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Aggregation behaviour of a novel series of polyamidoamine-based dendrimers in aqueous solution

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Dendrimers composed of G1 polyamidoamine branched with poly(propylene oxide) (PPO)-*block*-poly(ethylene oxide) (PEO) were synthesised for the first time. Surface tension results showed an increase in the critical aggregation concentration (cac) with PPO-*b*-PEO chain lengthening. The thermodynamic parameters associated with aggregate formation were determined by isothermal titration microcalorimetry, indicating that both the cac and the Gibbs free energy for aggregation (ΔG°) ascended as the amphiphilic chain length increased. The gain of entropy (ΔS°) was the main contribution to aggregation due to $T\Delta S^\circ$ being larger than the enthalpy (ΔH°). Aggregate morphology and size distribution were studied through transmission electron microscope and dynamic light scattering measurements. Furthermore, the relationship between PEO chain length and aggregation behaviour was discussed.

Keywords: dendrimer; critical aggregation concentration; aggregation behaviour

1. Introduction

Dendrimers, possessing a highly symmetrical and branched three-dimensional architecture, represent an intriguing approach to controlling the molecular organisation on the colloidal scale in contrast to conventional colloids (1, 2). Since the pioneer work and development of related cascade molecules appeared in the past two decades (3–8), dendritic structures have been designed and created extensively. Polyamidoamine (PAMAM), one of the most famous dendrimer families with structures thoroughly investigated, can be obtained via the divergent synthesis of excess reagent method (9). It is constructed divergently from an initiator core unit (typically ammonia or ethylenediamine (EDA)) by stepwise branching attachment (e.g. methyl acrylate, MA), with the ordered branching and terminal functionality as a functional generation (G). The reaction with a large molar excess of a multifunctional nucleophile (e.g. EDA) produces a compound with terminal multiplicity and nucleophilic sites that can serve to expand the system further upon repetition of the growth cycle. Through such a reaction sequence, a highly symmetrically branched macromolecule can be prepared.

Up to date, various examples of PAMAM-based dendrimers functionalised with a rigid hydrophobic periphery or chromophoric units or binding metal ions have been intensively investigated (10–13). Little attention, however, has been paid to surface active

characteristics and aggregation behaviour of PAMAM molecules branched with amphiphilic segments (14), though this kind of dendrimers has great importance in many potential application fields, including biochemistry, crude oil industry, emulsion polymerisation, etc. (15–17). With this in mind, we synthesised a series of PAMAM (G1)-based dendrimers branched with poly(propylene oxide) (PPO)-*block*-poly(ethylene oxide) (PEO) whose scheme is shown in Figure 1, abbreviated to PPP_n ($n = 1-3$, standing for different PPO-*b*-PEO chains). The surface and aggregation properties of the interesting dendrimer series in an aqueous solution were investigated in the present work.

2. Experimental section

2.1 Materials

EDA, MA, propylene oxide (PO), ethylene oxide (EO) and all of the inorganic chemicals were obtained from the Beijing Chemical Reagents Company and were of analytical grade. The dendrimer solutions were prepared with triply distilled water.

2.2 Synthesis

Amine-terminated PAMAM (G1) dendrimer with tetra-functional EDA initiator was synthesised and purified according to the reported method (18). To an autoclave,

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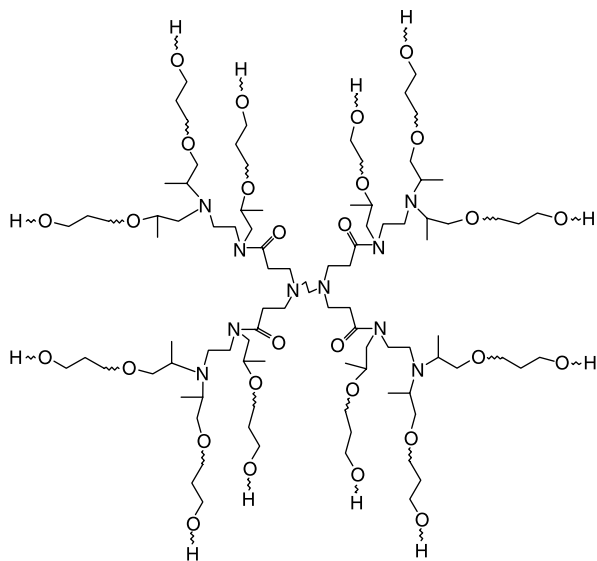


Figure 1. Scheme of PPP_n dendrimer.

