

A CONFORMATION STUDY OF POLYELECTROLYTE-DENDRITIC SURFACTANT COMPLEXES IN DILUTE SOLUTIONS*

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Abstract Three dendronized polymers from generation one to generation three have been prepared by complexing negatively charged Fréchet-type dendrons with a polyanion, poly(diallyldimethylammonium chloride) (PDADMAC). The grafting degree has been confirmed mainly by elemental analysis. In dilute solutions of tetrahydrofuran, static light scattering studies indicate that the first generation complex has a coil-like conformation, even more flexible than PDADMAC. The second and third generation complexes exhibit polyelectrolyte behavior. Dynamic light scattering experiments indicate that all the three complexes have almost the same hydrodynamic radius, indicating that they might own similar coil conformation. Atomic force microscopy shows the existence of disordered globules formed by one or a couple of complex coils. All these observations can be explained by the flowerlike coil conformation, which is formed by the intra-molecular association. This is totally different from the stretched chain conformation formed by covalently connected dendronized polymers. This result also explains why some ordered supramolecular structures, found in condensed state of the similar complexes, are not as perfect as those of conventional dendronized polymers.

Keywords: Polyelectrolytes; Dendrons; Complexes; Dendronized polymers; Flowerlike coils.

INTRODUCTION

Supramolecular synthesis based on non-covalent interaction has been a promising strategy in constructing new molecules and nano-objects^[1–3]. One of the most important fields is concerning the complexation between low molecular weight ionic surfactants and oppositely charged polyelectrolytes that can result in highly ordered polymer structures in solid state^[4–6] and in polyelectrolyte-gel-surfactant system^[7, 8]. This widely studied self-assembling strategy shows a number of advantages, such as facile preparation and purification, a wide range of available materials equipped with abundant important functions and so on. More importantly, these structures can be easily controlled on a nanoscale by tuning charge density and chain flexibility of polyelectrolytes as well as the alkyl chain length and tail topology of surfactants, thus have broad potential applications in catalytic, optical, electrical and biological systems^[9].

These polyelectrolyte-surfactant complexes are usually insoluble in water. Depending on alkane chain length and the hydrophilic/lipophilic balance, the complexes dissolve in organic solvents with different polarity^[6, 10]. Studies on their solution behaviors showed that these complexes had “comb-like” structures in which the surfactant head groups were electrostatically bound with the charged units of polyelectrolytes, whereas the hydrophobic tails of the surfactants were exposed to the bulk solvent^[11].

Meanwhile, as a novel polymer structure, dendronized polymers^[12–14] exhibit a series of unique properties

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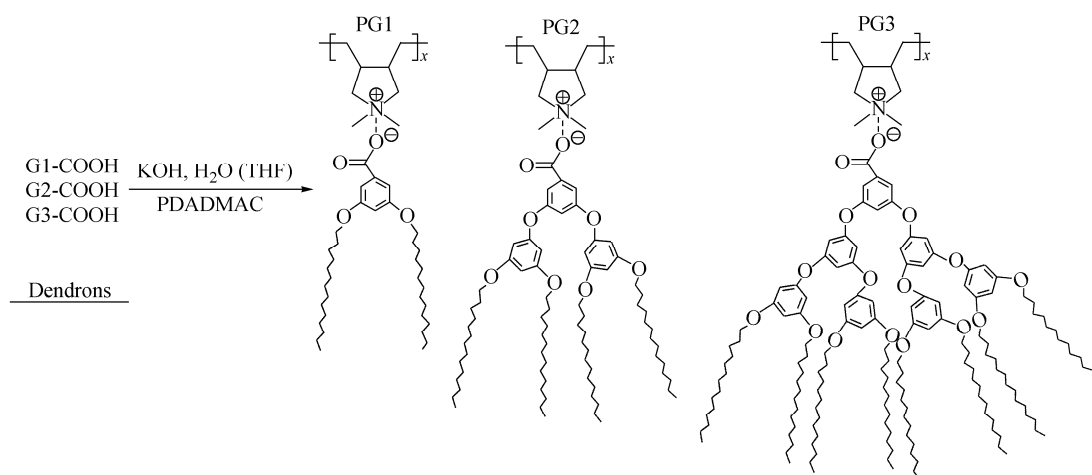
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for research and potential applications in the field of light-emitting devices, catalytic chemistry and individual conductive nanowires, thus have attracted a lot of research interests. However, at present their synthesis is still a great challenge^[13,15], so it is not easy to produce such macromolecules. In graft-to and graft-from strategies, the products with some defects along the backbone can be generated, and their separation to get the desired products is very difficult. Macromonomer strategy is the most successful method so far; however, the steric hindrance may have a large effect on the polymerization, being able to lead to oligomeric products with a very broad molecular weight distribution.

