Chemical structures of the Chol and Py functional RAFT chain transfer agents, *O*,*O*'-(((4-cyano-4-((phenylcarbonothioyl)thio)pentanoyl)azanediyl)bis (ethane-2,1-diyl))bis(10,13-dimethyl-17-(6-methylheptan-2-yl)-2,3,4,7,8,9,10,11, 12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl) disuccinate (**CTA1**) and 2-(4-cyano-4-((phenylcarbonothioyl)thio)-*N*-(2-((4-(pyren-1-yl)butanoyl)oxy)ethyl)pentanamido)ethyl 4-(4,6-dihydropyren-1-yl)butanoate (**CTA2**).

In this contribution we expand on this limited number of α,α-difunctional homopolymers and this novel self-assembly/organization technique, and report the RAFT synthesis of a library of hydrophilic homopolymers, including biologically relevant sugar species, employing the bis Chol RAFT chain transfer agent **CTA1**, Figure 1. In contrast to the previous report where hydrophilic monomers were polymerized directly, herein we utilized pentafluorophenyl

(meth)acrylate monomers to prepare reactive scaffolds amenable to quantitative post-polymerization functionalization with primary and secondary amines.[11-15] The primary aim of this contribution is to highlight facile synthetic approaches to novel α,α-bis functional (co)polymers and, in preliminary solution studies, demonstrate that these materials can undergo self-directed assembly in aqueous media.

2. Experimental Section

2.1 Instrumentation. NMR spectroscopic measurements were performed on a Bruker Avance 300 MHz instrument. The internal solvent signals were used as reference (δ ($CDCl_3$) = 7.26 ppm, δ (D_2O) = 4.79 ppm).

Fourier transform infrared spectroscopy (FT-IR) was performed on a Bruker IFS 66/S instrument under attenuated total reflectance (ATR) and data was analysed on OPUS software version 4.0.

Size exclusion chromatography (SEC) in tetrahydrofuran (THF) or dimethylacetamide (DMAc) was performed on a Shimadzu system with four phenogel columns operating at a flow rate of 1 mL/min. The system was calibrated with a series of narrow molar mass distribution polystyrene (PS) standards with molar masses ranging from 0.58–1820 kg/mol.

Scanning electron microscopy (SEM) was conducted on a FEI Nova NanoSEM 230. Freeze dried samples were carefully deposited on a sticky carbon film and plasma-coated with a thin layer of chromium.

2.2 Materials. All reagents were purchased from Sigma-Aldrich and were used as received unless stated otherwise. Azobis(isobutyronitrile) (AIBN) was recrystallized from methanol and stored at –24 °C. The double cholesterol-functional chain transfer agent, **CTA1**, was prepared as described elsewhere.[10]

2.3 Synthesis of poly(pentafluorophenyl (meth)acrylate)s (PPFP(M)As). The target homopolymers of different molecular weights were prepared in analogy to the example given. PFPA (3.5 g, 14.7 mmol, 50 equiv), **CTA1** (383 mg, 0.294 mmol, 1 equiv), AIBN (9.6 mg, 0.059 mmol, 0.2 equiv), and 1,4-dioxane (5.5 mL) were combined in a flask, which was equipped with a stir bar and sealed with a rubber septum. The mixture was purged with nitrogen for 20 min and placed into a preheated oilbath (70 °C) and polymerized for 8 hours. The target polymer was isolated by two precipitations into methanol. $\bar{M}_{n,SEC}$ (THF) = 8.3 kg/mol, $Đ_M = \bar{M}_{w,SEC}/\bar{M}_{n,SEC}$ = 1.21; ^{19}F NMR (282 MHz, $CDCl_3$), δ/ppm = −153.2 (bm, 2 F, *ortho*), −157.1 (bs, 1 F, *para*), −162.4 (bs, 2 F, *meta*). FT-IR: υ/cm^{-1} = 1780 (carbonyl C=O stretch), 1520 (aryl C=C bend).