1.78 g PAMAM and 0.44 g catalyst KOH were added, and then degassed by pulling vacuum and releasing with nitrogen. When the temperature increased to 100°C, 65.4 g PO was added, keeping the reaction for 2–5 h at 140°C. After an ageing time of 1 h, it was made sure that the system cools down to 100°C and 21.8 g EO was added, and then the reaction continued for another 2–5 h at 140°C. After cooling down to 60°C, H₃PO₄ was added to lower the pH to a value of 7. Finally, the product PPP₁ with 2 wt% content of PAMAM was obtained. Products PPP₂ and PPP₃, with 1 and 0.5 wt% content of PAMAM, respectively, were prepared with the same procedures stated above.

2.3 Characterisation

The structures of the products were confirmed by ¹H NMR, FTIR and gel permeation chromatography (GPC) methods. ¹H NMR was recorded on a Bruker Avance-400 NMR spectrometer in D₂O at room temperature. The FTIR films cast on KBr pellets were recorded on a Tensor-27 spectrometer (Bruker, Germany). The GPC was performed by a set of a Waters 515 HPLC pump, a Waters 2414 differential refractometer and three Waters Styragel

columns (HT2, HT3 and HT4), using THF as an eluent at a flow rate of 1.0 ml/min at 35°C. Polystyrene standards were used for the calibration. The key parameters of the PPP_n series are listed in Table 1.

¹H NMR of PPP₁: δ_{PEO}(-OCH₂CH₂-) = 3.70, δ_{PPO}(-OCH₂CHCH₃-) = 3.63, δ_{PAMAM}(-CONHCH₂-) = 3.55, δ_{PAMAM}(protons next to the tertiary amines) = 2.3–2.7, δ_{PPO}(-OCH₂CHCH₃-) = 1.15; FTIR peaks, ν: 1108, 1375, 1458, 1652, 2872, 2972, 3470 cm⁻¹. ¹H NMR of PPP₂: δ_{PEO}(-OCH₂CH₂-) = 3.69, δ_{PPO}(-OCH₂CHCH₃-) = 3.63, δ_{PAMAM}(-CONHCH₂-) = 3.56, δ_{PAMAM}(protons next to the tertiary amines) = 2.3–2.7, δ_{PPO}(-OCH₂CHCH₃-) = 1.15; FTIR peaks, ν: 1108, 1374, 1456, 1651, 2871, 2972, 3425 cm⁻¹. ¹H NMR of PPP₃: δ_{PEO}(-OCH₂CH₂-) = 3.69, δ_{PPO}(-OCH₂CHCH₃-) = 3.62, δ_{PAMAM}(CONHCH₂-) = 3.55, δ_{PAMAM}(protons next to the tertiary amines) = 2.2–2.6, δ_{PPO}(-OCH₂CHCH₃-) = 1.14; FTIR peaks, ν: 1109, 1374, 1459, 1556, 1645, 2872, 2972, 3300 cm⁻¹.

2.4 Measurements

Surface tension measurements were conducted by the drop volume method at 25.0 ± 0.1°C (19). The critical aggregation concentration (cac) was determined by the crossing point of two linear lines before and after the cac on the γ - log c curve. A TAM 2277-201 microcalorimetric system (Thermometric AB, Järfälla, Sweden) was used for calorimetric measurements. Both the sample cell and the reference cell of the microcalorimeter were 1 ml, and they were initially loaded with 0.7 and 0.8 ml pure water, respectively. Each aliquot of the 6–8 μl concentrated dendrimer solution was injected into the stirred sample cell using a computer-controlled syringe (Lund 612) through a stainless cannula. The interval between the two injections was kept sufficiently long for the system to reach equilibrium. The dynamic light scattering (DLS) measurement was introduced using an LLS spectrometer (ALV/SP-125) with a multi-τ digital time correlator (ALV-5000). Light (λ = 632.8 nm) from a solid-state He-Ne laser (22 mW) was used as the incident beam. The scattering angle was selected to 90° and the correlation function was analysed using the CONTIN method. The dendrimer

Table 1. Configuration parameters of PPP_n (n = 1–3) molecules.

Dendrimer	GPC results			Core content G1 PAMAM (wt%)	PO:EO (mass ratio)	PPO _x -b-PEO _y (x, y = group number per chain)
	Weight average mol. wt	Polydispersity M _w /M _n	Theoretical mol. wt			
PPP ₁	22,600	1.24	25,800	2	3:1	x = 27; y = 11
PPP ₂	50,600	1.30	51,600	1		x = 55; y = 24
PPP ₃	101,800	1.32	103,200	0.5		x = 110; y = 48

aqueous solutions were filtered through a 0.45 μm millipore filter to leach the dust before measurements. All the experimental temperatures were kept at $25.0 \pm 0.1^\circ\text{C}$. The transmission electron microscope (TEM) samples were obtained by the method of fracturing and replication, which were carried out in a high-vacuum freeze-etching system (Balzers BAF-400D, Germany). The samples were imaged under a JEM-100CX electron microscope.