In recent years, some efforts have been devoted to synthesis of non-covalent forces based on dendronized polymers^[16], especially the ones involving the ionic interaction that is sufficiently strong enough to provide adequate stabilities^[5]. The pioneering work on this goes back to Bilibin and coworkers^[17], who described the ionic binding of a polyelectrolyte with oppositely charged focal ionic groups of dendrons. Zhu *et al.*^[18] and Cheng *et al.*^[19] independently reported the liquid-crystalline behaviors of complexes formed by combination of wedged pendants and polymer chains through ionic interaction, and the formed supramolecular structures have a dependence on grafting degree and binding site. Stoddart and coworkers used the strong complexation between dialkylammonium ion centers and a crown ether unit to construct dendronized polyacetylenes. Because this complexation only occurs in acidic circumstance, the acid-base switching properties are realized^[20]. Very recently, our group successfully attached the poly(urethane amide) (PUA) dendrons to a linear polyelectrolyte through ionic interaction and found that using a polyelectrolyte as templates the ability of forming organogel of this PUA dendron was greatly enhanced^[21].

In the systems described so far we can see that most of the work were focused on their supramolecular structures in solid states, little study about the influence of dendritic structure on the properties of individual macromolecules, which is of fundamental interest in this system, was carried out. In this work we will try to reveal some behaviors of individual macromolecules of polyelectrolyte-dendritic surfactant complexes in solution. Our main aim is to understand the effect of the defects along the backbone on the properties of the complexes, not only in solution but also in the solid state. To achieve this goal, three dendronized polymers from generation one to generation three were prepared through ionic interaction. Their chemical structures are shown in Scheme 1.



Scheme 1 Preparation and chemical structure of the three dendronized polymer complexes, PG1, PG2 and PG3, respectively

Clearly, the dendron size increases with the dendron generation and is much larger than that of conventional surfactants. Therefore, we argue whether all dendritic surfactants can completely and homogeneously graft to the polyelectrolyte backbone to form a defect-free dendronized polymer. In this work, the grafting degree will be determined mainly using element analysis. Meanwhile, the behaviors of the polymers

in dilute solutions will be studied by static and dynamic light scattering (SLS and DLS), and the polymer aggregates formed in the solution will be characterized by atomic force microscopy (AFM). Our results will indicate that the grafting degree will decrease with increasing dendron generation. So, the polymers are not fully dendronized and a couple of ions remained along the backbone will be able to result in an intra-molecular aggregation of the dendronized polymers in dilute solutions. This behavior is different from conventional polyelectrolyte-surfactant complexes or dendronized polymers in which polymers and dendrons are covalently linked.

EXPERIMENTAL

The preparation and purification procedure of the complexes has been described in the literature^[22].

Techniques

Nuclear magnetic resonance (¹H-NMR) spectra were recorded in CDCl₃ (D 99.0% + TMS 0.03%, CIL) on a Bruker AM-400 spectrometer at 400.13 MHz at room temperature. All δ values downfield from the signal of tetramethylsilane (TMS) were given. Elemental analysis (EA) was carried out on a VarioEL III system (C H N modus).

