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Synthesis of Core Cross-Linked Star Polymers with Adjustable Coronal Properties

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ABSTRACT: A range of functionalized core cross-linked star (CCS) polymers were synthesized via the “arms first” approach and subsequently modified postsynthesis to manipulate the size, density, and chemical composition of the CCS corona. Poly(ϵ-caprolactone)-*b*-poly(methyl methacrylate) (PCL-*b*-PMMA) macroinitiator was used to synthesize a novel CCS polymer with a degradable outer PCL coronal layer. Subsequent hydrolysis of the PCL layer reduced the CCS arm length and effectively reduced the overall hydrodynamic diameter of the polymer. Surface-functionalized CCS polymers capable of initiating either ring-opening polymerization (ROP) or atom transfer radical polymerization (ATRP) from the periphery of the arms were also synthesized through the use of a multifunctional initiator, 2-hydroxyethyl 2′-methyl-2′-bromopropionate. ROP and ATRP chain extensions from the CCS surface were shown to be possible, resulting in increased arm lengths and hydrodynamic diameters with the initiation efficiency being found to be adversely affected by the sterically hindered structure of the CCS polymer. Core functionalization to generate novel CCS polymer capable of simultaneously initiating ATRP from the core as well as the periphery of the arms was also investigated. ATRP-initiated chain extension of this core/surface-functionalized CCS polymer was shown to increase the preexisting arm length as well as the number of arms. This resulted in an increased hydrodynamic diameter, with the protected initiating sites within the core being found to undergo a higher degree of polymerization than the functionalized arms.

Introduction

Core cross-linked star (CCS) polymers represent an interesting class of macromolecules due to their unique three-dimensional architecture and properties. They consist of a highly cross-linked core domain surrounded by a number of radiating linear arms,[1,2] typically ranging from anywhere between 10 and 100 arms per star depending on the reaction conditions. The architectural makeup of this type of polymer generates some very interesting rheological properties in that the CCS polymers have very high molecular weights (>100 000 g/mol) but their solubility and viscosity characteristics are similar to linear or branched polymers of relatively low molecular weights.[3] Properties such as these have led to a wide range of potential applications for CCS polymers particularly in the areas of drug delivery,[4,5] membrane formation,[6,7] and paint additives.[8]

Synthesis of this class of polymer is usually carried out in a two-step process known as the “arm first” approach, where living linear arms capable of further chain extension are initially synthesized. These terminally reactive linear polymer chains are subsequently used to initiate the polymerization of a cross-linkable monomer such that the active arm ends are coupled together to form a star-shaped polymer with a cross-linked core. Since the initiating functionalities are preserved within the core of the CCS polymer, a second type of arm can be grown out from the core to produce what is known as a miktoarm star polymer via the “in-out” method.[3,9−11] Other, more complex, architectures can also be generated such that CCS polymers with block copolymer arms[12,13] or dendron terminated arms[12,14] can easily be synthesized. Controlled radical polymerization techniques such as nitroxide-mediated radical polymerization (NMP),[12,15] atom transfer radical polymerization (ATRP),[16] and reversible addition−fragmentation chain transfer (RAFT)[17] polymerization are typically employed to synthesize CCS polymers, resulting in a high degree of structural control and narrow molecular weight distributions. Recently, another form of controlled polymerization known as ring-opening polymerization (ROP) has also been used to successfully synthesize CCS polymers[18−20] such that the lactone-based structures, both arm and core moieties, can easily be synthesized to yield degradable star polymers, a subject which has been covered in a recent review by our group.[5]

One of the defining properties of CCS polymers is that their structure can be divided into two distinct regions, that of the cross-linked core and that of the arms or corona. The coronal domain is of particular importance since it significantly influences the physical properties displayed by the CCS polymer. Properties such as crystallinity or hydrophilicity of a CCS polymer can easily be modified by changing the type of polymer used to generate the arms. For example, Connal et al.[7] showed that the glass transition temperature (T_g) of CCS polymers could be decreased from 123 to −122 °C by simply changing the polymeric composition of the arms from poly(methyl methacrylate) to poly(dimethylsiloxane), whereas no such effect is observed on changing the polymeric composition of the core domain. The length and the number of arms, i.e., the size and density of the corona, also play a significant role in determining the properties of CCS polymers. A reduction in arm length has been shown to reduce the viscosity of CCS polymer solutions due to the structure becoming more compact and hence reducing the degree of entanglement experienced between adjacent star polymers.[21]

Therefore, in order to achieve a greater degree of control over the physical properties displayed by CCS polymers, we have to be able to control the coronal properties. Here, we present the synthesis of a range of CCS polymers with adjustable coronal properties such that it is possible to manipulate the size, density, and nature of the CCS corona postsynthesis. In this

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paper, a novel CCS polymer with semidegradable block copolymer arms was synthesized and subsequently hydrolyzed to reduce the size of the CCS corona. Functionalized CCS polymers capable of initiating ATRP and ROP from the periphery of the arms were also synthesized and subsequently used to initiate chain extension reactions with the effect on coronal size being investigated. Further functionalization was used to generate a novel CCS polymer capable of initiating ATRP from both the periphery of the arms and the core, which was investigated for its potential to simultaneously increase the number and the length of the arms within the CCS corona.

Experimental Section

Materials. 2-Bromoisobutyrylbromide (98%), anisole (anhydrous, 99.7%), copper(I) bromide (CuBr, 98%), and stannous 2-ethylhexanoate (Sn(Oct)$_2$, 95%) were purchased from Aldrich and used as received. Toluene (99.9%, Merck) was distilled from sodium benzophenone ketyl and sodium metal under argon and stored over 4 Å molecular sieves. ϵ-Caprolactone (CL, Aldrich, >99%), dichloromethane (99.8%, Merck), and triethylamine (99%, Ajax) were dried over CaH$_2$ for 24 h and distilled prior to use. Methyl methacrylate (MMA, 99%), styrene (St, 99%), ethylene glycol dimethacrylate (EGDMA, 98%), and *N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine (PMDETA, 99%) were all purchased from Aldrich and washed three times with 5% w/w aq NaOH, once with water, then distilled from calcium hydride, and stored at −5 °C. 2-Hydroxyethyl 2′-methyl-2′-bromopropionate and [4,4′]-bioxepanyl-7,7′-dione (BOD) were synthesized according to literature.[19]

Instrumentation. Size exclusion chromatography was performed on a Shimadzu system with a Wyatt DAWN DSP multiangle laser light scattering detector (690 nm, 30 mW) and a Wyatt OPTILAB EOS interferometric refractometer (690 nm). THF was used as the eluent with three Phenomenex phenogel columns (500, 10^4, and 10^6 Å porosity; 5 μm bead size) operated at 1 mL/min with column temperature set at 30 °C. Astra software (Wyatt Technology Corp.) was used to process the data using known d*n*/d*c* values (or with the assumption of 100% mass recovery of the polymer where the d*n*/d*c* value was unknown) to determine the molecular weight. ^{1}H NMR spectra were collected in deuterated chloroform using a Varian Unity Plus 400 MHz spectrometer. Monomer conversion was determined by gas chromatography using a Shimadzu GC 17-A gas chromatograph equipped with an Agilent JW DB-5 capillary column (30 m, 5% phenyl siloxane) and coupled to a GCMS-QP5000 mass spectrometer (injector temperature = 250 °C; detector temperature = 250 °C; column initial temperature = 40 °C; heat ramp = 10 °C/min; column final temperature = 320 °C). Dynamic light scattering measurements were performed using a Malvern HPPS particle sizer with a 3.0 mW He−Ne laser operated at 633 nm. Analysis was performed at an angle of 173° and a constant temperature of 25 °C.