3. Results and discussion

Figure 2 shows the plots of surface tension against concentration (C) of the PPP_n series in water. The cac values are obtained from the measurement results as listed in Table 2, from which it can be seen that the values increased gradually with PPO-*b*-PEO chain lengthening. When the amphiphilic chain length increases, the PEO units become longer, which makes the PPP_n molecules more hydrophilic probably because of the hydrogen-bond formation between the ether oxygen and water molecules (20) and, consequently, aggregation occurs at higher C .

The calorimetric titration curves, plotting the variation of ΔH_{obs} against $\log C$, are given in Figure 3. The curves are all approximately sigmoid in shape, and each one can be subdivided into two C regions separated by a transition region associated with aggregate formation. As illustrated in the inset, cac is extrapolated from the crossing point of the two tangent lines of the fitted curves. The values of the enthalpy change for aggregation (ΔH°) are obtained by taking the enthalpy difference between the two segments. The Gibbs free energy (ΔG°) can be calculated using the following expression: $\Delta G^\circ = RT \ln \text{cac}$, where cac is expressed in molarity (21). The entropy change (ΔS°) can

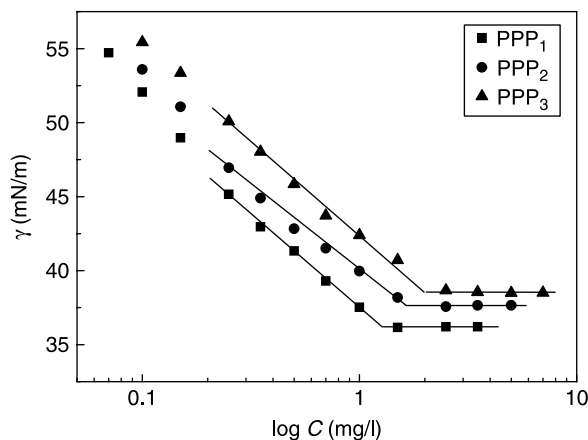


Figure 2. Surface tension of PPP_n ($n = 1-3$) as a function of concentration (C , logarithmic scale) at 25.0°C .

Table 2. Cac values of PPP_n ($n = 1-3$).

Dendrimer	PPP_1	PPP_2	PPP_3
Cac (mg/l)	1.5	1.8	2.5

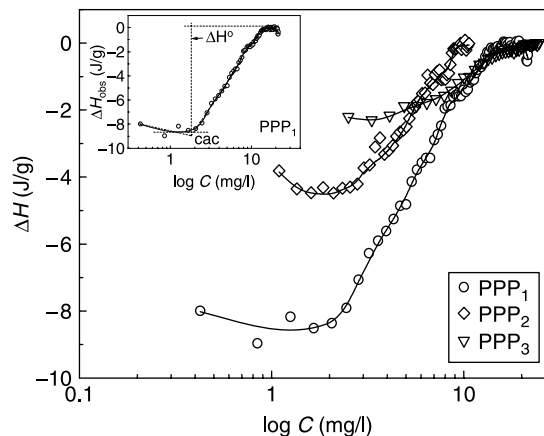


Figure 3. Variation of enthalpy (ΔH_{obs}) versus $\log C$ of PPP_n ($n = 1-3$) at 298.15 K .

Table 3. Cac values and thermodynamic parameters of PPP_n ($n = 1-3$) at 298.15 K .

Dendrimer	Cac (mg/l)		ΔH° (J/g)	ΔG° (J/g)	$T\Delta S^\circ$ (J/g)
	Microcalorimetry	Drop volume			
PPP_1	1.4	1.5	8.7	-1.6	10.3
PPP_2	1.9	1.8	4.5	-0.8	5.3
PPP_3	2.9	2.5	2.3	-0.4	2.7

be derived from the Gibbs–Helmholtz equation: $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$.

