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Thermoresponsive Polyphosphazene-Based Molecular Brushes by Living Cationic Polymerization

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Summary: A series of polyphosphazenes with molecular brush type structures have been prepared with controlled molecular weights and narrow polydispersities. The polymers show lower critical solution temperatures (LCST) between 18 and 90 °C, which can be easily tailored by choice of side-substituent to suit the required application. A temperature triggered self-assembly is observed to give stable colloidal aggregates with dimensions in the region of 100–300 nm.

Keywords: biodegradable polymers; lower critical solution temperature; polyphosphazenes; self-assembly; thermoresponsive polymers

Introduction

Polymers with precisely controlled molecular structures have become ever more common place in recent years and in this context the living cationic polymerization route to polyphosphazenes[1,2] is an important development, enabling not only controlled molecular weights and narrow polydispersities (1.1–1.4), but also access to block copolymers[3–6] and a variety of star[7,8] and brush-type[9,10] architectures. The poly(dichlorophosphazene) precursor, otherwise prepared via the ring-opening polymerization of hexachlorocyclotriphosphazene with limited molecular weight control and broad polydispersities,[11,12] undergoes a facile substitution with a host of nucleophiles to give the inorganic/organic hybrid polymers poly(organophosphazenes). Since the properties of the resultant hybrid polymers are largely dependent on the organic substituents, polymers with a wide range of properties can be prepared.[12] An important property of many poly(organophosphazenes) is the tunable biodegradability of the phosphorus-nitrogen backbone, a property which could be of particular advantage for biomedical applications.[13,14]

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Polyphosphazenes showing thermoresponsive behaviour have been developed through the coupling of N-isopropylacrylamide side groups onto the polyphosphazenes backbone,[15,16] as well as through side-chain combinations of hydrophilic polyethylene glycol oligomers and hydrophobic amino acid esters.[17,18] Such responsive materials possess a number of potential applications, including drug delivery systems,[19–21] targeted cancer therapy,[22] as well as in tissue engineering[23] and biomimetic materials.[24]

In this contribution, we report a new route to thermosensitive polyphosphazenes with a combination of controlled structures, biodegradability and lower critical solution temperatures (LCST) by simple tuning of the macromolecular structure. To do this we coupled a series of statistical mono amine-capped PEO/PPO copolymers (tradename Jeffamine, Huntsman Cooperation) that possess several interesting properties, including enhanced cell uptake compared to the less lipophilic PEG,[25] and importantly an LCST, the value of which varies with the proportion of ethylene oxide/propylene oxide units. Examples of the thermosensitive behaviour of Jeffamines include poly(L-glutamic acid (PGA) spherical micelles consisting of a Jeffamine core with a temperature controlled response,[26] as well as thermosensitive hydrogels based on polysaccharides with grafted Jeffamine side

groups.[27] In this work such oligomeric Jeffamines were grafted onto the biodegradable polyphosphazene backbone to impart a thermosensitive response onto the polymers. The thermosensitivity of these molecular brush type polymers was investigated.

Experimental Part

Materials and Methods

All synthetic procedures were carried out under inert atmosphere in a glovebox (MBRAUN) or using standard Schlenk line techniques. The glassware was dried in an oven at 120 °C prior to use. PCl_5 was purified by sublimation and stored under argon. NEt_3 was dried over molecular sieves and distilled prior to use. Solvents were dried using standard laboratory methods. The monomer trichlorophosphoranimine was synthesized according to literature procedures as described previously.[28] Amino capped statistical poly(ethylene oxide-co-propylene oxides) PEO-PPO-NH_2, sold under the trade name Jeffamine M-1000/M-2070/M-2005 were donated by Huntsman Performance Products (Netherlands) and used as received. The PEO-PPO-NH_2 M-1000 has a nominal molecular weight of 1000 and an ethylene oxide/propylene oxide ratio of 19/3, M-2070 and M-2005 have a molecular weight of 2000 and an ethylene oxide/propylene oxide ratio of 31/10 and 6/29, respectively. All other chemicals were purchased from Sigma Aldrich and used without further purification.