Light scattering (LS) experiments were performed on an ALV/DLS/SLS-SP 5022 F compact goniometer with an ALV 5000 E/E correlator and a He-Ne laser ($\lambda = 632.8$ nm). Dynamic light scattering (DLS) was conducted at a fixed scattering angle of 90°. CONTIN analyses were performed for the measured intensity correlation functions. Apparent hydrodynamic radii, R_H , were calculated according to Eq. (1):

$$R_H = \frac{k_B T}{6\pi\eta D_0} \quad (1)$$

where k_B is Boltzmann's constant, T is the absolute temperature, and η is the coefficient of viscosity of the solvent. SLS experiments were measured in the range from 40° to 140° with a step of 10°. The radii of gyration (R_G) and M_w were obtained from the intercepts and slopes of the extrapolated data (*i.e.* $c \rightarrow 0$ and $\theta \rightarrow 0$), respectively, according to Eq. (2):

$$Kc/\Delta R_\theta = (1/M_w)[1 + (16\pi^2 \langle R_G^2 \rangle / 3\lambda^2) \sin^2(\theta/2) + \dots] + 2A_2c + \dots \quad (2)$$

where ΔR_θ is the excess Rayleigh ratio of a polymer solution at a scattering angle θ , λ the wavelength of incident light, A_2 the second virial coefficient, $\langle R_G^2 \rangle$ the mean square radius of gyration of polymers in a solution, and c the polymer concentration. For vertically polarized incident light, the optical constant, K , is given by $K = 4\pi^2 n_0^2 (dn/dc)^2 / (\lambda^4 N_A)$, where n_0 is the refractive index of the solvent, N_A the Avogadro's number, and dn/dc the differential refractive increment of a polymer solution. All the LS measurements were carried out at $(25 \pm 0.1)^\circ\text{C}$. For the SLS measurements the samples were dissolved in THF at different concentrations in the range of $0.1 \text{ g/L} \leq c \leq 1.0 \text{ g/L}$. To remove dust, before measurements all the solutions were filtrated twice through PTFE filters with pore size of $0.2 \mu\text{m}$.

Atomic force microscopy (AFM) measurements were performed on a Digital Instruments Dimension 3100 microscope operated in tapping mode. The micro-cantilever used for the AFM measurements was from Olympus with resonant frequency between 284.3 kHz and 386.0 kHz, and the spring constant ranging from 35.9 N/m to 92.0 N/m. For AFM experiments, the samples were prepared on silica by a spin-coating method (2000 r/min) from a THF solution of 0.01 g/L. The fresh solution was prepared immediately before deposition by dilution of the stock solution of 1.0 g/L.

RESULTS AND DISCUSSION

Physical Properties of Dendronized Polymer Complexes

In our previous study we have presented experimental evidence to indicate the formation of the polyelectrolyte-

dendritic surfactant complexes^[22]. We also observed some changes in some physical properties such as viscosity and solubility after the formation of these complexes. The complexes are very sticky, indicating themselves as a kind of polymer. Meanwhile, their solubility differs much from the parent polyelectrolyte. Upon complexation, the polyelectrolyte, which was soluble in water, is embraced by plenty of alkyl chains and becomes highly hydrophobic. That is the reason why the complexes are soluble in low polar solvents, such as tetrahydrofuran (THF) and chloroform, and can not be dissolved in high polar solvents, such as water, dimethylformamide and dimethylamine.

Grafting Degree

It seems impossible to get a reliable grafting degree and molecular weight by means of peak integration in ¹H-NMR spectra (Fig. 1) due to the different relaxation time in such high molecular weight materials as well as the shieldness of dendrons to the backbone^[13]. We can see that in the ¹H-NMR spectra the backbones only show a broad peak, and in PG3 spectrum the shieldness becomes so serious that the signals from the backbone become very weak and are hardly distinguished as shown in the inset of Fig. 1.