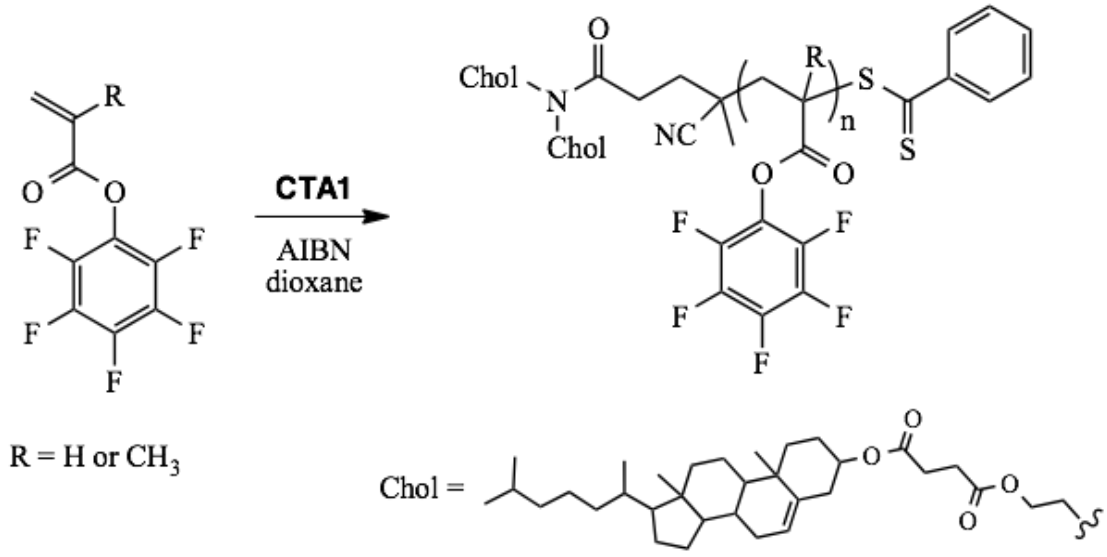
2.4 (Meth)Acrylamido homopolymers via conversion of PPFP(M)A with amines. A general procedure is given. PPFP(M)A (1 mmol of PFP units) was dissolved in THF (6 mL) and triethylamine (1.5 mmol) and amine (2-hydroxypropylamine, isopropylamine, *N*,*N*-diethylamine, *N*-ethylamine, or *N*-hydroxyethoxyethylamine, 10 mmol) and an acrylamide (isopropylacrylamide, hydroxyethylacrylamide, *N*,*N*-diethylacrylamide (3 mmol) were added and the mixture was stirred overnight before being subjected to dialysis in methanol (MWCO 3500 g/mol) for 3 days. The product poly(meth)acrylamides were isolated by removing methanol. The statistical copolymer poly(*N*-isopropyl methacrylamide$_{30}$-*co*-*N*-2-glucosmethacrylamide$_{70}$) was prepared by employing a mixture of isopropylamine,

glucosamine hydrochloride, and 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) in DMF. The molar composition was determined by ^{1}H NMR analysis. FT-IR: υ /cm^{-1} = 1650 (amide C=O stretch), 1550 (amide N–H bend). Poly(*N*-2-hydroxypropyl methacrylamide). ^{1}H NMR (300 MHz, $CDCl_3$), δ/ppm = 4.70 (bs, 1 H, –C<u>H</u>(OH)–); 3.68, 2.92 (2 bs, 2 H, –NHC<u>H</u>$_2$–); 2.08–1.40 (bm, 2 H, backbone –CH_2–); 1.15–0.78 (bm, backbone –CH_3, side group –CH_3). Poly(*N*-hydroxyethoxyethyl methacrylamide). ^{1}H NMR (300 MHz, $CDCl_3$,), δ/ppm = 3.69–3.04 (m, –CH_2–). Poly(*N*,*N*-diethyl acrylamide). ^{1}H NMR (300 MHz, $CDCl_3$,), δ/ppm = 3.16 (bm, 4 H, –N(C<u>H</u>$_2$CH$_3$)$_2$); 2.65 (bs, 1 H, backbone –CH$_2$C<u>H</u>R–), 1.63 (bm, 2 H, backbone –C<u>H</u>$_2$CHR–); 1.01 (bs, 6 H, –N(CH$_2$C<u>H</u>$_3$)$_2$). Poly(*N*-isopropyl acrylamide). ^{1}H NMR (300 MHz, $CDCl_3$,), δ/ppm = 3.92 (1 H, –C<u>H</u>(CH$_3$)$_2$, 0.94 (6 H, –CH(C<u>H</u>$_3$)$_2$). Poly(*N*-ethyl acrylamide). ^{1}H NMR (300 MHz, $CDCl_3$,), δ/ppm = 3.14 (bs, 2 H, –NHC<u>H</u>$_2$CH$_3$); 1.05 (bs, 3 H, –NHCH$_2$C<u>H</u>$_3$).