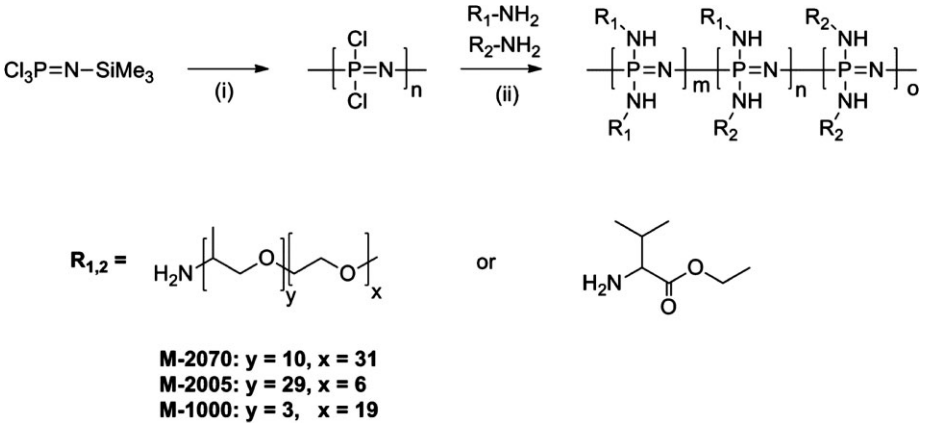
^{1}H NMR (300 MHz) spectra were measured on a Bruker 300 MHz spectrometer using $CDCl_3$ as an internal reference. ^{31}P NMR (121 MHz) spectroscopy was carried out using 85% phosphoric acid as an external standard. Gel permeation chromatography (GPC) was performed on a Viscothek GPCmax instrument using a PFG column from PSS (Mainz, Germany) (300 mm × 8 mm, 5 μm particle size). DMF containing 5 mM LiBr was used as the mobile phase at a flow rate of 0.75 ml min^{-1} at 60 °C. The molecular weights were calculated using a conventional calibration versus linear polystyrene standards from PSS (Mainz, Germany). UV turbidity measurements were carried out on a Varian UV-Visible Spectrophotometer Cary 100 BIO at 500 nm of aqueous polymer solutions with a concentration of 2 wt %. The optical transmittance was measured over a given temperature range after 10 minutes to equilibrate the system. The data points were fitted with a Boltzmann sigmoidal function and the given cloud point values correspond to the temperature at 50% transmittance. Dynamic light scattering (DLS) was performed on a Malvern Zetasizer Nano ZS instrument with a detection angle of 173° and a 4 mW He-Ne laser operating at a wavelength of 633 nm. The samples were prepared in deionized H_2O (0.5 mg ml^{-1}) and filtered through a 0.2 μm nylon filter at 5 °C. The size of the polymer was determined from the intensity size distribution at 5 °C and 37 °C.

Poly(dichlorophosphazene)

The living cationic polymerization of chlorophosphoranimine (scheme 1) was used to synthesize poly(dichlorophosphazenes).[1,29] All polymers were synthesized with the same ratio of monomer to initiator (25/1). $Cl_3P=N\text{-}TMS$ (0.70 g, 3.12 mmol) and PCl_5 (0.03 g, 0.12 mmol) were dissolved in 5 ml CH_2Cl_2 and stirred for 12 hours at room temperature in the glovebox. The solvent was removed under vacuum and the polymeric precursor, poly(dichlorophosphazene), was used for subsequent macromolecular substitution without further purification. Yield quantitative. ^{31}P NMR ($CDCl_3$): −18.42 ppm.