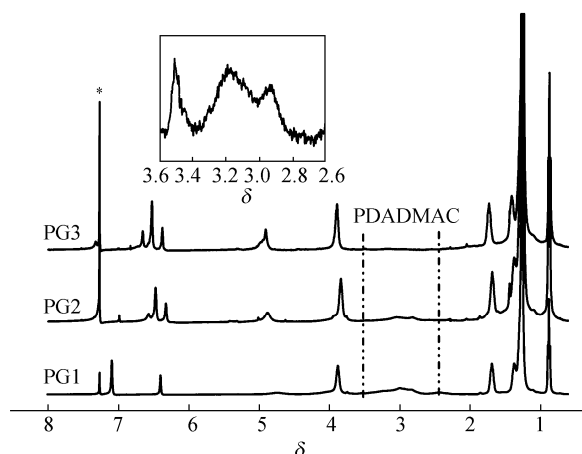


Fig. 1 ¹H-NMR spectra of PG1, PG2 and PG3
The inset shows the main signals of backbone in PG3 (* the peak of CDCl₃).

In this work, element analysis has been used to provide the accurate grafting degree^[23]. The EA experimental results of three complexes studied in the work are listed in Table 1. From the C and H contents the grafting degrees can be calculated as 83%, 74% and 64% for PG1, PG2 and PG3, respectively, showing that increasing the generation will lead to a decrease in the grafting degree. These values are reasonable compared with theoretical values for cation-anion 1:1 systems^[24].

Table 1. Surface elemental compositions for three dendronized polymer complexes
Theoretical composition is obtained according to the 100% grafting

Sample	Experimental composition (wt%)			Theoretical composition (wt%)		
	C	H	N	C	H	N
PG1	76.17	12.78	1.730	76.96	11.57	2.09
PG2	77.29	11.96	1.07	78.05	11.17	0.901
PG3	77.98	12.19	0.54	78.64	10.97	0.357

The grafting degree is an important parameter to determine the properties of complexes, and in most of previous studies in which single tail surfactants were utilized to prepare polyelectrolyte-surfactant complexes, a 100% grafting degree was realized. The decrease in grafting degree for the system studied in this paper should arise mainly from the bulky structure of dendritic surfactants. Clearly, increasing the dendrons generation will accordingly increase their volume, thus the steric hindrance constitutes a near-insuperable obstacle for high

grafting degree. Moreover, due to the high hydrophobic properties of high generation dendrons, it becomes more difficult to disperse the salts of dendrons in aqueous solutions, which may also be contributed to these decreasing grafting degrees.

From the grafting degrees, some basic information about the chemical constitution of prepared complexes is obtained and shown in Table 2. We can see that the structural constitution is the function of the dendron generation. As the generation increases, the numbers of C14-alkyl chains and M_w have notable increases, reflecting the more densely packing side chains caused by the increase of generation. Meanwhile, the number of charges is also increasing, which can generate the different miscibility with the dendrons-neutralized polyion chains. These different factors might have different effects on the behaviors of the polymers in solution, and the following discussion will focus on these issues.

Table 2. Some basic information of the three dendronized polymer complexes

Sample	Grafting degree	Theoretical M_w	Number of charges on each backbone	Number of alkyl chains on each backbone
PG1	83%	4.1×10^5	119	1162
PG2	74%	7.1×10^5	182	2072
PG3	64%	1.2×10^6	252	3584

Chain Conformation Characterization by LS

Light scattering was used to characterize the conformation of all the three complexes in THF solutions. In the SLS measurement, PG1 did not show polyelectrolyte behavior, which is in contrast with the observation reported by Antonietti and his coworkers^[10]. As there were a certain number of charges along the backbone, we attribute it to the hyper branched pendants that shield the inter-particle correlation between charges. From the Zimm plots shown in Fig. 2, M_w of PG1 is obtained as 4.2×10^5 , which is in a good agreement with the theoretical M_w (4.2×10^5) from its grafting density of 83%. Since the scattering intensity was very low, we can conclude that the PG1 was dispersed in solutions as individual chains, and the light signals were mainly scattered from them. From this measurement the R_G and R_H can be generated as 20.5 nm and 15.4 nm, respectively, so $R_G/R_H = 1.33$. According to a previous study^[25], $R_G/R_H = 1.33$, close to 1.5 of coil conformation, suggests that the dendronized polymer PG1 has a collapsed-coil conformation. This result is in accord with the result on covalently connected dendronized polymers found by Förster *et al.*^[26] that the dendrons of first generation are not bulky enough to stretch the backbone.