Synthesis of HO−PCL−Br Macroinitiator. A round-bottom flask was charged with a mixture of CL (9.00 g, 78.9 mmol), Sn(Oct)$_2$ (0.743 g, 1.83 mmol), 2-hydroxyethyl 2′-methyl-2′-bromopropionate (0.774 g, 3.67 mmol), and toluene (80 mL). A condenser and a CaCl$_2$ drying tube were attached to the flask which was heated to 110 °C. After 24 h, the reaction was stopped, and the mixture was precipitated into cold methanol. The precipitate wascollected by filtration and dried for 16 h in a desiccator to yield HO−PCL−Br macroinitiator (yield = 7.78 g, $M_\mathrm{n} = 4.6 \times 10^3$ g/mol, $M_\mathrm{w}/M_\mathrm{n} = 1.11$).

Synthesis of HO−PSt−Br Macroinitiator. A mixture of St (3.26 mL, 28.4 mmol), CuBr (68.0 mg, 0.474 mmol), PMDETA (99.3 μL, 0.474 mmol), and 2-hydroxyethyl 2′-methyl-2′-bromopropionate (0.100 g, 0.474 mmol) was added to a Schlenk flask and degassed by three freeze−pump−thaw cycles. The flask was then backfilled with argon and immersed in an oil bath at 80 °C for 16 h. The reaction was stopped via exposure to air, and the contents diluted with THF before being passed through a column of basic alumina to remove the copper complex. The solution was then concentrated and precipitated into cold methanol. The precipitate was collected by filtration and dried for 16 h in a desiccator to afford the HO−PSt−Br macroinitiator (yield = 1.90 g, $M_\mathrm{n} = 7.7 \times 10^3$ g/mol, $M_\mathrm{w}/M_\mathrm{n} = 1.03$).

Synthesis of PCL-*b*-PMMA−Br Macroinitiator. HO−PCL−Br macroinitiator (1.00 g, 0.217 mmol; $M_\mathrm{n} = 4.6 \times 10^3$ g/mol) was added to a round-bottom flask and dissolved in 10 mL of anisole. A mixture of CuBr (35.9 mg, 0.250 mmol), PMDETA (52.4 μL, 0.250 mmol), and MMA (1.23 mL, 11.5 mmol) was added to the reaction solution and purged with argon for 2 h. The flask was then sealed and heated at 100 °C for 1 h. The reaction was stopped by quenching in liquid nitrogen, and the contents diluted with THF before being passed through a column of basic alumina to remove the copper complex. The product was isolated by precipitation into cold methanol. The precipitate was filtered and dried in a desiccator for 16 h (yield = 0.711 g, $M_\mathrm{n} = 8.3 \times 10^3$ g/mol, $M_\mathrm{w}/M_\mathrm{n} = 1.07$).

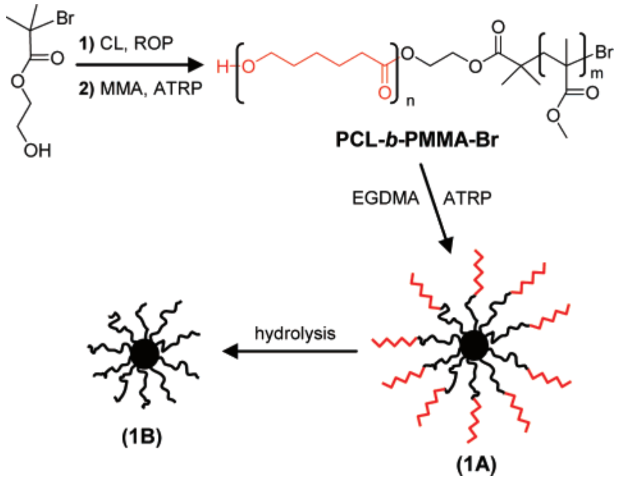
Degradable Block Copolymer CCS. A round-bottom flask was charged with a mixture of PCL-*b*-PMMA−Br macroinitiator (0.30 g, 0.036 mmol; $M_\mathrm{n} = 8.3 \times 10^3$ g/mol), CuBr (6.7 mg, 0.047 mmol), PMDETA (9.8 μL, 0.047 mmol), EGDMA (0.102 mL, 0.542 mmol), and anisole (4.7 mL) and purged with argon for 2h. The reaction vessel was then sealed and immersed in an oil bath at 100 °C. After 48h (70% EGDMA conversion), the reaction was stopped via exposure to air, and the mixture was fractionally precipitated into methanol to remove any unreacted macroinitiator. The precipitate was collected by filtration and dried under vacuum ($M_\mathrm{n} = 2.262 \times 10^5$ g/mol, $M_\mathrm{w}/M_\mathrm{n} = 1.18$).

ROP of Surface-Functionalized CCS Polymer. HO−PSt−Br macroinitiator (0.50 g, 0.065 mmol; $M_\mathrm{n} = 7.7 \times 10^3$ g/mol) was reacted with a mixture of CuBr (0.012 g, 0.084 mmol), PMDETA (35.2 μL, 0.168 mmol), EGDMA (0.183 mL, 0.970 mmol), and anisole (8.4 mL) in a Schlenk flask and degassed by three freeze−pump−thaw cycles. The flask was then backfilled with argon and immersed in an oil bath at 100 °C. After 46 h (82% EGDMA conversion), the reaction was stopped and the mixture was fractionally precipitated into methanol. The polymer was collected by filtration and dried under vacuum ($M_\mathrm{n} = 2.657 \times 10^5$ g/mol, $M_\mathrm{w}/M_\mathrm{n} = 1.16$). The hydroxyl surface functional CCS polymer (0.151 g, 0.0115 mmol arms) was then used to initiate the ROP chain extension via reaction with a mixture of CL (0.127 mL, 1.15 mmol), Sn(Oct)$_2$ (1.9 μL, 0.0057 mmol), and toluene (1.15 mL) in a dry round-bottom flask at 110 °C with a condenser and a CaCl$_2$ drying tube attached. After 24 h (>99% CL conversion), the reaction solution was precipitated into methanol. The precipitate wascollected by filtration and dried under vacuum ($M_\mathrm{n} = 5.444 \times 10^5$ g/mol, $M_\mathrm{w}/M_\mathrm{n} = 1.25$).

ATRP of Surface-Functionalized CCS Polymer. HO−PCL−Br macroinitiator (2.57 g, 0.559 mmol; $M_\mathrm{n} = 4.6 \times 10^3$ g/mol) was added to a mixture of Sn(Oct)$_2$ (70.8 μL, 0.219 mmol), BOD (0.988 g, 4.37 mmol), and toluene (22.7 mL). A condenser and a CaCl$_2$ drying tube were attached to the flask, which was then heated at 110 °C with stirring. After 31 h (81% BOD conversion), the reaction was stopped by quenching in liquid nitrogen and the solvent removed under reduced pressure. The crude polymer was dissolved in THF and fractionally precipitated into methanol. The precipitate was collected by filtration and dried under vacuum ($M_\mathrm{n} = 1.794 \times 10^5$ g/mol, $M_\mathrm{w}/M_\mathrm{n} = 1.15$). The alkyl bromide surface functional CCS polymer (0.05 g, 0.007 mol arms) was then used to initiate the ATRP chain extension via reaction with a mixture of MMA (1.60 mL, 14.9 mmol), CuBr (10.7 mg, 0.0746 mmol), and PMDETA (15.7 μL, 0.0749 mmol). Argon was bubbled through the reaction solution for 2 h, and then the vessel was sealed and immersed in an oil bath at 100 °C. The reaction was stopped after 45 min by exposure to air, and the mixture was precipitated into methanol. The precipitate was collected by filtration and dried under vacuum ($M_\mathrm{n} = 6.185 \times 10^5$ g/mol, $M_\mathrm{w}/M_\mathrm{n} = 1.24$).

