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SHORT COMMUNICATION

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Self-aggregation of dendritic poly(benzyl ether)–poly(acrylic acid), an amphiphilic block copolymer, studied by ^{1}H NMR

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Abstract The dynamic properties of the micelles of a novel synthesized amphiphilic block copolymer, dendritic poly(benzyl ether)–poly(acrylic acid) (Dendr.PBE-PAA), formed in aqueous solutions were studied by the ^{1}H self-diffusion coefficient, relaxation measurements and 2D nuclear Overhauser enhancement spectroscopy. The experimental results show that Dendr.PBE-PAA molecules self-aggregate in aqueous solution. The dynamic properties of the Dendr.PBE-PAA micelles vary with their total concentration in the solution. The motion of the molecules in the micelles of a concentrated solution is more restricted than that in a less concentrated one. The main chains of PAA are densely packed in the surface layer of the hydrophobic core with the carboxyl side chain pointing to the aqueous medium and the hydrophobic phenoxy rings stay in the interior. The self-aggregate becomes larger as the degree of polymerization of PAA increases. However the phenoxy rings situated in the interior of the hydrophobic core become more loosely packed. *n*-Hexadecane is solubilized in the micelles. The optimal position of *n*-hexadecane is between the phenoxy rings next to the PAA chains.

Keywords Self-diffusion coefficient · NMR relaxation · Self-aggregate · dendritic poly(benzyl ether)–poly(acrylic acid) · Amphiphilic block copolymer

Introduction

Dendritic poly(benzyl ether)–poly(acrylic acid) (Dendr. PBE-PAA) is a novel dendritic amphiphilic molecule [1–3]. Its specific supermolecular properties in aqueous solution, the structure of its self-assemblies and the mechanism of the coaggregation received much attention. Recently, the self-assembling behavior of amphiphilic block copolymer having a linear hydrophilic block and a hydrophobic block has received attention [4–6]. The dendrimer obtained in the last few years is a kind of macromolecule having a regular 3D suprabranched structure [7, 8]. It can be used as a building block of nanometric size to combine covalently with linear polymers to form a kind of dendrimer–linear polymer amphiphilic block copolymer. Its specific properties both in solution and in its solid states are of great interest. Not long ago, Van Hest et al. [9] synthesized an amphiphilic block copolymer from a hydrophilic poly(propylimide) dendrimer and hydropholic linear polystyrene. They found that the structure of this copolymer varies significantly with the generation of the dendrimer, and observed the change in the structure of the self-assembly from a reverse micelle to wormlike vesicles, a rodlike micelle, and finally to a spherical micelle. Gistov et al. [10] and Chapman et al. [11] also reported, respectively, an amphiphilic block copolymer of polyether dendrimer with polyethylene oxide and polylysine dendrimer with polyethylene oxide. The study of the self-assembling behavior of these nonionic amphiphilic block copolymers in aqueous solution was limited by their poor solubility. The titled copolymer is easily soluble in water [1]. Several spectroscopic methods, for example, fluorescence probe, dynamic laser light scattering, etc., have shown that Dendr.PBE-PAA self-aggregates in aqueous solution and that its critical micellar concentration (cmc) is very low [12, 13]; however, the structure of this self-assembly at a molecular level remains to be understood. The development of NMR demonstrates its specific multifunctional method. It is a noninvasive method of determining the properties of different components in the system at a time [14–20]. The cmc of a nonionic polymer surfactant was determined by the ^{1}H NMR self-diffusion method [21]. Few works deals with the dynamic properties of Dendr.PBE-PAA (an anionic polymer surfactant). The aim of this work was to study the micellization of Dendr.PBE-PAA in aqueous solution, the variation of its micellar structure with its total concentration and with the degree of polymerization of PAA by the ^{1}H NMR self-diffusion coefficient, ^{1}H and ^{23}Na relaxation measurements and 2D nuclear Overhauser enhancement spectroscopy (NOESY).