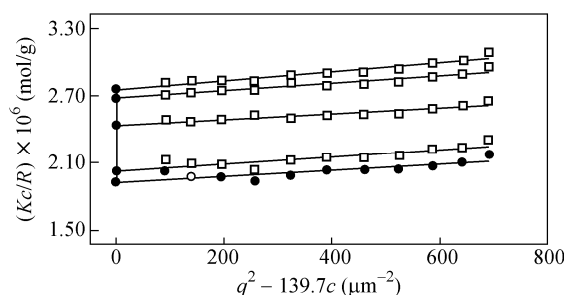


Fig. 2 Zimm plot of PG1 in THF solution: (□) experimental data of scattering ratio (Kc/R), (●) Data of Kc/R linear extrapolation to $c \rightarrow 0$ and $\theta \rightarrow 0$

As we know, the value of R_G/R_H is an indicator of the compactness of polymers in solvents. The R_G/R_H of PDADMAC in salt-free aqueous solutions was reported as 2.0^[27], higher than 1.33 of PG1, indicating PDADMAC had a more extended conformation. This can be easily explained by the fact that due to the introduction of the dendrons most of charges were neutralized by these pendants, as a result the mutual repulsive interaction between the positive charges along the polyelectrolyte chains was greatly reduced.

In the SLS experiments of PG2 and PG3, the scattering intensity was still low, however the scattering ratio Kc/R was decreasing as the angle increased, which is shown in Fig. 3. This is a polyelectrolyte behavior usually

caused by inter-particle correlation. Taking into consideration that PG1 did not show this property, we attribute this property to the strong electrostatic interaction between large quantity of charges in PG2 and PG3. This reveals the important role of the dendrons generation and grafting degree in the behavior of these complexes in dilute solutions.

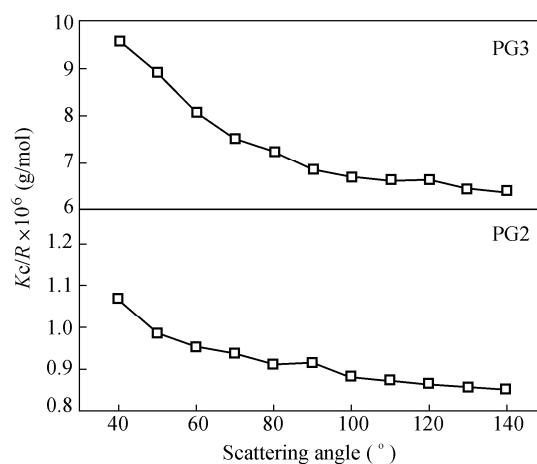


Fig. 3 Kc/R versus scattering angle curves of PG2- and PG3-THF solutions at 1.0 g/L

DLS is the most convenient tool for the determination of R_H with a great accuracy, so we performed such experiments to determine the R_H of all the three complexes in THF solutions. Their correlation functions $g^{(1)}(t)$ recorded at the scattering angle 90° are shown in Fig. 4. We can see that in dilute THF solutions they have almost the same R_H . Because the three complexes studied in this work were prepared from the same polyelectrolyte, they own the same contour length, making the comparison of their R_H reasonable. If the backbone extendedness of these dendronized polymers happens as the generation increases, which was predicted by Zhang *et al.*^[28] and observed by Das *et al.*^[29], there should be a notable increase in R_H . Thus, combining the SLS and DLS results we may deduce that in our system all the three complexes are dispersed in THF as single molecules and they own similar conformation in the concentration used.