2.5 Synthesis of a statistical copolymer of poly(*N*-2-hydroxypropyl methacrylamide$_{89}$-*stat*-pentafluorophenyl methacrylate$_{11}$). A copolymer containing residual reactive PFP units was prepared by incomplete conversion of PPFPMA: PPFPMA (100.8 mg, 0.4 mmol of PFP groups) was dissolved in THF (1 mL). In parallel, 2-hydroxypropylamine (26.6 µL, 0.345 mmol), DBU (51 µL, 0.341 mmol), and 2-hydroxyethyl acrylamide (10.5 µL) were dissolved in THF (1 mL). The amine solution was added quickly into the polymer solution with rapid stirring overnight. A sample of the reaction was withdrawn and diluted with $CDCl_3$. A ^{19}F NMR measurement indicated 89% conversion of PFP groups by comparison of the broad PFP ester signals at δ/ppm = −150.5 (*ortho*), −157.9 (*para*), −162.4 (*meta*) with the signals of free pentafluorophenol at δ/ppm = −169.9 (*ortho*), −170.9 (*meta*), −187.5 (*para*). The product was isolated by dialysis as described above.

3. Results and Discussion

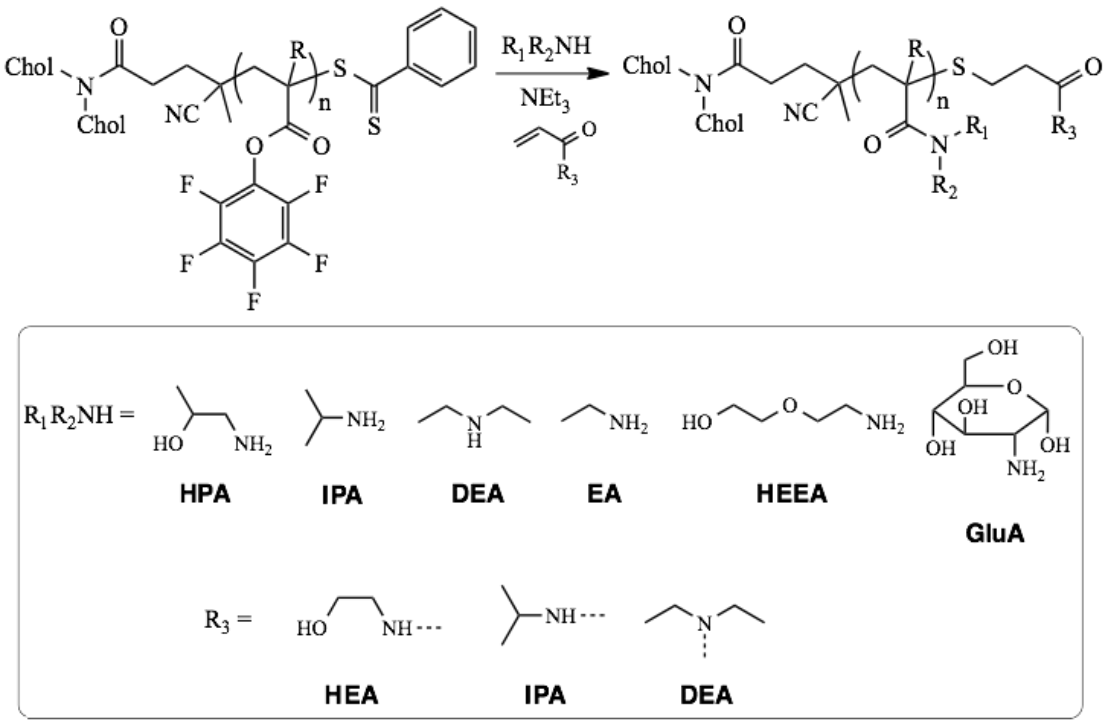
The general synthetic approach for the RAFT synthesis of pentafluorophenyl (meth)acrylate (PFP(M)A)-based homopolymers bearing two Chol groups at the α-terminus is shown in Scheme 1. Direct homopolymerisation of the PFPA and PFPMA species was accomplished under standard conditions in dioxane with **CTA1** as the RAFT chain transfer agent and AIBN as the radical source. In total, three homopolymers were prepared – one acrylic species (polyPFPA, $\bar{M}_{n,\,SEC}$ = 8,300 and $Đ_M$ = 1.21) and two methacrylic samples (polyPFPMA1, $\bar{M}_{n,\,SEC}$ = 9,400, $Đ_M$ = 1.25 and polyPFPMA2, $\bar{M}_{n,\,SEC}$ = 12,000 and $Đ_M$ = 1.30).