ATRP of Core/Surface-Functionalized CCS Polymer. HO−PCL−Br macroinitiator (3.20 g, 0.696 mmol; $M_\mathrm{n} = 4.6 \times 10^3$ g/mol) was reacted with a mixture of CuBr (0.115 g, 0.800 mmol), PMDETA (0.168 mL, 0.800 mmol), EGDMA (1.74 mL, 9.23 mmol), and anisole (80 mL) in a Schlenk flask and degassed by

Scheme 1. Combination of Ring-opening Polymerization (ROP) and Atom Transfer Radical Polymerization (ATRP) to Synthesize Degradable Block Copolymer Core Cross-Linked Star and Subsequent Hydrolysis to Reduce Arm Length[a]



[a] Key: CL = caprolactone, MMA = methyl methacrylate, EGDMA = ethylene glycol dimethacrylate.

three freeze−pump−thaw cycles. The flask was then backfilled with argon and immersed in an oil bath at 100 °C. After 21h (80% EGDMA conversion), the reaction was stopped, and the mixture was fractionally precipitated into methanol. The polymer was collected by filtration and dried under vacuum ($M_n = 1.523 \times 10^5$ g/mol, $M_w/M_n = 1.18$). The resultant CCS polymer (0.50 g, 0.061 mmol arms) was dissolved in a mixture of dichloromethane (40 mL) and triethylamine (0.754 mL, 5.44 mmol), to which was added 2-bromoisobutyrylbromide (0.673 mL, 5.44 mmol) slowly under argon. The reaction was stirred at 25 °C for 18 h, and the mixture was then precipitated twice in methanol to purify. The alkyl bromide core/surface functionalized CCS polymer (0.20 g, $M_n = 1.550 \times 10^5$ g/mol, 0.024 mmol arms) was then used to initiate the ATRP chain extension via reaction with a mixture of MMA (4.71 mL, 44.0 mmol), CuBr (31.6 mg, 0.220 mmol), and PMDETA (46.1 μL, 0.220 mmol). Argon was bubbled through the reaction solution for 2 h, and then the vessel was sealed and immersed in an oil bath at 100 °C. The reaction was stopped after 30 min by exposure to air, and the mixture was precipitated into methanol. The precipitate was collected by filtration and dried under vacuum ($M_n = 5.146 \times 10^5$ g/mol, $M_w/M_n = 1.26$).

Hydrolysis. In a typical example of hydrolysis reaction, a degradable block copolymer CCS (0.040 g, 1.76×10^{-7} mol; $M_n = 2.262 \times 10^5$ g/mol) was dissolved in a solution of THF (4.0 mL) and HCl (3 M, 0.4 mL), which was subsequently heated at 60 °C for 24 h. The reaction was stopped by precipitating into cold methanol, and the isolated polymer was collected by filtration and dried under vacuum (yield = 0.032 g, $M_n = 2.071 \times 10^5$ g/mol).

Results and Discussion

Degradable Block Copolymer CCS. The CCS polymer with a degradable outer coronal layer was synthesized from semidegradable poly(ϵ-caprolactone)-*b*-poly(methyl methacrylate) (PCL-*b*-PMMA−Br) macroinitiator (Scheme 1). The incorporation of degradable functionality within the CCS corona is achieved through the use of PCL, which contains ester linkages that can easily be hydrolyzed without affecting the remaining CCS structure. The difunctional initiator 2-hydroxyethyl 2′-methyl-2′-bromopropionate was used to synthesize the PCL-*b*-PMMA−Br macroinitiator since it has previously been shown to be an efficient initiator for the ATRP of vinyl monomers as well as for the ROP of lactone-based monomers.[22] The hydroxyl functionality of this initiator was first used to initiate the ring-opening polymerization of CL in the presence of $Sn(Oct)_2$ as a catalyst. The resultant linear HO−PCL−Br polymer ($M_n = 4.6 \times 10^3$ g/mol, $M_w/M_n = 1.11$) retained the alkyl halide functionality of the initiator, which was subsequently used to initiate the polymerization of MMA under ATRP conditions with CuBr/PMDETA as the catalyst. The resultant PCL-*b*-PMMA−Br block copolymer ($M_n = 8.3 \times 10^3$ g/mol, $M_w/M_n = 1.07$) showed good initiation efficiency, with the gel permeation chromatography (GPC) analysis indicating that all of the HO−PCL−Br macroinitiator underwent chain extension (Figure 1). The composition of the block copolymer was confirmed by ^{1}H NMR spectroscopy, and the molar fraction of MMA in the copolymer was calculated to be $F_{MMA} = 0.44$ (Figure 2).

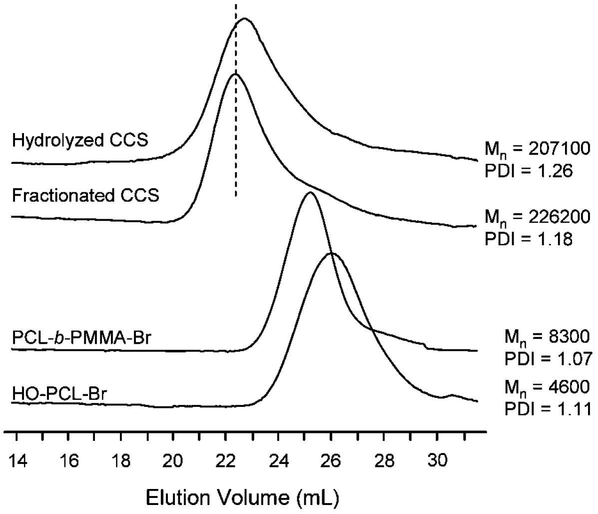


Figure 1. Gel permeation chromatography traces of the degradable block copolymer core cross-linked star (CCS) and its subsequent hydrolysed product. The GPC traces of the components involved in the synthesis are also included.

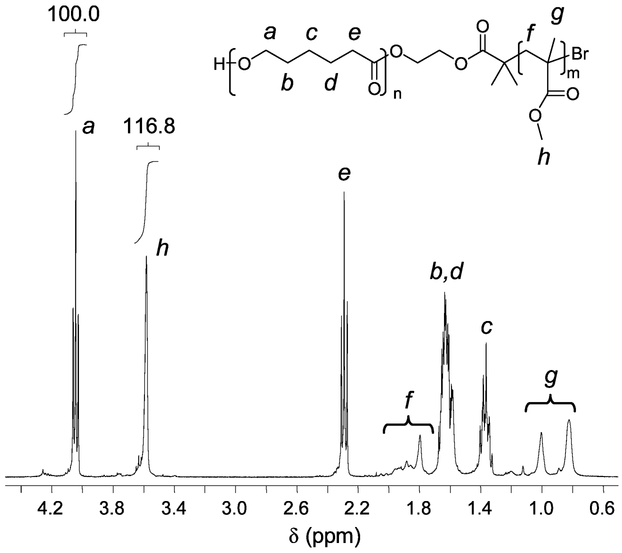


Figure 2. ^{1}H NMR spectra of polycaprolactone-*b*-poly(methyl methacrylate) block copolymer (PCL-*b*-PMMA-Br macroinitiator).