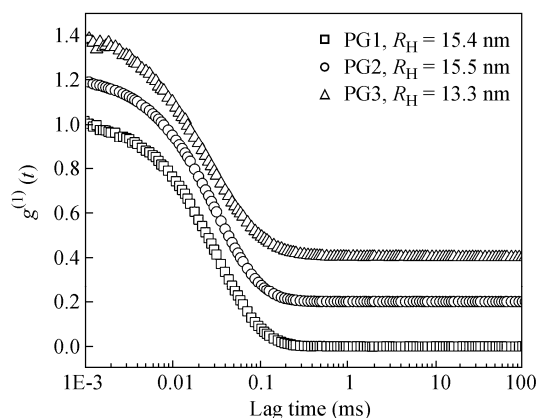


Fig. 4 The correlation function $g^{(1)}(t)$ at the scattering angle (90°) for PG1, PG2 and PG3 THF solutions at a concentration of 1.0 g/L

AFM Studies

AFM is a strong tool to investigate the conformation of dendronized polymers^[12, 13]. Here we applied it to obtain information in real space about the conformation of the complexes spin-coated on the silica surface. Unlike

previous report^[30], we did not observe individual polymer chains but some collapsed round particles as shown in Fig. 5. Increase the generation of the dendritic pendants does not result in any remarkable increase of the height of the particles and most of them retain rather uniformly low height, only about 1.0 nm. However, the measured average lateral dimensions of particles are significantly increasing with the increase of the dendrons generation, consistent with the increasing volume (molecular mass) of single complex molecules.

