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SHORT COMMUNICATION

Guiying Li
Linqi Shi
Qing Ye
Wenyuan Zhou
Jianguo Tian

Electric-field-assisted assembly and alignment of polystyrene-*b*-poly(acrylic acid) micelles

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G. Li · L. Shi (✉)
Key Laboratory of Functional Polymer Materials, Institute of Polymer Chemistry, Nankai University,
Tianjin 300071, China
e-mail: shilinqi@nankai.edu.cn
Tel.: +86-22-23501945
Fax: +86-22-23503510

Q. Ye · W. Zhou · J. Tian (✉)
Photonics Center, College of Physics,
Nankai University,
Tianjin 300071, China
e-mail: jjtian@nankai.edu.cn

Abstract In this paper, we describe an efficiently physical method of electric-field-assisted assembly and alignment of block copolymer micelles. Amphiphilic block copolymer polystyrene-*b*-poly(acrylic acid) (PS-*b*-PAA) self-assembles into spherical micelles in water consisting of a core formed by the insoluble PS blocks and a shell formed by the soluble PAA blocks. When applying an alternating voltage to micelles solution dispersed onto a thin gap of coplanar metallic electrode, we generate directional arrays of highly ordered aggregates in long range. The formation of the ordered aggregates is due to the adjustment of interactions between micelles induced by dielectrophoretic forces in alternating electric field. The morphologies and arrays of particles become more regular with increasing of the strength and frequency of electric field. Voltage and frequency of the electric field and other parameters, such as particles concentration and, the viscosity and dielectric constant of the medium, affect the assembly process.

Keywords Polystyrene-*b*-poly (acrylic acid) · Self-assemble · Micelles · Electric field · Ordered aggregates

Introduction

Self-assembly of nanoscale particles into complicated two- or three-dimensional structures has attracted significant interest in recent years for wide applications [1–3]. The collective properties of molecules or nanoparticles are dependent on the supramolecular structures or relative molecular alignments. Understanding and utilizing the unifying principles of the self-assembly of complex systems such as block copolymer micelles is the key to future advances in nanoscience. Amphiphilic block copolymers can self-assemble into various morphological micelles such as spheres, vesicles, cylinders, hollow spheres, nanotubes, and nanofibers in block-selective solvent, which has been extensively studied [4–6]. Because of their very interesting properties, block copolymer micelle systems play an important role in many areas, such as chemical and biological sensors, colloid science, drug and gene delivery, advanced materials formation, etc. However, the nanomicelles tend to form a disorderly aggregate when the solvent is removed. Up to the present time, only a few accounts on controlling the ordered aggregation of nanomicelles into shape-controlled polymeric nano- and microparticles have been reported [7–10]. Thus, developing new techniques to fabricate well-defined micelle aggregates is necessary for advancing the potential applications.

One way for rapid assembly of micro- and nanoparticles is based on the theory of dielectrophoresis (DEP): a non-uniform alternating electric field inducing a dipole moment on an object in solution. Dielectrophoresis has been studied in many fields, such as the separation of submicron bioparticles [11], assembly of complex particles [12, 13], manipulating of colloidal crystals [14, 15], and assembly of metallic particles [16–19]. For example, O. D. Velev [20] have done many researches on the assembly and alignment of colloidal crystals to various two- and three-dimensional functional structures in electric field. The use of external fields offers a combination of speed, easy control, and precision, which may be not available through the inherent

particle–particle interactions. But the influence of electric field on the morphology of block copolymer micelles has not been previously reported. In this paper, we present a practical method for assembling separate PS-*b*-PAA spherical micelles into long-range ordered directional arrays in alternating electric field.

Experimental

Materials

Polystyrene-*b*-polymethacrylate (PS_{200}-*b*-PMA_{78}) (the subscript numbers indicate the number of repeat units of the blocks) was synthesized by atom transfer radical polymerization and the detail can be seen in one of our previous studies [21]. The polydispersity index of PS_{200}-*b*-PMA_{78} measured by gel permeation chromatography was 1.20. The composition of PS_{200}-*b*-PMA_{78} was determined from the ratio of the ^1H NMR intensities of the OCH_3 signal (at δ=3.7) and the aromatic signal (at δ=6.6–7.3) of the block copolymer, of which the degree of polymerization was calculated. PS_{200}-*b*-PAA_{78} was obtained from hydrolysis of PS_{200}-*b*-PMA_{78} in 20 wt % NaOH aqueous solution at 90 °C for 72 h or more.