Ethylene glycol dimethacrylate (EGDMA) monomer was used to cross-link the ATRP-active end group of the PCL-*b*-PMMA−Br macroinitiator to synthesize the CCS polymer with semidegradable block copolymer arms. The extent of CCS formation was limited (10% conversion of arms into CCS polymer) and as such was fractionated to remove any unconverted macroinitiator to yield the pure CCS polymer. GPC-MALLS was used to measure the absolute molecular weight ($M_n = 2.262 \times 10^5$

Table 1. Synthesis of Core Cross-linked Star (CCS) Polymers with Adjustable Coronal Properties

entry[a]	M_n (g/mol)[b]	PDI[b]	av no of arms(f)[c]	arm M_n (g/mol)[b]	D_H (nm)[d]
1A	226 200	1.18	7.2	8300	23.3
1B	207 100	1.26	7.2	3910	18.6
2A	265 700	1.16	20.2	7700	11.7
2B	544 400	1.25	20.2	21 400[e]	23.7
2C	277 800	1.21	20.2	7700	
3A	179 400	1.15	26.8	4600	18.8
3B	618 500	1.24	26.8	21 000[e]	25.0
3C	159 000	1.29	N/A	N/A	
5A	152 300	1.18	18.7	4600	15.3
5B	514 600	1.29	[f]	[f]	36.9
5C	373 400	1.21	[f]	[f]	14.2

[a] Sample reference numbers as mentioned in Schemes 1−5, reaction conditions as defined in text. [b] Number average molecular weight (M_n) and polydispersity (PDI) measured by GPC-MALLS. [c] Average number of arms in CCS polymer, $f = M_{n,CCS} \times \text{arm}_{wt\%}/M_{n,arm}$. [d] Average hydrodynamic diameter (D_H) measured by dynamic light scattering. [e] Theoretical molecular weight of the arm based on 100% initiation efficiency of the extension reaction. [f] Values could not be determined due to unknown efficiency of the core/surface extension reaction.

g/mol) and polydispersity ($M_w/M_n = 1.18$) of the fractionated CCS polymer (Table 1, entry 1A). Using equations reported in the literature,[19] it is possible to calculate the average number of arms (f) being incorporated into the CCS polymer as 7.2 arms per star. Using this information, it is possible to calculate and deduce that a large proportion of this CCS polymer's molecular weight (~70%) is attributed to the core domain. This is relatively big for a CCS polymer core, with typical values being more in the range of 40−50% by weight although this does depend greatly on the particular reaction conditions employed. One of the unique properties of this novel CCS polymer lies in the ability to manipulate the size of the corona and hence alter the overall dimensions of the CCS polymer. This is made possible due to the presence of the degradable PCL block in the outer corona of the star, which essentially surrounds a nondegradable CCS polymer with PMMA arms and EGDMA cross-linked core.

Removal of the coronal PCL layer was achieved through the use of acidic conditions, which have previously been shown to be capable of hydrolyzing PCL without affecting the PMMA/EGDMA structure of the CCS polymer.[19] GPC traces of the hydrolyzed CCS polymer (Figure 1) show a reduction in molecular weight in that the resultant CCS polymer had a M_n of 2.071×10^5 g/mol and a polydispersity of 1.26 (Table 1, entry 1B). ^{1}H NMR analysis of the hydrolyzed polymer confirmed that all of the PCL had been removed to yield the CCS polymer with PMMA arms. Since the number of arms remains the same ($f = 7.2$) and the molecular weight of the degradable PCL arm segment is known ($M_n = 4{,}390$ g/mol), it is possible to calculate the theoretical molecular weight of the CCS polymer after hydrolysis. For the block copolymer CCS reported here, the theoretical M_n after hydrolysis was calculated to be 1.946×10^5 g/mol, which is in agreement with that measured by GPC-MALLS (2.071×10^5 g/mol).

Dynamic light scattering (DLS) was used to measure the hydrodynamic diameter of the PCL-*b*-PMMA arm CCS polymer before and after hydrolysis (Figure 3). It was found that as the length of the arms was reduced from 8.3×10^3 to 3.9×10^3 g/mol the hydrodynamic diameter also decreased (23.3 to 18.6 nm). The technique of using semidegradable block copolymers to synthesize CCS polymer not only allows for precise control of the arm length, through manipulation of the ratio of degradable to nondegradable polymer in the macroinitiator, but also allows for the modification of coronal properties. For example, the CCS polymer reported here initially has surface properties characteristic of PCL which, through simple hydrolysis, can be modified to display properties characteristic of PMMA. By employing a range of different degradable and nondegradable monomers to synthesize the block copolymer arms, the potential to control properties such as the hydrophilicity or the crystallinity of the CCS corona is increased.

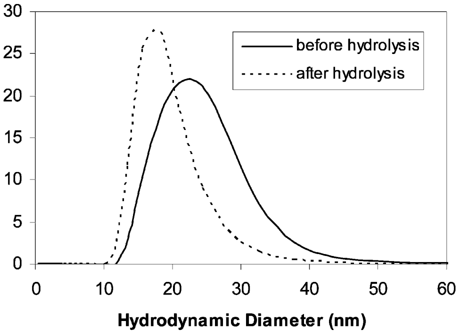
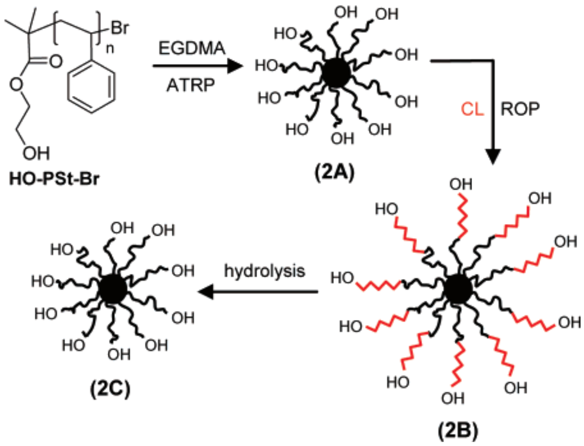


Figure 3. Dynamic light scattering traces of the degradable block copolymer core cross-linked star (CCS) before and after hydrolysis (Table 1, entries 1A and 1B).

ROP of Surface-Functionalized CCS Polymer. Postsynthesis modification of CCS polymers to increase the length of the arms can be achieved in various ways, one of which involves chain extension of the arms out from the surface of the CCS polymer. This technique requires that the arms be end functionalized with an appropriate functionality capable of initiating polymerization but not be active toward the cross-linking reaction during CCS formation. Rather than protecting the initiating functionality or attempting to functionalize the arms after star formation, it is much easier to incorporate two different initiating functionalities which can be utilized independently of one another. In order to achieve this, 2-hydroxyethyl 2′-methyl-2′-bromopropionate was used to initiate the polymerization of styrene under ATRP conditions to generate a difunctional macroinitiator (HO−PSt−Br, $M_n = 7.7 \times 10^3$ g/mol, $M_w/M_n = 1.03$). The resultant structure of this polystyrene macroinitiator is such that it contains an alkyl bromide group at one end capable of initiating ATRP reactions and a hydroxyl functionality at the other end capable of initiating ROP reactions.

The HO−PSt−Br macroinitiator was cross-linked through the ATRP-initiating end group with EGDMA to generate the CCS polymer with hydroxyl terminated arms (Scheme 2). Any unconverted macroinitiator was removed via fractional precipitation to yield the pure CCS polymer with a number average molecular weight of 2.657×10^5 g/mol ($M_w/M_n = 1.16$) and an average of 20.2 arms (Table 1, entry 2A). The hydroxyl end functionalized arms of the CCS polymer were subsequently used to initiate the ring-opening polymerization of ϵ-caprolactone to increase the arm length. GPC results (Figure 4) confirmed that the chain extension of the arms occurred, generating the CCS polymer with a number average molecular weight of 5.444×10^5 g/mol and a polydispersity of 1.25 (Table 1, entry 2B). The average extension of each arm was calculated to be 120 caprolactone units per arm, resulting in an increased arm molecular weight from 7.7×10^3 to 2.14×10^4 g/mol. The calculated molecular weight of the extended arm is based on the assumption that the initiation efficiency of the ROP chain extension reaction from the surface of the functionalized star is 100%. Unfortunately, the initiation efficiency in this case cannot be directly measured but is likely to be less than 100%, as later demonstrated for the case of ATRP-initiated surface extension. This reduced initiation efficiency means that fewer arms would undergo chain extension with the molecular weight of the extended arms being greater than predicted by theory.

