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Self-assembly behaviour of amphiphilic diblock copolymer in selective solvents studied by synchrotron small-angle x-ray scattering

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The aggregation behaviour of styrene-vinyl benzoic acid (PS_m-b-$PVBA_n$) amphiphilic diblock copolymers in selective solvents with different m and n was investigated by synchrotron small-angle x-ray scattering (SAXS). We have carried out a detailed analysis of scattering intensity, dimension, shape and microstructure of the diblock copolymers of narrow distribution in water, methanol, ethanol and isopropanol selective solvents, respectively. We have found that the aggregation behaviour of the copolymer depends on the nature of the solvent and the micelle forms flat disc objects with the ratio of radius ω=0.4. The average radius gyration R_g of the copolymer decreases as solvents change from isopropanol to ethanol and to methanol, and increases with increasing pH in aqueous solution, but decreases with the addition of $CoCl_2$ in ethanol solvent. The scattering intensity of diblock copolymer micelle follows $I(h) \propto h^{-\alpha}$ in different selective solutions, suggesting that the PS_m-b-$PVBA_n$ coils have self-similar structure behaviour or a fractal structure in the selective solvents. All of these revealed that the aggregation behaviour of the diblock copolymer changes dramatically with experimental condition in the selective solvent. The increase of mass fractal dimension (D_m) from 2.12 to 2.47 indicates that the copolymer chain changes from a swollen coil to a rather compact disc in the course of changing solvents, decreasing surface fractal dimension (D_s) from 2.98 to 2.58 indicates that the copolymer micelle change from a rather rough surface to a smooth form in the course of increasing pH in aqueous solutions, and increasing D_m and D_s from 2.29 to 2.35 and 2.70 to 2.90, respectively, indicates the shrinkage of copolymer micelle to a rather compact and rough disc form by adding $CoCl_2$ in ethanol solvents.

Keywords: styrene-vinyl benzoic acid amphiphilic diblock copolymers, small-angle x-ray scattering, aggregation behaviour

PACC: 6110, 2920, 8270

1. Introduction

Amphiphilic block copolymers are made up of two or more blocks with different chemical identities, which can exist as star, random, graft, block, or branched architectures. A solvent is considered as selective if it is a thermodynamically good solvent for one block and a poor solvent for the other. In selective solvent, amphiphilic diblock copolymers can form micella-like aggregates due to the association of the insoluble blocks. Such micella aggregates may have the form of spherical objects, or they may be elongated to rod- or worm-like systems, flat discs or vesicles, depending on a number of factors such as the chemical composition of the block copolymers, the polarity of the solvent and the relative solubility of the blocks in the solvent.[1,2] They can produce numerous phase-separated microstructures and nanostructures that are of wide scientific and technological interest.[3−5] It is obvious that investigation of the aggregation behaviour of the diblock copolymers has both theoretical and practical importance because of their conventional and potential applications in biomaterials, optics, microelectronics, thermoplastic elastomers, pressure-sensitive adhesives, colloidal dispersants, compatibilizers of polymer blends, foams, and surface modification.[6,7]

The intricate structures and the complex morphologies of block copolymers usually show a dimension in the range of 2–100nm, which is ideal for SAXS measurement.[8−10] The SAXS technique provides us

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some opportunities to study block copolymer system either in the solid state or in solution, e.g. directly probing the self-similar structure behaviour or fractal structure on the basis of the scattered intensity and the size dependence of the molar mass.[11,12] With synchrotron x-rays, the high-power density and small beam divergence of the incident x-ray beam permit relatively high experimental resolution, short experimental time and expanded application fields. Since a large number of studies have been reported on the micella formation and the structural characteristics of polymeric micelle for diblock copolymers in selective solvents, Chu and Hsiao[13] recently have reviewed the work of synchrotron SAXS studies on polymers. In the present paper, the synchrotron SAXS technique is used to study the aggregation behaviour of PS_m-b-$PVBA_n$ in several selective solvents. We are greatly interested in the variations of conformation and microstructure of PS_m-b-$PVBA_n$ copolymer in the course of changing selective solvents, as well as the relationship between selective solvents and the macroscopic properties of the aggregation behaviour. To avoid the complication related to intermolecular interactions, our experiments deal mainly with the dilute solutions. We focus on: (1) the investigation of the aggregation behaviour of the PS_m-b-$PVBA_n$ system; (2) the thermodynamics of copolymer solutions with emphasis on the fundamental parameters, such as the average radius gyration R_g and the radio of radius ω over a wide range of different solvents; and (3) the structure of the PS_m-b-$PVBA_n$ chain by using the scattering intensity $I(h)$. The analysis of $I(h)$ from the copolymer chain, which allows extraction of information on the structure properties of PS_m-b-$PVBA_n$ chain as a function of selective solvent by fractal theory.