Preparation of the micelles solution

The block copolymer PS_{200}-*b*-PAA_{78} was first dissolved in *N*, *N*-dimethylformamide (DMF) to make a polymer solution (2.0 mg/ml). The polymer solution was subsequently added dropwise into water with stirring. The formation of the micelles of PS_{200}-*b*-PAA_{78}, as indicated by the appearance of turbidity in the polymer solution, typically occurred when the water content reached 10–40 vol. %, depending on the concentration of the block copolymer in DMF. The micelles solution was lastly dialyzed against water for 4 days to remove DMF.

Electric-field-assisted assembly of PS_{200}-*b*-PAA_{78} micelles

The electric-field-assisted assembly of PS_{200}-*b*-PAA_{78} micelles is studied by dispersing drops of micelle solutions onto a glass slide placed in a thin gap of coplanar metallic electrode. The gap between electrodes is ranging from 2 to 10 mm. A glass coverslip is placed on the electrode to prevent the dispersion from drying during the experiment. The voltage of the alternating electric field was varied from 5 to 250 V and the frequency from 50 Hz to 10 kHz. An outline of the experimental setup is shown in Fig. 1. The electric field is not removed before the assembly process is finished. The resultant samples were observed on a HITACHI S-3500N scanning electron microscopy (SEM) at 20 kV. X-ray fluorescence spectroscopy (XRF) (Rigaku 1800) was used to characterize the composition of the polymer and the micelle aggregates. Transmission electron microscopy (TEM) observation was performed on a Philips EM400ST microscopy at 80 kV. The diameter of the micelles in aqueous solution was measured by a laser light scattering spectrometer (BI-200SM) equipped with a digital correlator (BI-9000AT).

Results and discussion

Single micelles of PS_{200}-*b*-PAA_{78}

PS_{200}-*b*-PAA_{78} is a typical amphiphilic block copolymer and self-assembles into spherical core-shell micelles in water consisting of a core formed by the insoluble PS block and a shell of the soluble PAA block. Figure 2a displays the TEM images of PS_{200}-*b*-PAA_{78} micelles. We can clearly see the perfectly spherical shape with diameters ranging from 30 to 50 nm. Figure 2b shows the hydrodynamic diameter (D_h) distribution $f(D_h)$ of the PS_{200}-*b*-PAA_{78} micelles in aqueous solution obtained from dynamic laser scattering (DLS) at 25 °C. The diameter distribution of the micelles is obviously very narrow and the average D_h of the micelles is about 65 nm.

Aggregates from assembly of single micelles in electric field

Figure 3 shows SEM images of PS_{200}-*b*-PAA_{78} micelles assembled in direct field and alternating electric field with different voltage and frequency. When applied a direct field, cube-like aggregates and a few of irregular spherical particles randomly coexisted on glass slide. The size of the cube-like aggregates is in the range from 200×200×200 to 500×500×500 nm^3, which is much larger than the single micelles. After being applied with an alternating voltage of 100 V and frequency of 5 kHz, the PS_{200}-*b*-PAA_{78} micelles formed a straight structure of cube-like aggregates as shown in Fig. 3b. With further increasing the voltage and frequency, parallel arrays of directional aggregates in long range with about equal spacing and size appeared (see Fig. 3c,d). The most intriguing feature of the structures is that they are