Scheme 2. Synthesis of Hydroxyl Surface Functionalized Star Polymer with Polystyrene (PSt) Arms and Ethylene Glycol Dimethacrylate (EGDMA) Cross-Linked Core Capable of Initiating Ring-opening Polymerization (ROP) from the Periphery of the Arms[a]



[a] Key: ATRP = atom transfer radical polymerization, CL = caprolactone.

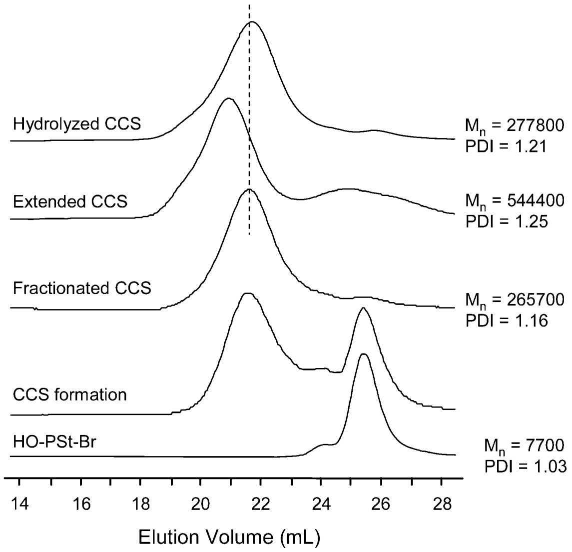


Figure 4. Gel permeation chromatography traces of the hydroxy surface functional core cross-linked star (CCS) polymer chain extended by ring-opening polymerization and its subsequent hydrolysed product. The GPC traces of the components involved in the synthesis are also included.

A small amount of low molecular weight polymer is also formed (Figure 4, extended CCS 24−27 mL elution volume) during chain extension of the CCS polymer. This is due to the presence of the linear macroinitiator which was not completely removed during the fractionation step. Since this residual macroinitiator contains hydroxyl groups capable of initiating ROP, a small amount of diblock copolymer is therefore formed during the chain extension and is present as the low molecular weight contaminant.

The change in hydrodynamic diameter of the CCS polymer as a result of the ROP chain extension was monitored by DLS (Figure 5). It was found that as the arm length of the CCS polymer increased in molecular weight from 7.7×10^3 g/mol to a theoretical value of 2.14×10^4 g/mol the corresponding hydrodynamic diameter also increased, changing from an average of 11.7 up to 23.7 nm. Another advantage of increasing the CCS polymer arm length via a postsynthesis chain extension reaction is that it provides a simplistic route for the synthesis of CCS polymers with a large number of high molecular weight arms. Traditionally this type of CCS polymer has been difficult to synthesize by the “arms first” approach due to the fact that the number of arms incorporated into the star polymer is strongly dependent on the molecular weight of the macroinitiator (i.e., the arm length). It has been shown that as the length of the macroinitiator is increased the number of arms incorporated into the CCS polymer tends to decrease.[6,23,24] This relationship can be controlled to a certain extent through the manipulation of reaction conditions; however, this is not an easy task due to the large number of reaction variables and the complex nature of their relationship to the structure of the CCS polymer. Therefore, a more attractive route for synthesizing CCS polymers with many high molecular weight arms would be to synthesize the CCS polymer using lower molecular weight macroinitiator to achieve high arm incorporation and then chain extend the arms to increase their molecular weight.

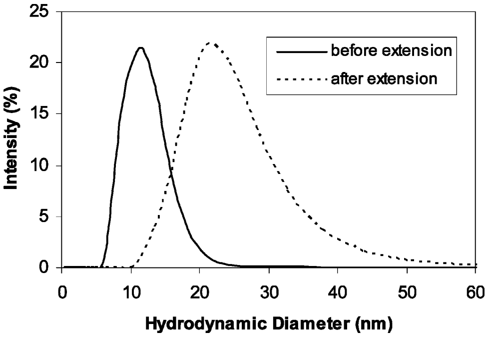


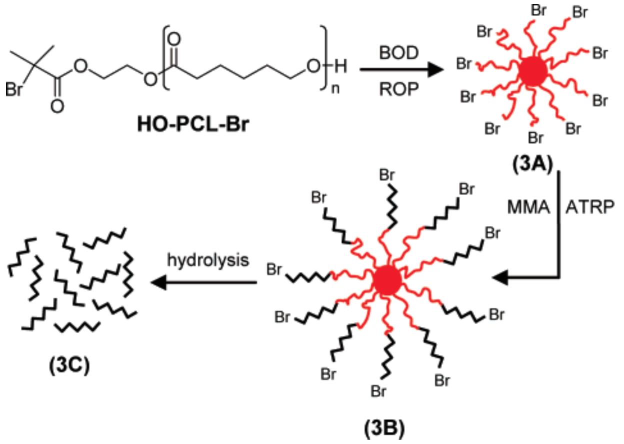
Figure 5. Dynamic light scattering traces of hydroxyl surface functionalized core cross-linked star polymer before and after ring-opening polymerization initiated from the periphery of the arms (Table 1, entries 2A and 2B).

The use of caprolactone as the chain extension monomer allows for recovery of the original CCS polymer. This is possible since the extended PCL segment can easily be removed by hydrolysis without affecting the PSt/EGDMA structure of the original CCS polymer. Experimental results showed this to be the case, with ^{1}H NMR analysis of the hydrolyzed polymer confirming that all of the PCL has been removed to regenerate the original CCS polymer. GPC analysis (Figure 4) also supported these findings, with hydrolysis of the chain-extended CCS yielding a polymer with a molecular weight close to that of the original polymer (2.778×10^5 g/mol compared to 2.657×10^5 g/mol) (Table 1, entry 2C). There was however a slight increase in the polydispersity of the star (1.16 to 1.21) with a very minor shoulder peak being detected in the GPC trace of the hydrolysis product (Figure 4, hydrolyzed CCS, 19 mL elution volume). This is believed to be due to the coupling of a small fraction of the stars, through termination of the preserved ATRP-initiating functionalities within the core, facilitated by the high reaction temperature used for ROP chain extension.

ATRP of Surface-Functionalized CCS Polymer. By utilizing similar principles to those employed in the synthesis of the surface-functionalized CCS polymer capable of initiating ROP, it is possible to generate CCS polymers capable of initiating other types of polymerization. By changing the surface functionality to something capable of initiating ATRP reactions, it is possible to vastly increase the range of monomers that can be utilized in the extension reaction. Consequently, the ability to modify the physical properties of CCS polymers is also increased since many of these properties are directly related to the nature of the polymer present in the corona.

In order to synthesize the CCS polymer capable of initiating ATRP from the periphery of the arms, the terminal hydroxyl group of the linear HO−PCL−Br macroinitiator (M_n = 4.6 ×

Scheme 3. Synthesis of Alkyl Bromide Surface Functionalized Star Polymer with Polycaprolactone (PCL) Arms and 4,4′-Bioxepanyl-7,7′-dione (BOD) Cross-Linked Core Capable of Initiating Atom Transfer Radical Polymerization (ATRP) from the Periphery of the Arms[a]



[a] Key: ROP = ring-opening polymerization, MMA = methyl methacrylate.