2.Experimental procedure

The general procedure for the preparation of the diblock copolymer PSt-b-PVBA is as follows: (1) The synthesis of monomer *t*-butyl *p*-vinylbenzoate (BVB), according to the procedures reported in Ref.[14] The yield of BVB was 82% and the boiling point was 107°C/40Pa. Its structure was confirmed by nuclear magnetic resonance spectrum (^{1}H-NMR). (2) The synthesis of macroinitiators PBVB-Br and PSt-Br. The procedure for the synthesis of macroinitiator was as follows: 0.5ml of degassed anisole and 0.5ml of monomer BVB or St were charged to a polymerization tube with 3.75mg of CuBr and 12.2mg of 2,2′-Bipyridine (bpy), and then 3.54μl of initiator 1-Bromoethylbenzene (BEB) was introduced. The tube was purged with nitrogen for about 5min, then degassed under vacuum and sealed after three cycles of freezing and thawing. The polymerization was carried out in an oil bath at 110°C under magnetic stirring. At an interval of time, the tube was broken and the contents were dissolved in tetrahydrofuran (THF). The polymer was recovered by precipitation in methanol and was dried overnight in vacuum. The yield was calculated from the weight of recovered polymer. (3) Synthesis of diblock copolymers PSt-b-PBVB. The synthetic procedure for the diblock copolymers was similar to that of the macroinitiator, except that PSt-Br or PBVB-Br was used as an initiator instead of BEB. (4) Synthesis of amphiphilic diblock copolymer PSt-b-PVBA. The diblock copolymer PSt-b-PVBA was obtained by the hydrolysis of PSt-b-PBVB. The general procedure was as follows: 1.0g of PSt-b-PBVB was dissolved in 10 ml of dioxane, then 0.5ml of concentrated hydrochloric acid was added. The mixture was allowed to react at 85°C for 7h and then was precipitated in hexane. The precipitate was washed with hexane and dried under vacuum overnight. The removal of the *t*-butyl group and the formation of the carboxyl group were confirmed by ^{1}H-NMR.

The property of PS_m-b-$PVBA_n$ solutions was investigated in the course of changing different solvents, increasing pH in aqueous solutions and adding polar salt in ethanol solvents, by means of synchrotron SAXS. The SAXS data were collected on 4B9A beamline at the SAXS station at Beijing Synchrotron Radiation Facility (BSRF).[15] x-rays were from a bending magnet, focused in both horizontal and vertical directions by a Pt coated toroidal mirror, monochromatized by a double S(11) crystal monochromator with fixed exit. The energy range of the beamline was 3keV to 12keV with 3×10^{-4} resolution when the storage ring was operated at 2.2GeV. In our experiments, the data accumulation time was 2 min. The angular range was chosen to provide data from h=0.005Å^{-1} to h=0.15Å^{-1}, where the magnitude of scattering vector $h = 4\pi\sin\vartheta/\lambda$, and 2θ and λ being respectively the scattering angle and incident x-ray wavelength of 1.54Å. The distance between the sample chamber and the detector is 1.495m. Two ionization chambers were used to measure the sample transmission. The detector for SAXS data collection is the image plate

(IP) system Fuji BAS-2500, with an active area of 400mm×200mm and a minimum pixel size of 50μm. The sample cell is a U-type metal groove with different thickness, whose window is made of thin films. The sample cell was flushed with corresponding solvent at least three times, before a suitable amount of PS-b-PVBA solution was filled into the cell. Background scattering from the slit collimator, the solvent, and the residual air path between the vacuum chamber and the detector was measured and subtracted. It should be mentioned that all the block copolymer solution were dilute with the concentration of 0.5mg/ml in this work. Excess SAXS scattering from the copolymer solution was also corrected for the incident beam decay and sample transmission.

3. Results and discussion

In this work, water, methanol, ethanol and isopropanol were used as the selective solvents for PS_m-b-$PVBA_n$ diblock copolymers. The scattering intensity for PS_{68}-b-$PVBA_{38}$ and PS_{56}-b-$PVBA_{48}$ in these selective solvents was measured at a concentration of 0.5mg/ml. Figure 1 shows the double logarithm plot of scattering intensity $I(h)$ versus scattering vector h for PS_{68}-b-$PVBA_{38}$ in methanol, ethanol and isopropanol. The scattering curve is obtained by subtracting the scattering of the solvent (background scattering) from the scattering of the copolymer plus solvent solution, so that we could obtain the information on the micellar behaviour of the diblock copolymer.