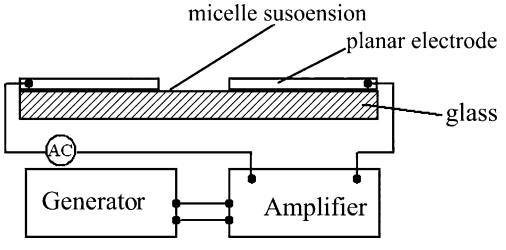

Fig. 1 Schematics of the experimental setup

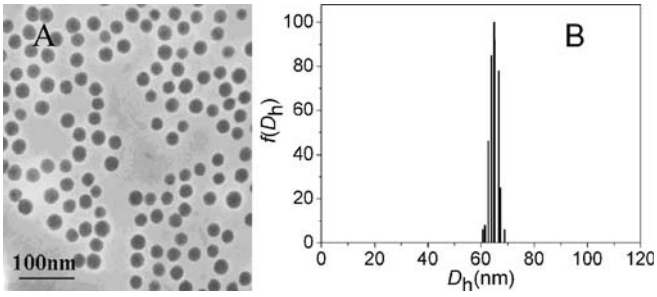

Fig. 2 **a** TEM images of PS_{200}-*b*-PAA_{78} micelles in water and **b** the hydrodynamic diameter distribution of micelles measured by DLS at 90°

perpendicular to the electrodes and parallel to the direction of the electric field. The length of the directional arrays is about 2 or 3 mm. Moreover, some smaller-sized spherical particles still existed. But the arrangement of the nanoscale particles is not regular as that of the cube-like aggregates.

The exact mechanism that caused the spherical nanomicelles to form microcubic aggregates is not clear to us at this current stage. To our best knowledge, only inorganic compounds and a few organic compounds can form a highly symmetrical crystal. The reports on amorphous polymer-forming crystal structures have been rarely seen [7, 22]. To confirm the composition of the cube-like aggregates, XRF was used to analyze the powder of PS-*b*-PAA. From the result, we did not detect any signals corresponding to inorganic compounds, such as Na and Ca elements, indicating that our purification of the copolymer of PS-*b*-PAA eliminated any inorganic impurity. Therefore, we believe that the cube-like structures are formed by the PS-*b*-PAA micelles.

In our previous study, we reported the evaporation-induced ordered aggregation of PS_{115}-*b*-PAA_{63} micelles into microcubic particles in an additive/water solvent mixture [7]. The formation of the microcubic structures is owed to the kinetics of the solvent casting and the effect of the organic additive, which forms a ternary system of copolymer/water/additive and facilitates the aggregating of micelles due to hydrogen bonding [7, 23]. As for PS-*b*-PAA core-shell micelles, the shell of the soluble PAA block can be influenced by addition of electrolytes and electric field. We suppose herein that the formation of cube-like aggregates is also partly due to the adjustment of the interactions between micelles in electric field.

The forces acting on particles in an alternating electric field include the long-range anisotropic interaction and a short-range isotropic interaction. The former originates from the dielectrophoretic force (F_{DEP}), which attracts or repulses the particles moving along the direction of the electric field gradient. The magnitude and direction of the F_{DEP} depend on the frequency, changes in surface charge density, and free charges in the vicinity of the particle and is given by

$$\overrightarrow{F}_{DEP} = 2\pi v \in_m K(\omega)\overrightarrow{\nabla}\left(\overrightarrow{E}^2_{rms}\right)$$

where v is the volume of the particles, $\overrightarrow{E}_{rms}$ is the root mean square value of the electric field, and $K(\omega)$ is the real part of the complex Clausius–Mosotti factor relating to the frequency-dependent complex dielectric constant of the medium and particle [20].