Scheme 1. Outline for the preparation of α,α-bis cholesteryl functional polyPFP(M)A homopolymers via RAFT radical polymerization mediated by **CTA1**.

The PFP(M)A monomers were chosen in this study for two important reasons. Firstly, polyPFP(M)A's react readily, and in most cases quantitatively, with both 1° and 2° amines in nucleophilic acyl substitution reactions yielding the corresponding amide derivatives;[11, 15] and secondly, the application of common reactive parent scaffolds facilitates an evaluation of the effect of monomer structure on the self-assembly process since the amide derivatives will possess identical average degrees of polymerization ($\bar{X}_n$). With three well-defined parent

homopolymers in hand we next converted then to a library of amide derivatives as outlined in Scheme 2. Two points are worth noting.



Scheme 2. Modification of parent poly(PFP(M)A) homopolymers with a library of small molecule amines in the presence of a suitable Michael acceptor for end capping reactions.

A wide range of functional polymers can be easily produced via this approach in straightforward reactions with simple small molecule amines to give 'common' polymeric derivatives. For example, reaction of polyPFP(M)A with 2-hydroxypropylamine (**HPA**) yields poly(*N*-(2-hydroxypropyl) (meth)acrylamide)s while treatment with isopropylamine (**IPA**) gives the corresponding poly(*N*-isopropyl (meth)acrylamide) derivatives. Additionally, reaction of the polyPFP(M)A parent scaffolds with a small excess of primary amines also results in the aminolysis of the thiocarbonylthio groups at the ω chain ends. This is not unexpected and represents the most common approach for removing such end groups in

RAFT-synthesized (co)polymers.[16, 17] However, to avoid oxidative coupling of the resulting macromolecular thiols the acyl substitution reactions of the polyPFP(M)A precursors were performed in the presence of an acrylamido-based Michael acceptor (3-hydroxypropyl acrylamide, *N*-isopropylacrylamide or *N,N*-diethylacrylamide) resulting in a thiol-Michael addition reaction following aminolysis of the thiocarbonylthio species. These were chosen to be structurally similar/identical to the small molecule amines employed in the side chain modification which offers the possibility of producing (co)polymers with no chemically distinct end group(s). The trapping of such polymeric thiols via sulfa-Michael coupling is well documented and also represents one of the more common approaches for end-modifying RAFT-prepared (co)polymers.[18, 19]