10^3 g/mol, $M_w/M_n = 1.11$) was used to initiate the ring-opening polymerization of the bislactone [4,4′]-bioxepanyl-7,7′-dione (BOD) (Scheme 3). The BOD monomer consists of two caprolactone rings bridged at the 4-position and consequently acts as a cross-linker to couple the ROP-active end group of the macroinitiators together to form the CCS polymer. GPC analysis (Figure 6) of the reaction product revealed that ~68% of the linear HO−PCL−Br macroinitiator was converted into the CCS polymer with subsequent fractionation yielding the pure CCS polymer ($M_n = 1.794 \times 10^5$ g/mol, $M_w/M_n = 1.15$) (Table 1, entry 3A). The average number of arms incorporated into the CCS polymer was calculated to be 26.8, each of which is end functionalized with an alkyl bromide group capable of initiating the ATRP.

The alkyl bromide surface functionalized CCS polymer was used to initiate the ATRP of methyl methacrylate monomer in the presence of CuBr/PMDETA catalyst. GPC traces of the reaction product (Figure 6) showed a shift to a higher molecular weight product, indicating that chain extension of the CCS polymer arms occurred. The number average molecular weight of the chain-extended CCS polymer was determined by GPC-MALLS to be 6.185×10^5 g/mol ($M_w/M_n = 1.24$) (Table 1, entry 3B). With the assumption that all of the arms were involved in the extension reaction, the average extension per arm was calculated to be 1.64×10^4 g/mol, resulting in an increased arm molecular weight from 4.6×10^3 up to 2.10×10^4 g/mol.

The extension reaction was closely monitored such that the polymerization could be stopped before the onset of gelation. The high local concentration of the active initiating sites within the surface functional star polymer increases the probability of the radical−radical termination reactions to occur. These termination reactions can take place either intra- or intermolecularly resulting in the coupling of arms within the individual star polymers or between that of the neighboring stars (star−star coupling) which can lead to gelation. The use of a controlled polymerization technique such as ATRP minimizes the concentration of growing radicals present at any given moment and effectively suppresses these termination reactions. However, as the extension reaction proceeds to higher conversions, these coupling reactions start to become more prevalent due to the reduced amount of available monomer and eventually lead to gelation of the reaction system.

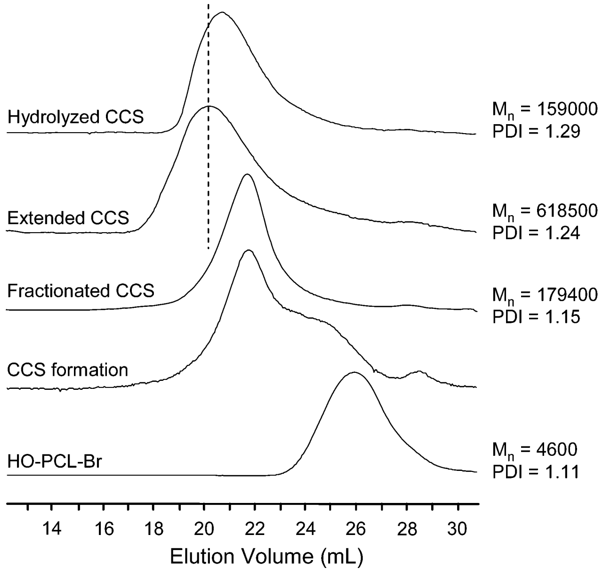


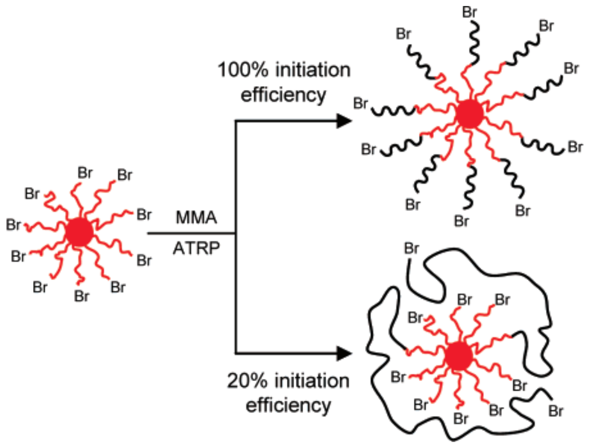
Figure 6. Gel permeation chromatography traces of the synthesis of alkyl bromide surface functional core cross-linked star (CCS) polymer chain extended by atom transfer radical polymerization (ATRP) and its subsequent hydrolysed product. The GPC traces of the components involved in the synthesis are also included.

The use of lactone-based polymers to synthesize the initial alkyl bromide surface functionalized CCS polymer (PCL arms and BOD core) means that the original star polymer can be completely hydrolyzed.[18,19] This allows for recovery of the extension product since the PMMA chains extended from the arms are nondegradable and as such can be liberated via hydrolysis of the extended CCS polymer. This was found to be the case with hydrolysis of the ATRP chain extended CCS polymer yielding the pure PMMA polymer, as confirmed by ^{1}H NMR spectroscopy. The molecular weight of this extension product ($M_n = 1.590 \times 10^5$ g/mol, $M_w/M_n = 1.29$) (Table 1, entry 3C) was a lot larger than predicted by theory for 100% initiation efficiency of the arms (1.64×10^4 g/mol). Using this information, it is possible to calculate the initiation efficiency of the arms during the ATRP chain extension reaction, which was found to be only 10%. Consequently, the structure of the ATRP chain extended CCS polymer is not that of a star polymer with a uniform layer of short PMMA chains attached to the end of each arm. A more realistic representation would be that of a star polymer with long PMMA chains attached to only a few of the preexisting PCL arms (Scheme 4).

The structural difference brought about through a reduction in initiation efficiency would have a significant effect on the solution properties of the chain-extended CCS polymer. For example, the CCS polymer with an evenly distributed short polymeric layer added to the periphery of the star (i.e., 100% initiation efficiency) would be expected to have a significantly lower viscosity than that of a CCS polymer having only a few long polymer chains attached to the corona (i.e., 10% initiation efficiency). The reason for this is that the long polymer chains attached to the surface of the low initiation efficiency star would have a higher potential to interact with other CCS polymers and become entangled, essentially converting the compact low viscosity structure of the star into a pseudo high molecular weight linear polymer with increased viscosity.

The low initiation efficiency of the ATRP chain extension reaction could be due to the loss of functionality of some of the initiating sites located at the periphery of the CCS polymer. The occurrence of radical termination reactions during either star formation or extension of the arms could potentially destroy

Scheme 4. Effect of Reduced Initiation Efficiency of Chain Extension from Surface-Functionalized Core Cross-Linked Star Polymer[a]



[a] Key: ATRP = atom transfer radical polymerization, MMA = methyl methacrylate.