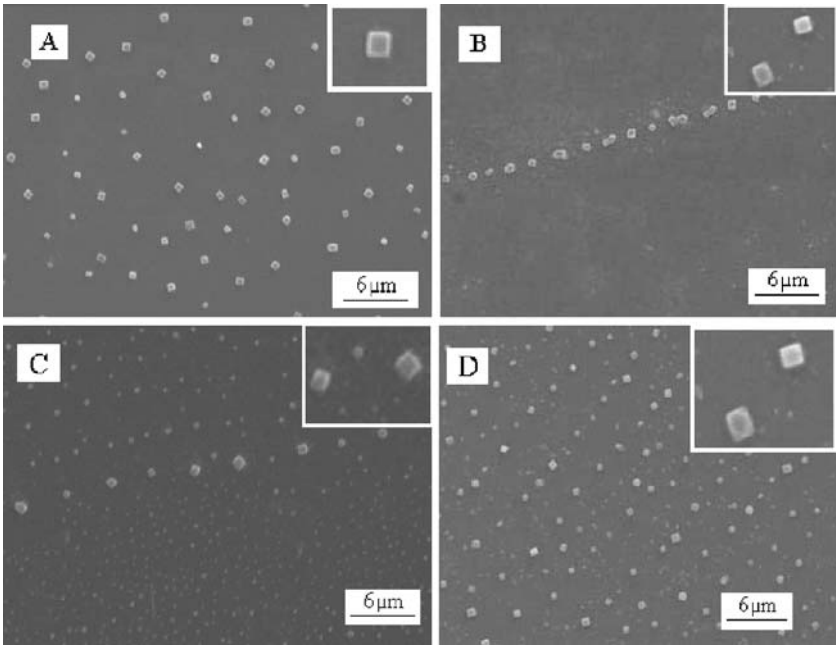

Fig. 3 SEM images of PS_{200}-*b*-PAA_{78} micelles assembled in electric field. The voltage applied to the electrodes was **a** direct current of 50 V and **b** alternating current of 100 V, 5 kHz, **c** 150 V, 5 kHz, and **d** 250 V, 10 kHz

The alignment of particles in long range is ascribed to the combination of the F_{DEP}-induced dipole field and dipole–dipole particle interactions. In the presence of an electric field gradient, F_{DEP} drives the particles moving along the direction of the electric field gradient. When the ratio of electric-to-thermal energy exceeds a critical value, their random distribution in a suspension becomes unstable, and the particles tend to aggregate [24]. Then the arrayed particles create fields of high intensity and gradient giving rise to the appearance of electrohydrodynamic currents around the particles and the lateral dipole–dipole interactions. The particle dipolar attraction can provide much-needed directional orientation during the assembly process. It is this large-field-induced force that results in alignment of the directional arrays between two electrodes. The spacing between aggregates is probably due to the repulsive electrostatic interactions from the charged PAA shell and also in part due to the shrinkage of particles during the process of drying. When the particle size approaches nanoscale, the thermal Brownian motion becomes increasingly important compared to the dielectrophoretic force, which disturbs the rearrangement in electric field.

Effect of parameters on assembly of micelles

The parameters that were recognized to affect the assembly process in the experiment include the field strength, frequency, viscosity and dielectric constant of the medium, and particles concentration.

The forces that drive particles moving towards high field gradient result from F_{DEP}, whose magnitude depends on the squared values of the field intensity and gradient. When the applied voltage is too low, the F_{DEP} is not strong enough to overcome the repulsive interparticle forces that stabilize the dispersion. As the voltage applied to the electrodes increases, the F_{DEP} on the particles increases, too, resulting in improved alignment. The alternating voltage allows achieving high field strengths without water electrolysis and electro-osmotic current, either of which can disrupt particle motion and affect the usability of direct current fields.

The frequency of the alternating electric field has a marked effect on the assembly process. Directional arrays of particles formed only when the frequency is sufficiently high. At the frequency below 1 kHz, PS_{200}-*b*-PAA_{78} micelles formed flower-like and dendritic aggregates as shown in Fig. 4. From the SEM image, we can see that the flower-like and dendritic aggregates comprise many single micelles and (semi)cubic aggregates. The result is very similar to our previous report for PS-*b*-PAA micelles assembled into flower-like aggregates when casting the micelles solution in the presence of 1-propanol at relatively high temperatures [9]. The frequency dependence can be interpreted such that the polar molecules in the dielectric medium at low frequency shield the charge separation on the particles, leading to relatively low alignment forces [25]. At low frequency, dissipation due to thermal fluctuations and Joule heating out compete alignment due to the field, so the particles deposited irregularly or formed dendritic structures on the substrate. When the frequency increases, the polar molecules lead to greater net polarization on the tip of the arrays and stronger alignment forces.