A small library of eight new α,α-bis Chol functional (meth)acrylamido (co)polymers were prepared as outlined above and summarized in Table 1. Quantitative conversion of the precursor reactive scaffolds to the (meth)acrylamido derivatives was confirmed using a combination of ^{1}H and ^{19}F NMR spectroscopy. For example, Figure 2 shows the ^{19}F NMR spectra for the polyDEAM sample (Table1) before reaction with DEA (A) showing resonances associated with the PFP residues in the parent polymer, the unpurified solution after reaction with DEA (B) showing F signals associated only with the small molecule pentafluorophenol by-product with no evidence of polymer-bound F, and finally the purified polyDEAM polymer (C) with the complete absence of any detectable F species. Similarly, Figure 2**B** shows a representative ^{1}H NMR spectrum of an amide derivative (with key resonances assigned), polyHPMAM Table 1.

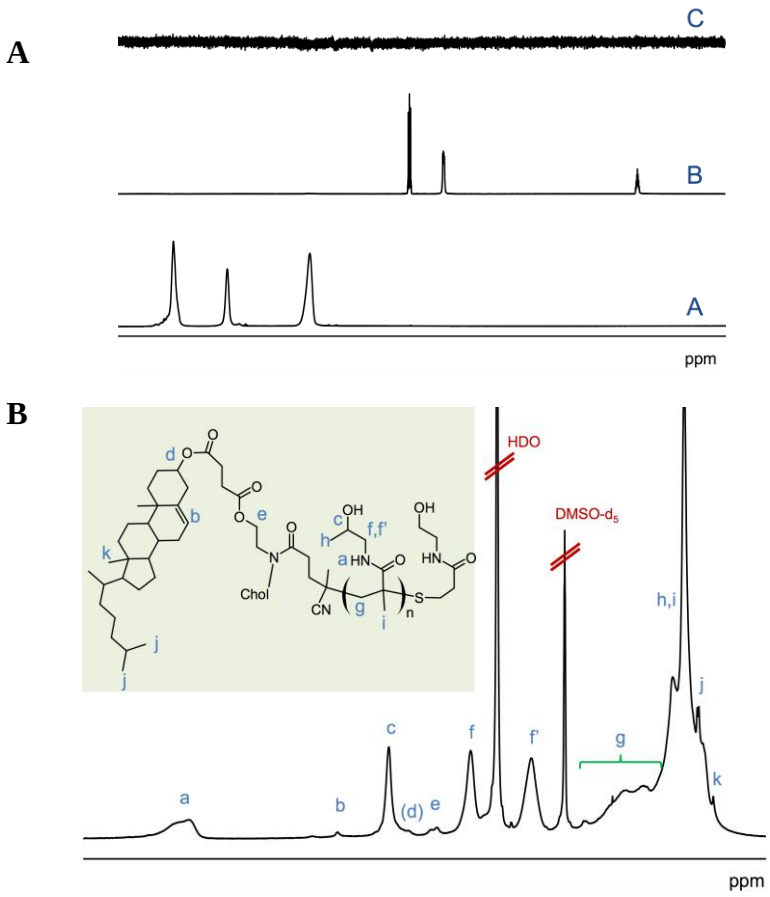


Figure 2. A ^{19}F NMR spectra of reactive precursor polyPFPA (A), after reaction with diethylamine before purification (B) and of polyDEAM after purification (C) and **B**, the ^{1}H NMR spectrum of polyHPMAM with assigned signals.

Table 1. Summary of the (meth)acrylamido derivatives prepared from parent polyPFP(M)A homopolymers including their SEC and NMR derived number average molecular weights ($\bar{M}_n$) and their SEC-measured dispersities ($Đ_M$).