Experimental

Dendr.PBE-PAA was synthesized as described in Ref. [1]. Its structure is shown schematically in Fig. 1. The assignments of the ^{1}H resonance are given in Ref. [3]. The generation (*i*) of the dendrate (G*i*) is 2. The degree of polymerization of PAA (*n*) is 16. $M_n = 2{,}248$ and $M_w/M_n = 2.01$. The concentrations of the Dendr.PE-PAA in D_2O solutions are 1 and 10 g/l. The D_2O (99.8% deuterium) was obtained from the Bo-Pu Co. of the Chinese Academy of Sciences. All the NMR experiments were performed using a Bruker ARX-500 spectrometer, with a ^{1}H frequency of 500.13 MHz. The self-diffusion coefficients were measured by the longitudinal Eddy current delay sequence with bipolar pulse pairs [17]. The spin–lattice and spin–spin relaxation times were measured by inversion recovery and Carr–Purcell–Meiboom–Gill pulse sequences, respectively. The 2D NOESY spectra were obtained under the phase-sensitive mode. For the 1 and 10 g/l solutions, the 90° pulses were 8.6 and 9.1 μs and the spectral widths were 4,761.9 and 5,376.3 Hz, respectively. Accumulations of 256 and 64, $2k \times 128$ and 1024×256 data points ($t_2 \times t_1$) and mixing times of 400 ms and 1 s for the solution of 1 g/l and of 200, 400 and 800 ms for the solution of 10 g/l were used, respectively. The data point array was $F_2 \times F_1 = 2k \times 512$ in the Fourier transformation after the zero filling. The probe temperature was maintained at 298.0 ± 0.1 K using a Bruker VT-200.

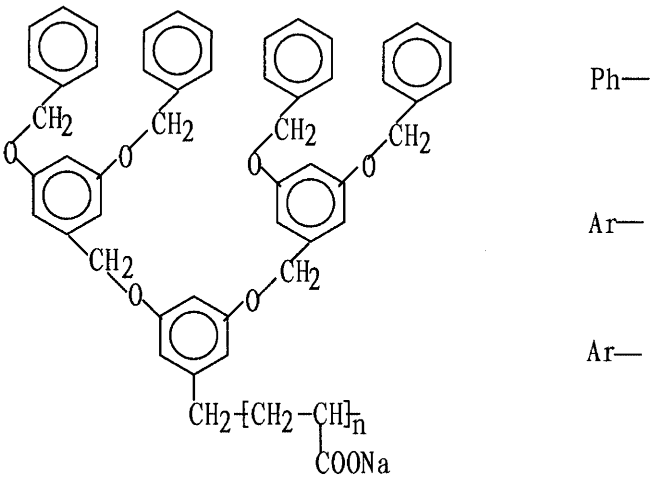

Fig. 1 Schematic structure of dendritic poly(benzyl ether)–poly(acrylic acid) (*Dendr.PBE-PAA*) (G2-16)

Results and discussion

The structural formula of Dendr.PBE-PAA is shown in Fig. 1, where Ph and Ar stand for the protons of the hydrophobic end phenoxy ring and the protons of the phenoxy ring next to the polymer main chain, respectively. CH and CH_2 stand for the protons of the PAA main chain.

Table 1 shows the spin–spin relaxation times (T_2), the ratios of T_2/T_1 and the average self-diffusion coefficients of all the proton resonances (*D*) of Dendr.PBE-PAA in aqueous solutions at concentrations of 1 and 10 g/l, which are probably well above its critical micelle concentration (2.5×10^{-6} mol/l measured by the fluorescence method [13]). According to the relaxation rate dependence on the correlation time of the molecule, T_2/T_1 is unity for free molecular motion in the extreme narrowing condition. A deviation of this ratio from unity shows that the motion is restricted. It is evident that T_2/T_1 of all the protons (Ph, Ar and those of the main chain of PAA) are less than unity. This indicates that the motion of the whole molecule is somewhat restricted by the interaction among the molecules. That is to say that the concentration of 1 g/l Dendr.PBE-PAA is above its cmc. These experimental facts agree well with the results obtained by dynamic light scattering methods [13] that the single molecules of the block