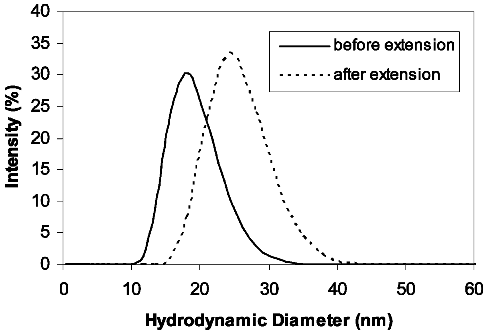
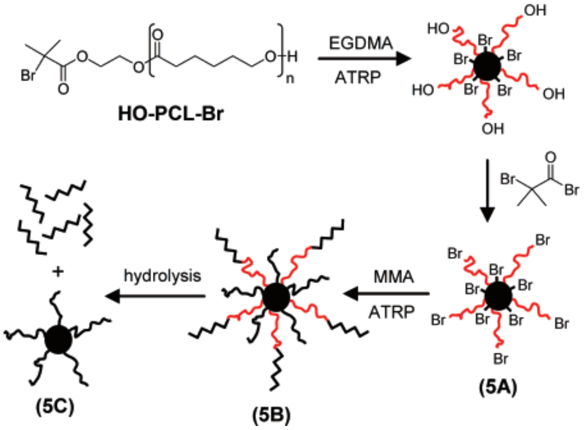


Figure 7. Dynamic light scattering traces of the alkyl bromide surface functionalized core cross-linked star polymer before and after atom transfer radical polymerization initiated from the periphery of the arms. (Table 1, entries 3A and 3B).

the initiating functionality of some of the arms and hence reduce the calculated efficiency. In addition to this, the accessibility of these initiation sites may be limited due to the compact nature of the CCS polymer and the potential for the initiating sites to be embedded within the corona of the star polymer rather than being situated at the periphery. Similar issues have been reported for the synthesis of molecular brushes[25] and miktoarm star polymers[26] where it has been found that the highly congested nature of the multifunctional macroinitiators resulted in reduced initiation efficiencies due to limited accessibility. Although the initiation efficiency of the ROP-based CCS extension reaction presented earlier in this paper could not be determined, it is expected to be higher than that of the ATRP-based extension reaction. This is due to the fact that the ROP proceeds via a coordination−insertion mechanism rather than a radical propagation as in the case of ATRP. This eliminates the potential loss of functionality due to radical termination reactions and therefore results in potentially higher initiation efficiencies. However, the ROP-based extension reaction is still expected to experience steric hindrance effects similar to that of the ATRP-based extension reaction and consequently will still have an initiation efficiency less than 100%.

The hydrodynamic size of the surface functional CCS polymer before and after ATRP chain extension was monitored via DLS (Figure 7). It was found that as the molecular weight of the CCS polymer increased due to the extension of 10% of the arms with $M_n = 1.590 \times 10^5$ g/mol PMMA the hydrodynamic diameter of the corresponding CCS polymer also increased, changing from an average of 18.8 up to 25.0 nm. This result shows that even though the initiation efficiency of the arms was quite low it was still possible to significantly increase the hydrodynamic size of the CCS polymer. This is an important result since it shows that even the extension of only a few arms is still sufficient to appreciably alter the coronal properties of a CCS polymer and therefore modify its solution behavior.

Scheme 5. Synthesis of Alkyl Bromide Core/Surface Functionalized Star Polymer with Polycaprolactone (PCL) Arms and Ethylene Glycol Dimethacrylate (EGDMA) Cross-Linked Core Capable of Initiating Atom Transfer Radical Polymerization (ATRP) Simultaneously from the Core and the Periphery of the Arms[a]



[a] MMA = Methyl Methacrylate.

ATRP of Core/Surface-Functionalized CCS Polymer. The synthesis of the CCS polymer capable of simultaneously initiating chain extension from both the core and the surface was also investigated. One of the consequences of using the "arms first" approach to synthesize star polymers is that the initiating functionality of the linear macroinitiator is preserved within the core of the CCS polymer. It has been well established that this embedded functionality can be used to grow a second type of arm out from the core to synthesize miktoarm star polymer in what is known as the "in−out" method. By modifying the functional groups located at the periphery of the CCS polymer arms to match those of the preserved initiating sites within the core, it is possible to generate the CCS polymer which can simultaneously initiate polymerization from the core as well as from the arms. This allows for not only manipulation of the size of the CCS corona but also the packing density of arms within the corona.

To achieve this, the CCS polymer capable of initiating ATRP from the core was first synthesized by cross-linking of the HO−PCL−Br macroinitiator ($M_n = 4.6 \times 10^3$ g/mol, $M_w/M_n = 1.11$) with EGDMA under ATRP reaction conditions (Scheme 5). GPC analysis of the reaction product (Figure 8) revealed that ~60% of the linear HO−PCL−Br macroinitiator has been converted into the CCS polymer, which was subsequently fractionated to yield the pure CCS polymer ($M_n = 1.523 \times 10^5$ g/mol, $M_w/M_n = 1.18$) with an average of 18.7 arms per star (Table 1, entry 5A). The structure of this CCS polymer is such that each arm is end functionalized with a hydroxyl group whereas the core contains an equivalent amount of alkyl bromide groups capable of initiating ATRP reactions. This CCS polymer was subsequently reacted with an excess of 2-bromoisobutyryl-bromide to convert the terminal hydroxyl groups into ATRP-initiating functionalities similar to the alkyl bromide groups preserved within the core. ^{1}H NMR analysis of the reaction product (Figure 9) showed that the peak corresponding to the methylene protons adjacent to the terminal hydroxyl group

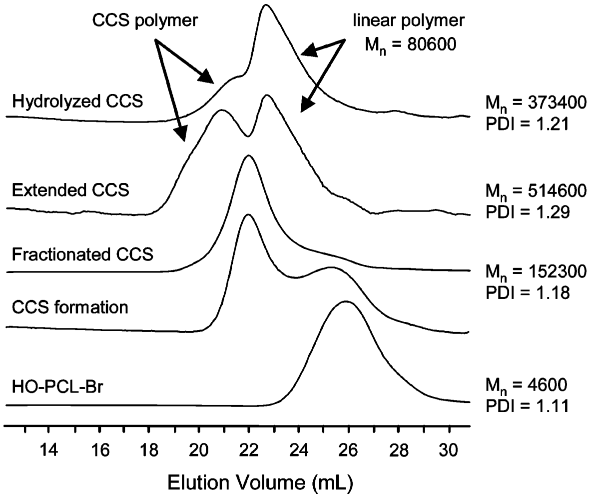


Figure 8. Gel permeation chromatography traces of the core/surface functional core cross-linked star (CCS) polymer chain extended by atom transfer radical polymerization (ATRP) and its subsequent hydrolysed product. The GPC traces of the components involved in the synthesis are also included.

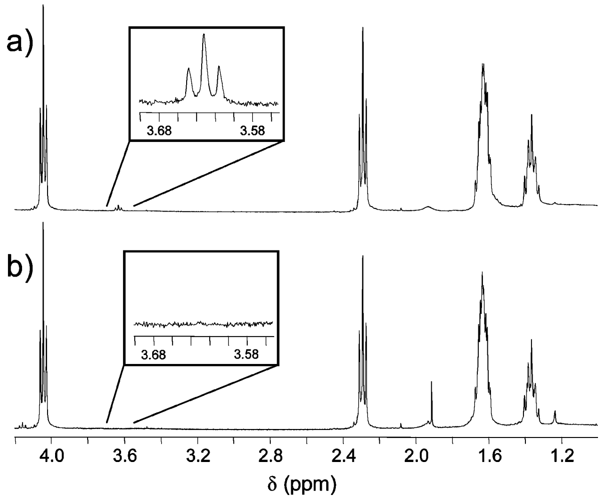


Figure 9. ^{1}H NMR spectra of (a) alkyl bromide core functionalized core cross-linked star (CCS) polymer and (b) alkyl bromide core/surface functionalized CCS polymer.

(CH_2CH_2OH, 3.62 ppm) disappeared upon functionalization indicating that all of the arms have been successfully end capped with ATRP-initiating groups.