Parent polymer	**Amine**	**End group**	**Modified Polymer**	**Name**	$\bar{M}_{n,\,SEC}$	$Đ_{M,\,SEC}$	$\bar{M}_{n,\,NMR}$
polyPFPMA1	HPA	HEA	poly(*N*-2-hydroxypropyl methacrylamide)	polyHPMAM	23,400 (DMAc)[1]	1.19	13,900
polyPFPMA1	HEEA	HEA	poly(*N*-hydroxyethoxy ethyl methacrylamide)	polyHEEMAM	23,000 (DMAc)[1]	1.20	16,500

polyPFPMA2	IPA	IPA	poly(*N*-isopropyl methacrylamide)	polyNIPMAM	4,400 (THF) [1]	1.41	nd[2]
polyPFPMA2	IPA/GluA	IPA	poly(*N*-isopropyl methacrylamide$_{30}$-*stat*-*N*-2-glucosmethacrylamide$_{70}$)[3]	poly(NIP$_{30}$-*stat*-Glu$_{70}$)	11,200 (DMAc) [1]	1.34	nd[2]
polyPFPA	IPA	IPA	poly(*N*-isopropyl acrylamide)	polyNIPAM	2,400 (THF) [1]	1.25	7,500
polyPFPA	DEA	DEA	poly(*N,N*-diethyl acrylamide)	polyDEAM	2,400 (THF) [1]	1.23	8,200
polyPFPA	EA	HEA	poly*(N*-ethyl acrylamide)	polyEAM	1,400 (THF) [1]	1.07	6,100
polyPFPMA1	HPA	HEA	poly(*N*-2-hydroxypropyl methacrylamide$_{89}$-*stat*-pentafluorophenyl methacrylate$_{11}$) [3]	poly(HP$_{89}$-*stat*-PFPMA$_{11}$)	22,900 (DMAc) [1]	1.23	14,900

1. SEC eluent.
2. The absolute molecular weight could not be determined as end groups were not clearly visible in the ^{1}H NMR spectrum.
3. Compositions were determined by ^{19}F NMR spectroscopy by analysis of residual PFP residues after reaction with the first amine.

The molecular weights of the modified polymers were determined by SEC in DMAc or THF (depending purely on the solubility characteristics of the modified polymers) and, where possible, the absolute molecular weights were determined by end group analysis employing NMR spectroscopy. Since the SEC-determined molecular weights are based on polystyrene equivalents coupled with analysis in different solvents, the measured values vary considerably even for polymers with identical parent precursor polymers.

The post-modification approach also allows for the facile preparation of a range of novel functional statistical copolymers via the reaction of the parent reactive scaffolds with two (or

more) small molecule amines. We also prepared one example of such a material, poly(*N*-isopropylmethacrylamide$_{30}$-*stat*-*N*-2-glucosmethacrylamide$_{70}$) obtained from the reaction of polyPFPMA2 with a mixture of isopropylamine and glucosamine (performed in the presence of *N*-isopropylacrylamide as the Michael acceptor). Finally, we reacted polyPFPMA1 with ca. 85 mol% 2-hydroxypropylamine, in the presence of 2-hydroxyethyl acrylamide, to give the amide derivative containing 11 mol% unreacted PFPMA repeat units that were utilized in later aggregation/crosslinking reactions and will be discussed elsewhere.[20]

With the library of well defined α,α-bis chol (meth)acrylamido (co)polymers in hand we performed a preliminary evaluation of their self-assembly in aqueous media based on the previously published protocol.[8] Specifically, we evaluated the self-assembly of the polyDEAM, polyNIPAM and polyHPMAM homopolymers as well as the sugar-based P(NIP$_{30}$-*stat*-Glu$_{70}$) copolymer in which 20 mg/mL DMF solutions were diluted with a 3-fold excess of water followed by lyophilisation and directly imaged by scanning electron microscopy (SEM), Figure 3. In all instances the hydrophilic homopolymers and the sugar-based statistical copolymer formed polymersomes with sizes ranging from ca. 250-800 nm, and in most instances gave particles with reasonably broad size distributions. However, while not optimized, this clearly demonstrates that hydrophilic *homopolymers* with appropriate $\bar{X}_n$'s and end groups can undergo self-assembly to give higher ordered nanostructures and, arguably, significantly simplifies access to such vesicular species. A more detailed evaluation of the self-assembly process and process conditions will be reported shortly.