Table 1 ^{1}H spin–spin relaxation times (T_2/ms), T_2/T_1 ratios and self-diffusion coefficients ($D \times 10^{-11}$ m^{2}s^{-1}) of dendritic poly(benzyl ether)–poly(acrylic acid) (*Dendr.PE-PAA*) (G2-16) at different concentrations (*c*/g/l)

c	Ph		Ar		CH		CH_2		*D*
	T_2	T_2/T_1	T_2	T_2/T_1	T_2	T_2/T_1	T_2	T_2/T_1	
1	870	0.53	460	0.34	120	0.30	45	0.12	8.3
10	80	0.08	97	0.19	50	0.13	32	0.08	5.4

copolymer disappear at concentrations higher than the critical aggregation concentration and the average size of the aggregate is 10 times that of the single molecule. The self-diffusion coefficients of Dendr.PBE-PAA in the solutions are typical values for micelles. This supports the existence of interaction among the molecules, i.e. the self-aggregation. On comparing the T_2/T_1 values of the proton resonances within the molecules we see that the protons of the main chain are most restricted and the farther the protons are from PAA the less the motion is restricted. According to the general rules of micelles, from the relaxation measurements one can deduce that the main chain of PAA forms the rigid surface layer of the hydrophobic micellar core. The end phenoxy rings, moving more freely, stay in the interior and the phenoxy rings next to the main chain stay in-between. The carboxyl groups are in the exterior of the hydrophobic core protecting it from contacting water. However, T_2/T_1 of all the protons decreased to about 0.1 and D decreased from 8.3×10^{-11} to 5.4×10^{-11} m^2s^{-1} and this shows that the molecules are more densely packed, and the micelles are larger in the concentrated solution (10 g/l) than in the dilute one (1 g/l). The ^{23}Na relaxation measurements (Table 2) support this observation.

Table 2 ^{23}Na spin–spin relaxation (T_2/ms) and T_2/T_1 of Dendr.PBE-PAA (G2-16) at different concentrations (*c*/g/l)

c	T_2	T_2/T_1
1	21.45	0.8
10	11.69	0.7

It is well known that 2D NOESY is an effective method to study the structure of macromolecules. It gives information about the distance in space between pairs of coupled protons. The intensity of the cross-peak of the pair of protons (A and B) is proportional to $r_{AB}{}^{-6}$. Contour plots of the 2D NOESY map of Dendr.PBE-PAA (G2-16) in aqueous solutions at concentrations of 10 and 1 g/l are shown in Fig. 2a and b, respectively. The unlabeled peak of the 1D spectrum at 3.6–3.9 ppm belongs to the protons of the methoxy group attached to the carboxyl group of the main chain. Surprisingly we found that a cross-peak between remote proton pairs (Ph and the protons of the main chain of PAA) appeared in the 2D map of the concentrated solution. Cross-peaks between Ar and the protons of the main chain were found in the 2D maps of both solutions. This suggests that the distances of these proton pairs are at least not greater than 5 Å [22], although they should be greater than 12 Å for a single molecule. This decrease in interproton distances could only originate from intermolecular interaction, i.e. the molecules come close to each other, forming self-aggregates. It gives direct evidence that the Dendr.PBE-PAA molecules are in the micellar state in these two aqueous solutions. It is worth mentioning that the 2D NOESY experiments were done with several mixing times, from 200 ms to 1 s, to ascertain that the appearance of these cross-peaks is not the result of spin diffusion. The appearance of the cross-peak between Ph and the protons of the main chain of PAA of the concentrated solution but no cross-peak between this proton pair in the dilute solution suggests that the Dendr.PBE-PAA molecules are more densely packed in the micelles of the concentrated solution. The broadening