Polymer Substitution

This typical example describes the synthesis of polymer **1**. To a solution of M-2005 (10.00 g, 5.00 mmol, 2.4 eq) in anhydrous THF and NEt_3 (0.51 g, 0.69 ml, 5.00 mmol) was added a solution of poly(dichlorophosphazene) (0.47 g, 2.08 mmol) in anhydrous THF and reacted for 24 hours at room temperature. The reaction mixture



Scheme 1.
Synthesis of poly(organophosphazenes) via the living cationic polymerization of chlorophosphoranimine to obtain poly(dichlorophosphazene) and subsequent macromolecular substitution reactions. Reagents and conditions: (i) PCl_5, CH_2Cl_2, room temperature, 12 hours and (ii) NEt_3, THF, room temperature, 24 hours.

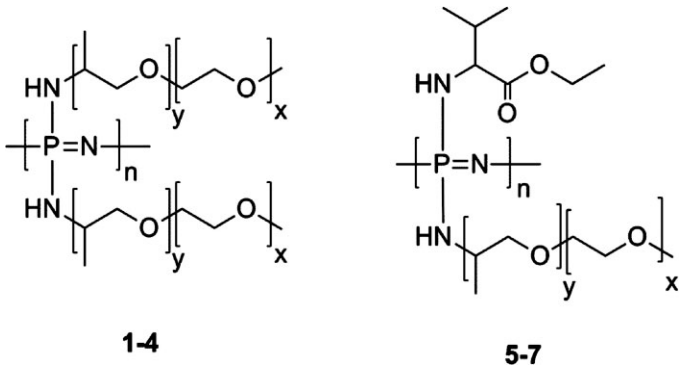
was filtered and the solvent was removed under vacuum. The product was dialyzed against ethanol for several days and dried under high vacuum to yield a colourless, highly viscous liquid. For polymers 2–7, the chemical structure of the side groups and the amounts of the side groups were varied in order to obtain the desired polymers (scheme 2). In case two different side groups were attached to the poly(dichlorophosphazene), the two substituents were mixed in the desired ratio in THF followed by the addition of the polymer precursor and NEt_3. All polymers were dried under vacuum to give viscous liquids in yields of 30 to 80%.

Polymer **1**. ^{1}H NMR ($CDCl_3$): δ 1.13 (m, 87H, CH_3 of PO), 3.37–3.42 (br, m, 32H, OCH_3 and CH of PPO), 3.48–3.59 (br, 55H, OCH_2), 3.64 (br, t, 14H, OCH_2) ppm. ^{31}P NMR ($CDCl_3$): δ 0.19 ppm.

Polymer **2**. ^{1}H NMR ($CDCl_3$): δ 1.13 (m, 72H, CH_3 of PO), 3.37–3.43 (br, m, 27H, OCH_3 and CH of PPO), 3.50–3.59 (br, 46H, OCH_2), 3.64 (br, t, 29H, OCH_2) ppm. ^{31}P NMR ($CDCl_3$): δ 0.72 ppm.

Polymer **3**. ^{1}H NMR ($CDCl_3$): δ 1.13 (m, 54H, CH_3 of PO), 3.37–3.43 (br, m, 21H, OCH_3 and CH of PPO), 3.50–3.57 (br, 34H, OCH_2), 3.64 (br, t, 33H, OCH_2) ppm. ^{31}P NMR ($CDCl_3$): δ1.13 ppm.

Polymer **4**. ^{1}H NMR ($CDCl_3$): δ 1.13 (m, 50H, CH_3 of PO), 3.37–3.42 (br, m, 19H, OCH_3 and CH of PPO), 3.47–3.56 (br, 30H, OCH_2), 3.64 (br, t,



Scheme 2.
Representative structures of polymers **1-7**.

58H, OCH_2) ppm. ^{31}P NMR ($CDCl_3$): δ −0.07 ppm.