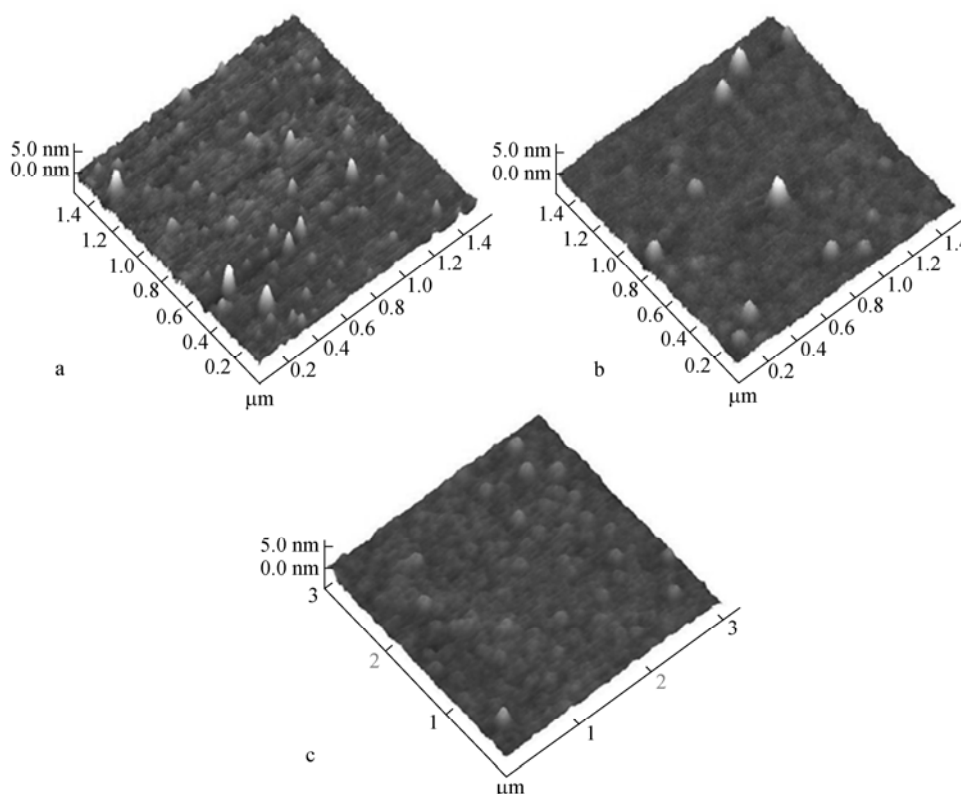


Fig. 5 AFM micrographs of PG1 (a), PG2 (b) and PG3 (c) deposited on silica from solution in THF. The scan sizes are $1.4\ \mu\text{m} \times 1.4\ \mu\text{m}$ (a), $1.4\ \mu\text{m} \times 1.4\ \mu\text{m}$ (b) and $3.0\ \mu\text{m} \times 3.0\ \mu\text{m}$ (c), respectively.

Molecular weight determination by AFM^[31] showed that the estimated number-average molecular weight is somewhat bigger than the theoretical M_w of the individual polymers, indicating that the complexes had a strong tendency to aggregate in solid state and those particles might be composed of one or several polymer coils.

Suggested Aggregate Model

As far back as 1990, Eisenberg *et al.* proposed a morphological model for random ionomers in solid state^[32]. In this model, ion pairs along the polymer backbone tend to aggregate to form ion-rich regions, while the steric effects of polymer chains can oppose this ions-enrichment process. As a consequence, only a certain number of ion pairs can be incorporated to form a micro-domain termed multiplet that plays the role of intra- and inter-polymer cross-linking. Similarly, in low polar solutions and at low ionomer concentrations, most of the polymer chains exist as single chains, and the microphase separation of ionic groups will lead to the flowerlike chain conformation^[33].

We apply this model to explain our observation on the behaviors of the dendronized polymer complexes in dilute solutions. Like ionomers, in dilute THF solutions solvophobic interaction of charges will lead to the formation of multiplets. The ions on the same chain would have a high possibility of being involved in the same multiplets, while the neighboring ions on one chain are difficult to form multiplets due to the steric hindrance

from bulky pendants. The neutralized polymer chains are confined in the vicinity of multiplets, and the elastic forces resulting from the steric effects of bulky pendants are attributed to keep these multiplets from aggregating further. That is, their conformation is controlled by intramolecular association, and polymer chains are in the form of flowerlike coils consisting of looped chains in which charged groups are located within multiplets.

As demonstrated in the previous study^[34], the polyelectrolyte-dendritic surfactant complexes are not fully grafted, so some charges are scattered along the backbone randomly, while due to the self-assembling properties of dendrons other charges can be distributed in the segment where all the charges were not neutralized by dendrons. This distribution will spatially advance the formation of multiplets. In addition, the fluidity property of ionic bonds may also play an important role in this process.

Apparently, this kind of structure will result in a flowerlike conformation of PG1. To PG2 and PG3, due to the introduction of more bulky pendants, the polymer chains should become more rigid, making the conformation theoretically elongated. However, we did not observe the more extended conformation as the generation of dendritic pendants increased. Actually, the R_H of PG3 is even somewhat smaller than PG1's, indicating PG3 has more coiled conformation. The reason may be that along the backbones PG2 and PG3 have more charges than PG1 thus more multiplets can form in individual molecules, which will greatly limit the expanding of polymer chains. Consequently, the expanding tendency and cross-linking effect compensate for each other and lead to the fact that all the complexes had almost the identical R_H . Considering that the molecular weight of PG3 is much bigger than PG1's, we have to conclude that the flowerlike conformation of PG3 is much more condensed than the one of PG1.

In PG1, those formed multiplets are surrounded by a thick covering of flexible loops of polymer chains. Differently, in the case of PG2 and PG3, there are more charges along the backbone and the more rigid polymer chains are difficult to coil to cover these charges, as a result some isolated charges will exist on the periphery of these coils and the electrostatic interactions among polymer chains are greatly enhanced. This is the reason why PG1 did not show polyelectrolyte behavior while PG2 and PG3 did. A schematic representation for these flowerlike coils is shown in Fig. 6.