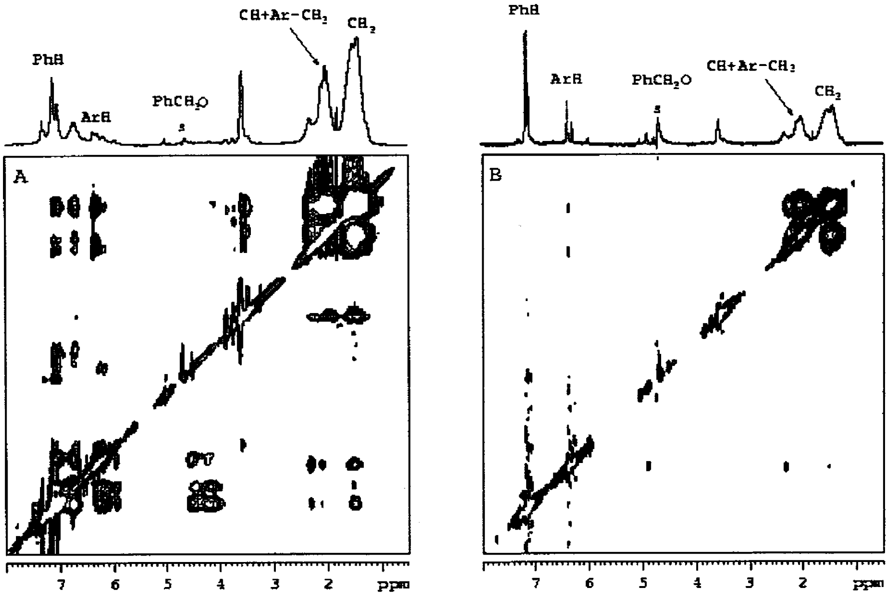

Fig. 2 Contour plots of the 2D nuclear Overhauser enhancement spectroscopy (*NOESY*) maps of Dendr.PBE-PAA (G2-16) aqueous solutions at different concentrations: **a** 10 g/l and **b** 1 g/l

Table 3 The effect of the degree of polymerization (n) of PAA on the ^{1}H spin–spin relaxation times (T_2/ms), T_2/T_1 ratios, intensity ratio of the cross-peaks to their corresponding diagonal peaks (I_c/I_d, %) and self-diffusion coefficients ($D \times 10^{-11}$ m^{2}s^{-1}) of Dendr.PBE-PAA at a concentration of 10 g/l

n	Ph			Ar			CH		CH$_2$		D
	T_2	T_2/T_1	I_c/I_d	T_2	T_2/T_1	I_c/I_d	T_2	T_2/T_1	T_2	T_2/T_1	
16	80	0.08	2.1	97	0.19	21.6	50	0.13	32	0.08	5.4
37	115	0.08	0.3	116	0.16	23.2	32	0.11	24	0.07	3.1
144	298	0.16	0	178	0.21	13.2	22	0.07	15	0.04	1.0

of the Ph resonance in the 1D spectrum of the concentrated solution further supports this observation.

Combining the results of the relaxation and the self-diffusion coefficient measurements and the 2D NOESY maps we come to the following conclusion: micelles of Dendr.PBE-PAA molecules are formed in the two solutions studied. The main chains of PAA form the dense surface layer of the hydrophobic micellar core with the carboxyl groups pointing outwards to the aqueous medium. The hydrophobic end phenoxy rings which move more freely stay in the interior of the micellar core and are farther from the surface layer of the micellar core, while the phenoxy rings next to the main chains of PAA are in-between.