Polymer **5**. ^1H NMR ($CDCl_3$): δ 0.93 (br, 6H, CH_3 of ValOEt), 1.13 (m, 27H, CH_3 of PPO), 3.38 (s, 3H, OCH_3), 3.64 (br, s, 148H, OCH_2) ppm. ^{31}P NMR ($CDCl_3$): δ 1.03 ppm.

Polymer **6**. ^1H NMR ($CDCl_3$): δ 0.91 (br, 9H, CH_3 of ValOEt), 1.13 (m, 75H, CH_3 of PPO), 3.37–3.43 (br, m, 28H, OCH_3 and CH of PPO), 3.48–3.59 (br, 49H, OCH_2), 3.64 (br, t, 12H, OCH_2) ppm. ^{31}P NMR ($CDCl_3$): δ 0.32 ppm.

Polymer **7**. ^1H NMR ($CDCl_3$): δ 0.93 (br, 12H, CH_3 of ValOEt), 1.14 (m, 6H, CH_3 of PPO), 1.25 (br, 6H, CH_3 of ValOEt), 3.38 (s, 3H, OCH_3), 3.64 (br, s, 76H, OCH_2) ppm. ^{31}P NMR ($CDCl_3$): δ 0.72 ppm.

Results and Discussion

The poly(dichlorophosphazene) precursor, previously prepared by the living cationic polymerization of trichlorophosphoranimine, was fully substituted with a range of substituents to give a series of molecular brush type[30] poly(organophosphazenes) (scheme 1). The rationale behind the choice of substituents for this polymer series was that subtle variations in the properties of organic side chains are known to have a defining influence on the properties of the resulting poly(organophosphazene).[13] Complete substitution of the chlorine atoms was confirmed (up to NMR detection limits) by ^{31}P NMR spectroscopy and the chemical structure was further confirmed by ^1H NMR spectroscopy (figure 1a-c).

As expected from the living, cationic polymerization, polymers with controlled molecular weights and relatively narrow polydispersities could be prepared, as shown by GPC analysis (figure 1d and table 1). The apparent absolute molecular weights measured in DMF against conventional polystyrene standards are grossly underestimated, as would be expected for such highly branched polymers.[31]

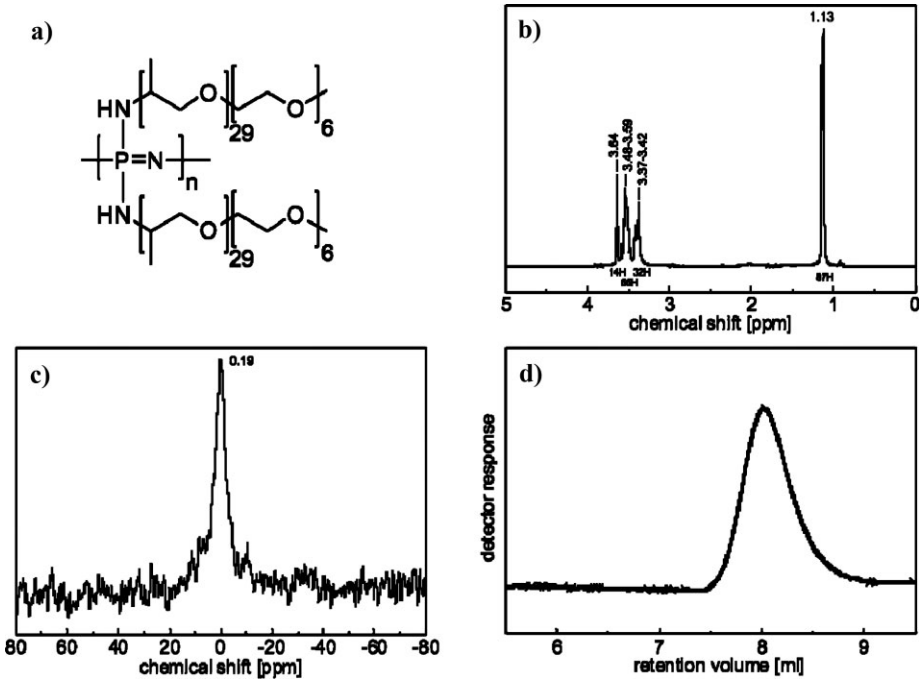


Figure 1.
Characterization of polymer **1**: a) Chemical structure; b) ^1H NMR spectrum in $CDCl_3$; c) ^{31}P NMR spectroscopy showing a single peak for the fully substituted poly(organophosphazene); d) GPC chromatogram.