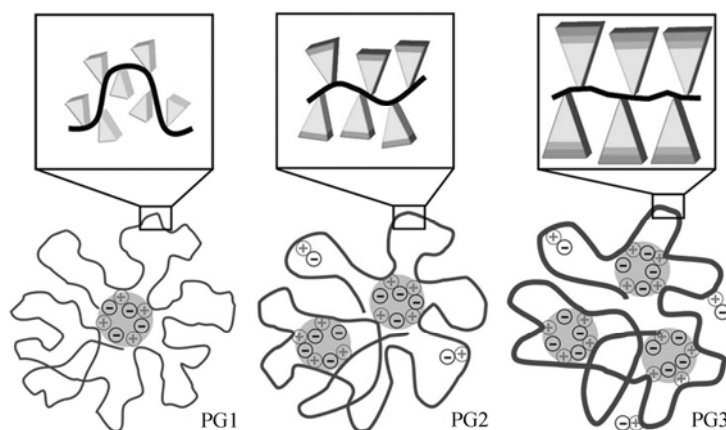


Fig. 6 Schematic representation of the flowerlike coil conformation of the three complexes in dilute THF solutions

An estimation was made based on the chemical structure of PG1. The average length of dendrons-neutralized polymer chains is: $L_w/N = 410/119 = 3.44$ nm where N is the charge number. Thus the loops formed should not be larger than 1.72 nm, which is much smaller than the size of the coils. We have to conclude that there is more than one multiplet even in the coils of PG1. Moreover, the polydispersity of the dendrons-neutralized polymer chains can favor the formation of this conformation, in which long polymer chains tend to form loops while short ones are located inside the coils and play the role in bridging the multiplets.

With the formation of multiplets, it is impossible to observe stretched individual macromolecular chains. As we know, multiplets not only play the role of intramolecular cross-linking, but also advance the intermolecular twist. The former can lead to the formation of globule-like conformation of the single molecules, while the latter will favor the fusion of a certain number of coils, producing larger aggregates. The unconventional shape of PG3 particles is not discussed here.

This fundamental understanding on solution behavior can provide an explanation for the self-organized structures of these complexes in bulk. Small angle X-ray scattering (SAXS) experiments (not displayed here) showed that PG1 can form lamellar structure and PG3 can be arranged into a columnar hexagonal phase, while PG2 might be experiencing the transition from lamellar to columnar structures. However, similar to previous studies^[18, 19, 23], the ordered structures found in such ionic binding dendronized polymers are not as well-defined as the ones formed by covalently linked dendronized polymers^[12, 35, 36]. This may be because in the ionic complexes the flowerlike conformation confines the polymer chains around the multiplets, keeping them from achieving higher order degrees of supramolecular structures.

CONCLUSIONS

Three dendronized polymers from generation one to generation three were successfully prepared through complexing ionic Fréchet-type dendrons with poly(diallyldimethylammonium chloride) (PDADMAC) by ionic interactions. Light scattering was used to study their behaviors in THF solutions. The results of SLS showed that PG1 has a coil-like conformation, more flexible than the PDADMAC, which is caused by the neutralization of charges along the backbone. In PG2 and PG3, there were more charges left on the backbone because of the more bulky pendants, making the polymers exhibit polyelectrolyte behavior. The DLS experiments proved that all the three complexes had almost the same hydrodynamic radiuses, indicating that they might own similar conformations in dilute THF solutions. Under AFM, some globules formed by one or several polymer coils were observed.

Based on our observations as well as previous models for conformation of random ionomers, the flowerlike chain conformation is deduced in which with the formation of multiplets, these polymers exist as individual coils. The entropy effect, elastic forces between bulky pendants, solvation of alkyl chains and electrostatic repulsion between multiplets can contribute to stabilizing these flowerlike coils. The presence of this kind of conformation can be contributed to the observation that the ionic binding dendronized polymers self-organize into less ordered supramolecular structures than covalently linked dendronized polymers. This study would provide insight into the influence of charges on the solution as well as solid behaviors of dendronized polymers.

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