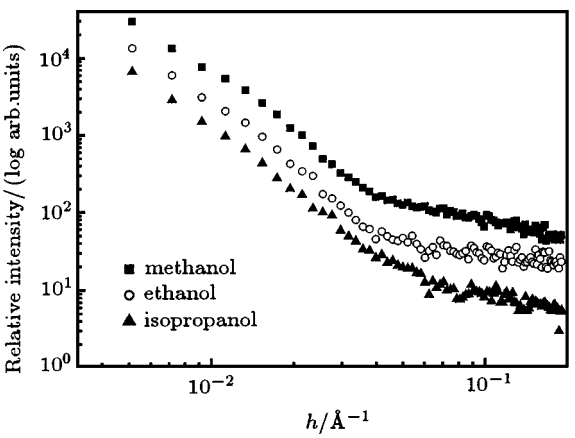


Fig.1. SAXS curves of PS_{68}-b-$PVBA_{38}$ block copolymer in methanol, ethanol and isopropanol solvent.

Table 1. Structure parameters of PS_{68}-b-$PVBA_{38}$ in different solvents.

Solvent	$< R_g^2 >^{1/2}$/nm	ω	a/nm	ωa/nm	D_m	D_s
methanol	11.84	0.4	18.01	7.02	2.12	2.79
ethanol	12.25	0.4	18.64	7.46	2.37	2.70
isopropanol	12.97	0.4	19.63	7.85	2.47	2.60

As shown in Fig.1, the scattering intensity increases as the solvents change from isopropanol to ethanol and to methanol. It is well known that variation in scattering intensity is due to the contrast produced by the difference of electron densities in the solute and solvent. The scattering intensity may reflect the aggregation behaviour of diblock copolymers in solutions. As we know, the average radius gyration of the copolymer coils in different selective solvents can be calculated by using the Guinier equation,[16]

$$I(h) = I_e N n^2 \exp[(-R_g^2/3)h^2], \qquad (1)$$

where I_e is the scattered intensity per electron, N is the number of the scatterers, n is the number of electrons per scatterer. Here the mean square radius of gyration $\langle R_g^2 \rangle$ is related to the size and conformation of the copolymer in the solution thus it could be used to characterize any kind and shape of scatterers,[17] and the results obtained for different solvent conditions are listed in Table 1, Table 2 and Table 3. In Table 1, the R_g decreases as the solvent changes from isopropanol, ethanol to methanol, indicating that the PS_m-b-$PVBA_n$ copolymer micella shrinks in the course of changing these solvents. It can also be found that the value of R_g increases in Table 2 with increasing pH in aqueous solvents, indicating that the copolymer micella experiences expanding in the course of increasing pH in aqueous solvents. In Table 3, R_g decreases with the addition of $CoCl_2$ in the ethanol solvents, indicating the shrinkage of the copolymer micella in the course of adding $CoCl_2$ in the ethanol solvent. All of these reveal that the average size of the copolymer coils might be related to the nature of the selective solvent. Further information about the microstructure of the copolymer can be obtained from the scattered intensity $I(h)$ in the

ellipsoids of revolution system with the half-axes a, a, ωa, which is given by

$$I(h) = I_e N n^2 \times \left[\int_0^{\frac{\pi}{2}} \phi^2(ha\sqrt{\cos^2\theta + \omega^2 \sin^2\theta}) \cos\theta \mathrm{d}\theta\right]. \quad (2)$$

To approximate the shape of the scatterers, the prolate rod-like scatterers can be looked as prolate ellipsoid with $\omega > 1$ and the oblate discs can be looked as oblate ellipsoid with $\omega < 1$. When $\omega = 1$, the scatterer is spherical and the intensity $I(h)$ is

$$I(h) = I_e N n^2 \phi^2(hR), \quad (3)$$

$$\phi^2(hR) = \left[3\frac{\sin(hR) - hR\cos(hR)}{(hR)^3}\right]^2, \quad (4)$$

where R is the radius of the spherical scatterers.