Table 1.
Characterization of polymers **1-7**.

Polymer	R_1	R_2	Ratio[a]	^{31}P NMR	M_n[b] (M_n^{theo})	M_w/M_n[b]	CP[c]
			R_1:R_2	ppm	kg mol^{-1}		°C
1	M-2005	–	1	0.19	44.2 (202.2)	1.31	18
2	M-2005	M-2070	0.85:0.15	0.72	36.9 (202.2)	1.22	56
3	M-2005	M-2070	0.75:0.25	1.13	40.5 (202.2)	1.24	60
4	M-2005	M-2070	0.50:0.50	−0.07	44.2 (202.2)	1.29	90
5	M-2070	ValOEt[d]	0.25:0.75	1.03	28.5 (63.0)	1.17	76
6	M-2005	ValOEt[d]	0.25:0.75	0.32	24.7 (63.0)	1.25	25
7	M-1000	ValOEt[d]	0.25:0.75	0.72	10.8 (38.0)	1.33	–

[a] Ratio added; [b] Determined by GPC analysis versus linear polystyrene standards (M_n^{theo} theoretical M_n); [c] Cloud point determined by UV-Vis spectroscopy at 50% decrease in optical transmittance; [d] ValOEt = Valine ethyl ester.

Although all polymers were prepared with the same backbone chain length, the theoretical (and measured) molecular weights vary due to the different sizes of the side-substituents, as well as their different hydrophobicity and thus hydrodynamic volume. The polymers formed were all highly viscous liquids, the characterization and properties of which are summarized in table 1. It should be noted that, due to their structural similarity, the reported ratios of M-2005 to M-2070 grafted to the polyphosphazenes backbone are the proportions added and thus assume approximately equal reactivity of the two oligomers.

The hydrophobicity/hydrophilicity of the polymers is clearly expected to have a critical impact on the thermosensitive behaviour of the resulting polymers and indeed the thermosensitivity could be simply varied through the propylene oxide/ethylene oxide (PO/EO) ratio of the Jeffamine side chains (polymers **1-4**). Representative structures are shown in scheme 2. M-2005 (PO/EO ratio 29:6) is considerably more hydrophobic than M-2070 (PO/EO ratio 10:31) thus imparting a considerably more hydrophobic character onto the given number of side-chains and as a consequence onto the macromolecule as a whole.

The thermosensitivity of aqueous solutions of the polymers was investigated by turbidity measurements observing the transmittance at 500 nm UV-spectroscopy (figure 2). Polymer **1**, with 100% M-2005 showed a sharp cloud point at 18 °C. Addition of the more hydrophilic M-2070 units, in ratios of 15 to 50%, resulted in a significant increase in the cloud points. The mixture of substituents also resulted in a pronounced broadening of the cloud point transitions, thought to occur as a result of the heterogeneity of the polymers.[32]