To characterize the effect of medium on the process of assembly, we prepared PS_{200}-*b*-PAA_{78} micelles solution with ethanol content of 50 vol. %. The dielectric constant of ethanol is lower and the viscosity is a little higher than that of water. On one hand, the speed of assembly in ethanol–water suspensions was lower than that in pure aqueous solution. This can be readily explained by the lower dielectrophoretic force at lower permittivity and the higher viscosity of the mixture medium. On the other hand, the addition of ethanol to the micelles solution favors the formation of ordered aggregates. Though the shape of particles formed at low voltage and frequency is not uniform, the size and arrangement of the cube-like aggregates formed at high voltage and frequency is more regular than those formed in pure aqueous solution (see Fig. 5). The low conductivity of mixture solutions achieves a strong electric field without substantial heating and electrolysis, a condition often impossible to attain in strong electrolytes. Furthermore, in aqueous solution, direct electrostatic interaction between the particles is negligible due to strong Debye screening effects [26], whereas in non-aqueous systems, this electrostatic interaction is often the dominant one, which opens the possibility to tune the

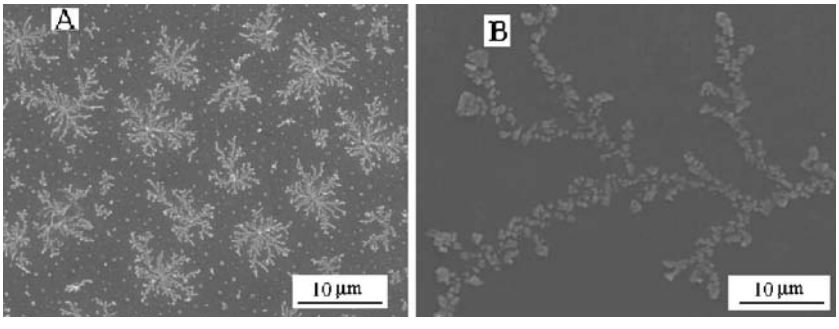

Fig. 4 SEM images of PS_{200}-*b*-PAA_{78} micelles assembled in alternating electric field **a** 250 V, 50 Hz and **b** 250 V, 500 Hz

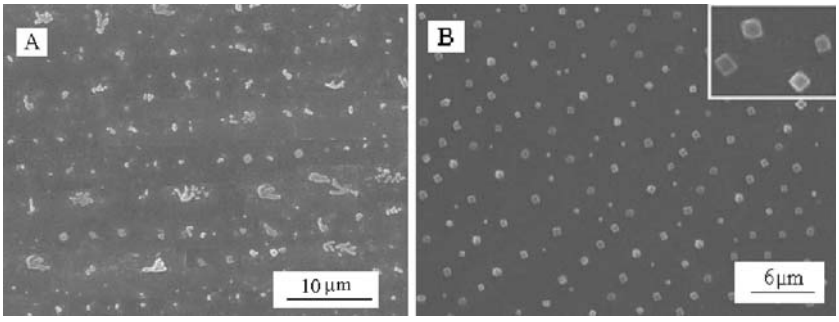

Fig. 5 SEM images of PS_{200}-*b*-PAA_{78} micelles with ethanol content of 50 vol. % assembled in electric field **a** 150 v, 500 Hz and **b** 250 v, 10 kHz

resulting particle patterns by adjusting the amplitude and frequency of the applied field.

Particle concentration is another parameter that affects the process of assembly because the aggregation can proceed only when the concentration of particles exceed a threshold value. In our study, the appropriate micelles concentration to form ordered aggregates is from 5×10^{-4} to 1×10^{-5} g/ml.

Conclusion

Block copolymer PS_{200}-*b*-PAA_{78} self-assembles into core-shell micelles in the block-selective solvent water. After applying an alternating electric field to micelles solution, PS_{200}-*b*-PAA_{78} spherical micelles formed directional arrays of cube-like aggregates or flower-like and dendritic aggregates with different voltage and frequency. The experimental results presented here indicate that the alignment forces result from the mobility and interactions of the particle dipoles induced by the non-uniform alternating electric field. Some parameters, such as voltage and frequency of the electric field, particles concentration, and the viscosity and dielectric constant of the medium, affect the assembly process. Morphologies and arrays of particles become more regular with increasing of the strength and frequency of electric field. Adding of ethanol to the micelles solution favors the formation of ordered aggregates. This new approach is not a passive self-assembly process but an active, electronically controlled one. Though the mechanism of the electric-field-assisted assembly needs further study, it leads to an increased understanding of the factors controlling the growth of nano- and microstructures and suggests a promising future for developing functional materials.

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