The effect of the degree of polymerization of PAA on the structure and dynamics of the Dendr.PBE-PAA micelles was also examined by relaxation and self-diffusion measurements of the solutions at the same concentration of 10 g/l (Table 3). It is evident that T_2/T_1 of the main chain of PAA decreases with the increase in the length of the main chain of PAA; however, the T_2/T_1 values of Ph and those of Ar scatter about 0.19. The D value decreases with the increase in the length of the main chain of PAA. These results suggest that with the increase in the length of the main chain of PAA the surface layer of the hydrophobic core became larger and more densely packed. Accordingly, the micelles became larger, providing more space in the interior of the micellar core for the phenoxy rings, especially for the Ph protons which are the farthest from the micellar core, to move. The weakening of the intensity of the cross-peaks between the protons of the phenoxy rings and those of the main chains of PAA (Fig. 3) supports these results. For more quantitative comparison the intensities of the cross-peaks between the phenoxy protons and those of the main chain are divided by the intensities of the diagonal peaks of the corresponding protons, respec-

Table 4 T_2/T_1 values of Dendr.PBE-PAA (G2-16) at a concentration of 10 g/l before and after the solubilization of n-hexadecane

$V_{\text{hexadecane}}/V_{\text{solution}}$	Ph	Ar	CH	CH$_2$
0	0.08	0.19	0.13	0.08
0.04	0.10	0.25	0.15	0.10

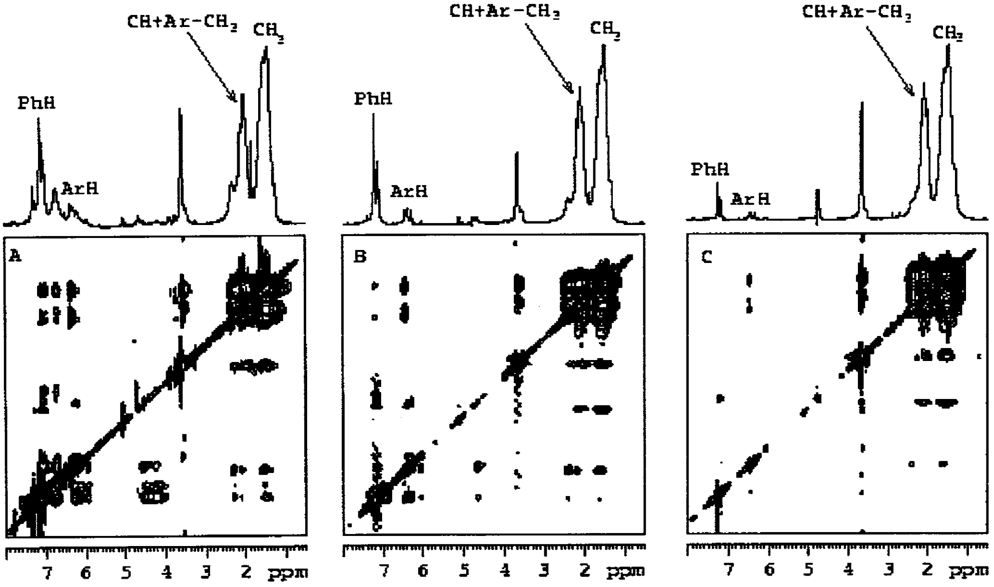

Fig. 3 Contour plots of the 2D NOESY maps of Dendr.PBE-PAA aqueous solutions at a concentration of 10 g/l with varying degrees of polymerization, n, of PAA: **a** 16, **b** 37 and **c** 144

tively, as shown in Table 3. It is evident that with the increase in *n* from 16 to 37 the contribution per Ph proton to the intensity of the cross-peak decreased from 2.1 to 0.3% and became 0 when *n* increased to 144. The variation of the Ar protons is far less pronounced. This shows that the relative distance between the end phenyl rings became longer as the degree of polymerization increased.

The relaxation measurements showed that *n*-hexadecane can be solubilized in the Dendr.PBE-PAA (G2-16) micelles at a concentration of 10 g/l, when the volume ratio of *n*-hexadecane to the volume of the solution is 0.04. The position of the *n*-hexadecane molecules in the micelles is between the phenoxy rings next to the main chain of PAA because the change in T_2/T_1 of Ar is most obvious after solubilization (Table 4).

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