Polymers **5-7** were prepared with a mixed substitution of Jeffamines (M-2005, M-2070, M-1000) and valine ethyl ester groups in molar ratios of approximately 25/75. This was carried out firstly as it is expected to alter the hydrophobicity and rigidity of the polyphosphazenes backbone, and hence the properties of the polymers, but more importantly as it increases the spacing between the otherwise densely packed side chains (two chains per repeat unit for polymers **1-4**). Furthermore, the addition of amino acid ester units is known to enhance the rate of biodegradation of the polymers.[33] It was observed from turbidity measurements (figure 3), that despite the relatively low molar ratio of Jeffamine to ethyl valinate (25/75), the thermoresponsive properties of the resulting poly(organophosphazene) was predominately influenced by the Jeffamine used, suggesting that the ratio of ethylene oxide to propylene oxide has a significant impact on the thermosensitive properties of the resultant poly(organophosphazenes) and thus is an effective option to tailor these properties. Despite the mixed substitution, only a small broadening in the cloud point transition was observed for polymers **5**

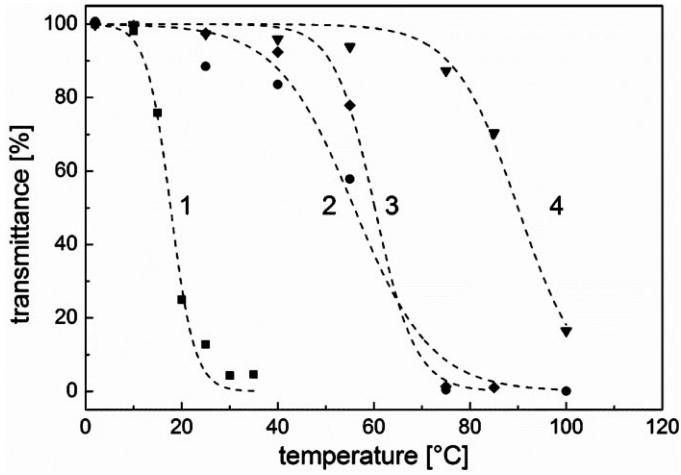


Figure 2.
Optical transmittance measurements for aqueous solutions of polymers **1** to **4** on 2 wt % solutions in deionized H_2O measured by UV-Vis spectroscopy at 500 nm.

and **6**. Polymer **7**, with the highly hydrophilic M-1000 side groups (PO/EO ratio 3/19) showed good aqueous solubility and no LCST behaviour below 100 °C.

Dynamic light scattering analysis at 5 °C, i.e. below the LCST temperatures for polymers **1** and **6**, showed hydrodynamic diameters of approximately 16 nm, as would be expected for single polymer molecules of this size (figure 4). A temperature triggered, intermolecular agglomeration was observed upon increasing the temperature above the LCST, with measurements at 37 °C showing a 10-20-fold increase in the hydrodynamic volumes. A slightly higher hydrodynamic diameter of the aggregates was observed for polymer **6** (280 nm), than was the case for polymer **1** (140 nm). Since the individual polymer chains are approximately the same size

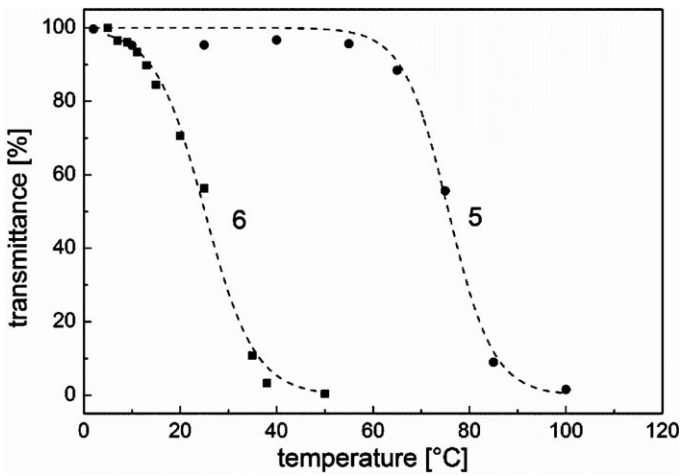


Figure 3.
Optical transmittance measurements for aqueous solutions of polymers **5** and **6** on 2 wt% solutions in deionized H_2O measured by UV-Vis spectroscopy at 500 nm.