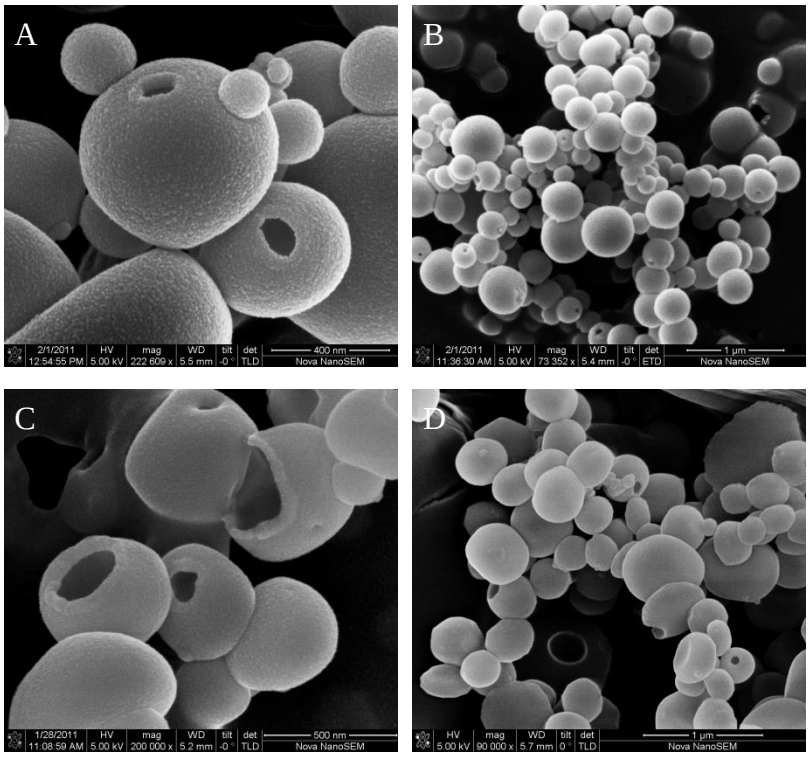


Figure 3. High-resolution SEM images of (A) polyDEAM, (B) polyNIPAM, (C) polyHPMAM and (D) poly(NIP$_{30}$-*stat*-Glu$_{70}$) (co)polymers highlighting vesicle formation. Scale bars 400 nm (A), 1µ (B), 500 nm (c) and 1µ (D).

4. Conclusions

Herein we have reported a straightforward approach to the synthesis of a library of (meth)acrylamido homo- and co-polymers containing two cholesteryl groups at the α-termius. The success of the approach relies on the use of an appropriate cholesteryl functional RAFT chain transfer agent in combination with pentafluorophenyl (meth)acrylates as monomers amenable to facile modification post-polymerization. We demonstrated that a wide range of novel end functional materials can be made and also highlighted that examples of these homopolymers (and one statistical copolymer) are capable of undergoing self-directed assembly in an aqueous environment to give polymeric vesicles spanning an impressive range of sizes.

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Keywords: RAFT, self-assembly, end-groups, cholesterol, vesicles

(Co)Polymers containing two cholesteryl groups at the α-terminus have been prepared using RAFT polymerization in combination with pentafluorophenyl (meth)acrylate monomers. Subsequent reaction of the activated ester precursors with a range of amines gives a small library of hydrophilic (meth)acrylamido (Co)polymers. Interestingly, these *homopolymers*, are capable of undergoing self-directed assembly in aqueous media to form polymersomes.

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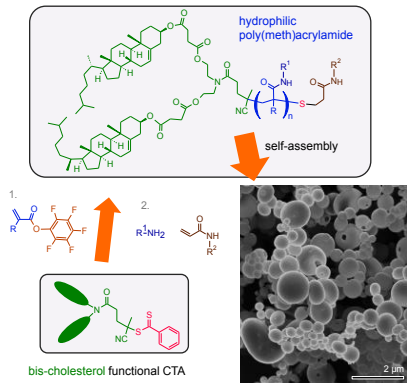
Novel α,α-Bischolesteryl Functional (Co)Polymers: RAFT Radical Polymerization Synthesis and Preliminary Solution Characterization



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