The cac values and thermodynamic parameters converted into mass C are listed in Table 3. It can be seen that the values of ΔH° and $T\Delta S^\circ$ are all positive and $T\Delta S^\circ$ is larger than ΔH° , which indicates that the gain of entropy is the main contributor to aggregation and overrides the unfavourable endothermic enthalpy term (22). The positive entropy of aggregation for the non-ionic surfactants is mainly related to the dehydration of EO units (23, 24). Aggregation can perform spontaneously due

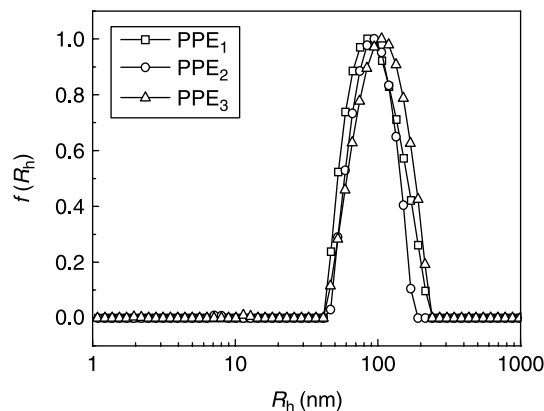


Figure 4. DLS measurements of the size distribution for PPP_n ($n = 1-3$) at 20 mg/l .

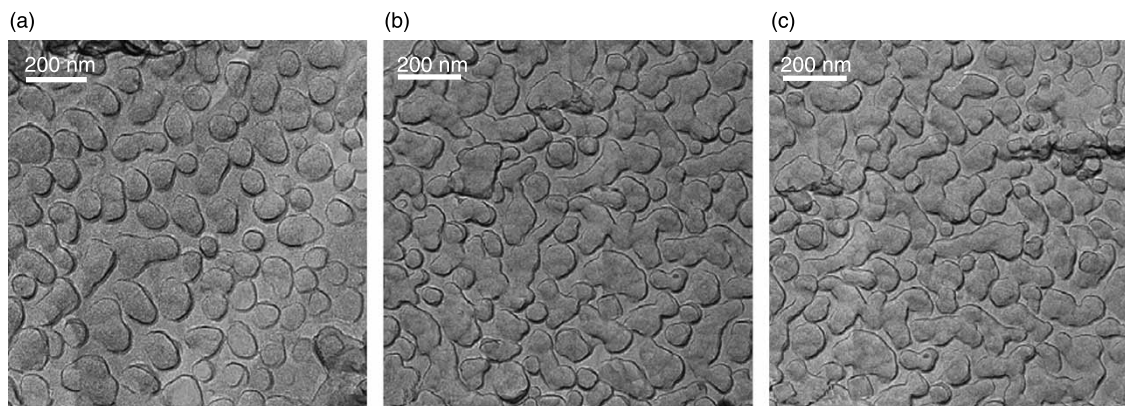


Figure 5. Freeze-fracture TEM images of PAMAM-based dendrimer aggregates: (a) PPP₁; (b) PPP₂; (c) PPP₃.

to the negative ΔG° values. The cac and ΔG° values are all increasing functions of the number of EO groups as expected, which is similar to the result reported previously (22, 24). With the EO chain lengthening, more oxygen atoms contribute to hydrogen bonding, which is responsible for the hydrophilicity of the non-ionic dendrimer molecules. Such an inherent stronger hydrophilicity probably leads to the formation of aggregates at higher C , resulting in larger cac and ΔG° .

To obtain the information of size distribution and morphology of aggregates formed by PPP_{*n*} molecules above the cac , DLS and TEM measurements were carried out and the results are shown in Figures 4 and 5, respectively. A narrow size distribution with a mean hydrodynamic radius (R_h) value of about 100 nm is shown in Figure 4. It can be observed that there is a trivial increase of R_h with PPO-*b*-PEO chain lengthening, which indicates that the amphiphilic chain plays a certain part in controlling the size of the PPP_{*n*} series.

A collection of spherical aggregates with the size around 200 nm is observed, as shown in Figure 5(a–c), and there are some bigger ones shown in Figure 5(b,c), which is in agreement with the DLS result.

4. Conclusion

A new class of PAMAM-based dendrimers with a different length of PPO-*b*-PEO branches was synthesised and the aggregation behaviour was studied. From the surface tension measurement results, it can be seen that cac increases gradually with the amphiphilic chain lengthening, which is consistent with that determined by microcalorimetry measurements. The gain of entropy is the main driving force for the spontaneous aggregation. In the case of longer amphiphilic chains, more EO oxygen atoms contribute to hydrogen bonding and, consequently, lead the aggregates to form at higher C , resulting in larger cac and ΔG° values. Spherical aggregates with a narrow size distribution around 200 nm are observed using the

DLS and TEM methods, which exhibit a trivial increase in the aggregate size with the amphiphilic chain lengthening.

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