The core/surface-functionalized CCS polymer was subsequently used to initiate the ATRP of methyl methacrylate monomer to extend the preexisting arms while simultaneously growing secondary arms out from the core (Scheme 5). GPC traces of the reaction product (Figure 8) showed a shift to a higher molecular weight product ($M_n = 5.146 \times 10^5$ g/mol, $M_w/M_n = 1.29$) (Table 1, entry 5B), indicating that the chain extension of the CCS polymer occurred. In addition to the extended CCS product, a peak corresponding to lower molecular weight ($M_n = 8.06 \times 10^4$ g/mol, $M_w/M_n = 1.08$) was also observed (Figure 8, extended CCS, 22−25 mL elution volume) representing linear PMMA chains generated by the presence of a contaminant capable of initiating ATRP. The source of this contaminant is most likely due to the presence of linear macroinitiator which was not completely removed by the fractionation step. Although this unconverted macroinitiator is considered to be “dead”, it is reactivated during the functionalization of the CCS polymer surface where hydroxyl groups are converted into ATRP-initiating sites. The presence of this linear macroinitiator can be observed in the GPC trace of the fractionated CCS polymer as a low molecular weight shoulder peak, which attributes to ~10% of the total peak area (Figure 8, fractionated CCS, 24−27 mL elution volume). Even though this peak only accounts for ~10% of the area, it is actually based on a mass percentage and consequently, when relative molecular weights are taken into account, is found to account for ~80% on a molar basis. As seen earlier, the initiation efficiency of this linear macroinitiator is close to 100% for ATRP-initiated chain extension whereas the congested structure of the CCS polymer tends to have a significantly reduced initiation efficiency. The reduced initiation efficiency of the star polymer and the presence of a large molar excess of the linear macroinitiator means that the majority of the mass added through the chain extension reaction will be associated with the contaminant macroinitiator. Therefore, while the same amount of contaminant is still present (i.e., ~80 mol %), it will appear as if to have increased substantially on a mass basis due to the uneven distribution of monomer during chain extension. In fact, this is exactly what is observed in the GPC trace of the chain extension product with the contaminant peak now attributing for approximately 50% of the total peak area.

The use of the PCL macroinitiator to synthesize core/surface-functionalized CCS polymer means that the chain-extended star polymer can be degraded to a certain extent (Scheme 5). Hydrolysis of the extended CCS polymer resulted in degradation of the PCL arms and subsequent cleavage of the linear PMMA chains which have been extended from the arms. In addition to this, the EGDMA cross-linked core with PMMA arms, grown out from the core as a result of core-initiated chain extension, was also liberated. GPC analysis of the hydrolysis reaction clearly shows the chain-extended core product (Figure 8, hydrolyzed CCS, 20−22 mL elution volume), which was determined to have a molecular weight of 3.734×10^5 g/mol ($M_w/M_n = 1.21$) (Table 1, entry 5C). The secondary peak in the GPC trace of the hydrolysis reaction (Figure 8, hydrolyzed CCS, 22−25 mL elution volume) can be attributed to the linear PMMA chains generated from chain extension of the contaminant macroinitiator. Since the degradable component of the PCL-*b*-PMMA contaminant is relatively small (4390 g/mol), the contaminant peak appears to be unchanged after hydrolysis having a molecular weight of approximately 7.62×10^4 g/mol. Unfortunately, this contaminant peak obscures the cleaved arm extension product generated from hydrolysis of the extended CCS polymer making it impossible to accurately determine the length of the extended arms and therefore the initiation efficiency of the arms.

The additional molecular weight added through chain extension of the core/surface-functionalized CCS polymer was calculated to be 3.623×10^5 g/mol. Of this additional mass, it is possible to calculate how much was added through chain extension initiated from the arms as opposed to the core. By subtracting the molecular weight of the core (theoretical $M_n = 7.01 \times 10^4$ g/mol) from that of the chain-extended core product (5C) (3.734×10^5 g/mol), the molecular weight contribution from the core-initiated extension was calculated to be 3.033×10^5 g/mol. This accounts for 83.7% of the total extended mass with the other 16.3% (5.90×10^4 g/mol) being attributed to the chain extension initiated from the arms. If it is assumed that the rate of polymerization from the different initiation sites (i.e., core, arm, and contaminant macroinitiator) is the same, then the molecular weight of the hydrolyzed contaminant product (7.62×10^4 g/mol) should be representative of the polymer chains extended from the core and the arms. While this assumption does not take into account the differing degrees

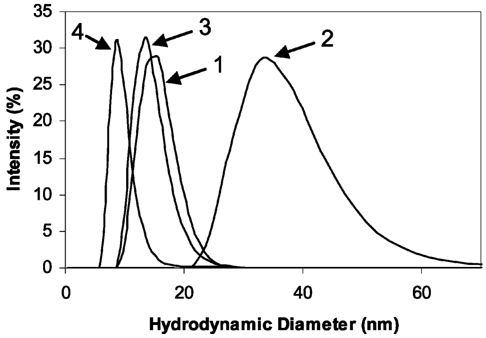


Figure 10. Dynamic light scattering traces of alkyl bromide core/surface functionalized core cross-linked star (CCS) polymer (1), atom transfer radical polymerization chain extended CCS (2), hydrolyzed CCS (3), and naked core (4) (Table 1, entries 5A−C).

of steric hindrance experienced at the core as opposed to the periphery of the arms, it can be used to give an estimation of the theoretical initiation efficiency of these sites, with theoretical efficiencies of 21% and 4% being calculated for the core and the arms, respectively. This shows that in this case the chain extension from the core occurred much more easily than from the arms, which is a counterintuitive result as it is expected that the initiation sites at the core would be more sterically hindered than those at the end of the arms. One potential explanation for this is that the high concentration of propagating radicals at the surface of the CCS polymer resulted in a higher rate of radical termination between the initiating groups of the arms as opposed to the more protected initiating sites within the core. The fact that rapid gelation of the reaction mixture was also a problem is further evidence that this was indeed the case.

The effect of ATRP chain extension on the hydrodynamic diameter of the alkyl bromide core/surface functionalized CCS polymer was studied via DLS (Figure 10). It was found that as the molecular weight of the CCS polymer increased from 1.523×10^5 to 5.146×10^5 g/mol the corresponding hydrodynamic diameter also increased changing from an average of 15.3 nm up to 36.9 nm. As discussed earlier in this paper, the extended CCS polymer can be hydrolyzed to remove the PMMA-*b*-PCL arms and generate the modified CCS polymer with PMMA arms that have been grown out from the core. The hydrodynamic diameter of this modified star polymer was found to be similar to that of the original CCS polymer having an average diameter of 14.2 nm. The effect of these core-extended arms can be seen by comparing the diameter of this modified CCS polymer to that of the core with no arms attached. Generation of the naked core was achieved by hydrolyzing the original core/surface-functionalized CCS polymer (5A) to remove the PCL arms and liberate the EGDMA cross-linked core. The hydrodynamic diameter of this naked core was determined to be 9.4 nm, showing that the core-extended arms add an extra 4.8 nm to the overall hydrodynamic size of the CCS polymer.

Conclusions

The synthesis of functionalized CCS polymers which can be structurally modified postsynthesis was shown to be an efficient method for manipulating properties such as the size, density, and chemical composition of the CCS corona. A novel CCS polymer with a degradable outer coronal layer of PCL was synthesized using semidegradable PCL-*b*-PMMA arms. Hydrolysis of the PCL layer was found to effectively reduce the arm length of the CCS polymer and consequently reduce the overall hydrodynamic size of the polymer. The opposite effect was observed for the case of surface-functionalized CCS polymer, which was shown to be capable of initiating both ROP and ATRP type reactions from the periphery of the arms. Chain extension of this type of CCS polymer resulted in increased arm lengths and hydrodynamic diameters even though initiation efficiencies were found to be adversely affected by the sterically hindered structure of the CCS polymer. The synthesis of a third class of CCS polymer capable of simultaneously initiating polymerization from the core and the arms was also investigated. Chain extension of this core/surface-functionalized CCS polymer under ATRP reaction conditions was shown not only to increase the length of the preexisting arms but also to increase the number of arms. This resulted in an increased hydrodynamic diameter with the better protected initiating sites within the core being found to undergo a higher degree of initiation than the functionalized arms.

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