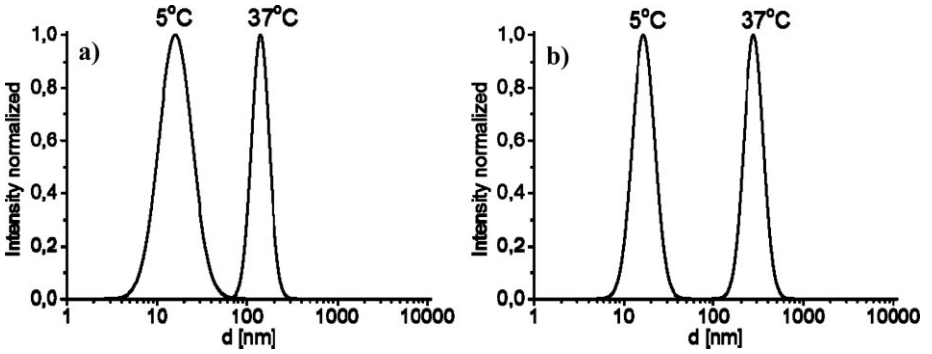


Figure 4.
Dynamic light scattering measurements for a) polymer **1** and b) polymer **6** measured at 5 and 37 °C and a concentration of 0.5 mg ml^{-1}. Thermally triggered aggregation can be observed.

(16 nm), this is possibly due to the less densely packed nature of the polymer branches, allowing greater agglomeration of polymer **6**.

The polyphosphazenes backbone is known to be highly flexible and similar polymers with N-isopropylacrylamide oligomers grafted to a polyphosphazene backbone have been shown to form micelles[16] and temperature-triggered nanospheres.[34] Internal inter-chain aggregation within one molecular brush polymer could also be expected.[35] It is possible that a shrinkage of the individual polymer chains occurs prior to and/ or during aggregation, due to a coil-to-globule transition within only one molecular brush type polymer.[35] However, with tests at extremely low concentrations (down to 0.1 mg ml^{-1}) it was not possible to observe a single molecule contraction.

Polymers **1** and **6**, with LCST's below 37 °C, were observed to degrade rather slowly in comparison to similar poly(organophosphazenes),[33] with no phosphate (a backbone degradation product) being detected after 4 weeks in aqueous solution at 37 °C. This is thought to be due to the highly hydrophobic nature of the Jeffamine M-2005 side chains, restricting H_2O attack on the polyphosphazenes backbone. Furthermore, above the LCST, the hydrophobic domains of the polymers can be reasonably expected to pack towards the backbone, further protecting it from hydrolytic attack. GPC analysis of the degradation medium also confirmed the relatively slow degradation of polymer **1** compared to similar brush-type poly(organophosphazenes), with no changes being observed after 4 weeks under aqueous conditions. Polymer **6**, however, did undergo slow degradation at reduced pH (pH 2) resulting in a shift of the polymer peak to longer retention times in the GPC chromatogram and another peak arising corresponding to the released Jeffamine M-2005 side chains at 2000 g mol^{-1}. It is therefore possible to alter the degradability using ethyl valinate as a co-substituent without losing the thermosensitive behaviour of the polymer. A more in-depth study of the biodegradation behaviour is currently underway.[36]

Conclusion

A series of thermosensitive poly(organophosphazenes) with variable LCST's could be prepared via the grafting of amphiphilic Jeffamine oligomers. The polymers had molecular brush type structures and could be prepared with controlled molecular weights and narrow polydispersities. A temperature triggered self-assembly is observed to give stable colloidal aggregates with dimensions in the region of 200 nm. The cloud point was observed to vary with differing ratios of EO/PO in the polymer side chains. It is envisaged that, with the structural control and the biodegradability

of the polymers, in combination with the high multifunctionality (two functional groups per polymer repeat unit), these materials could also be useful to prepare thermoresponsive controlled drug delivery vehicles.

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