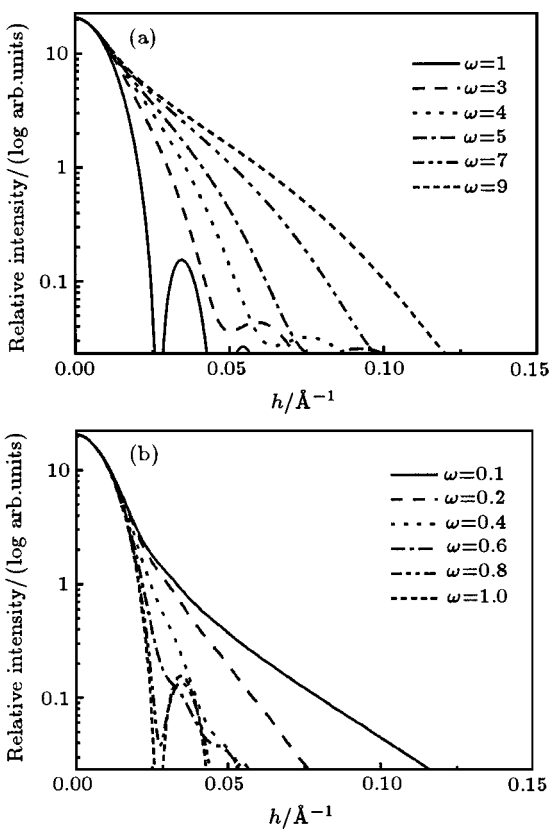


Fig.2. (a) Theoretical SAXS curves of long ellipsoid of rotation with $\omega > 1$ and $< R_g^2 >^{1/2}$=12.97nm; (b) Theoretical SAXS curves of flat ellipsoid of rotation with $\omega < 1$ and $< R_g^2 >^{1/2}$=12.97nm.

Thus, from the above equations and the relation between the average radius gyration R_g and the half-axes a, a, ωa,

$$R_g = a[(2 + \omega^2)/5]^{\frac{1}{2}}. \quad (5)$$

The shape of the scatterers can be determined by comparing the experimental and theoretical $I(h)$. Figure 2 shows the theoretical logarithmic scattering intensity plots of $I(h)$ versus h at different ω with the same $< R_g^2 >^{1/2}$=12.97nm of the copolymer. The experimental data plot cannot fit with any theoretical plots of prolate ellipsoid with $\omega > 1$, but it can fit very well with the theoretical plot of the oblate ellipsoid with ω=0.4 in small h at 0.5mg/ml of PS_{68}-b-$PVBA_{38}$ copolymer in isopropanol as shown in Fig.3. The ratios of the axes of ω of the copolymer aggregates with different chemical compositions in different selective solvents are similar in this work, indicating that the micella is just like a flat disc in the copolymer solution.

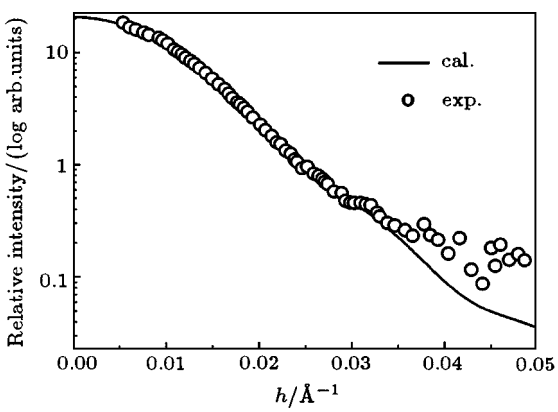


Fig.3. Comparison of theoretical and experimental SAXS curve of the copolymer with $< R_g^2 >^{1/2}$=12.97nm.

Aggregation information may be also obtained from the scattered intensity $I(h)$. The wide h-range of linear behaviour in $\ln I$ versus $\ln h$ plots as shown by experimental SAXS curves is expected when the scattering intensity is produced by objects with a fractal structure.[18–24] Then the scattering intensity produced by these objects is given by

$$I(h) \sim h^{-\alpha}, \quad (6)$$

where α is a positive constant. In this case, the fractal dimension can be determined from the asymptotic slope of $\ln I(h)$ versus $\ln h$. Two kinds of fractal disordered solid or liquid systems have been studied by small-angle scattering, these fractal systems are called mass-fractals and surface fractals.[25] The distribution of mass $M(r)$ in a mass fractal has the property that the mass inside a spherical surface of radius r is $M(r) = M_0 r^{D_m}$, where M_0 is a constant, and D_m is the mass fractal dimension. For mass fractals that are connected solids (not made up of isolated points), the meaningful values of D_m fall in the interval $1 \leq D_m < 3$ and $D_m = \alpha$. Surface fractals,

on the other hand, consist of one or more fractal surfaces that have a surface fractal dimension D_s. When the area is measured by covering the surface with the smallest possible number $N(r)$ of balls with radius r and thus with a cross-sectional area πr^2, the measured area $A(r)$ can be written as $A(r) = A_0 r^{2-D_s}$, where A_0 is a constant. The meaningful values of D_s lie in the interval $2 \leq D_s < 3$ and $D_s = 6 - \alpha$. Thus the value of α determined by small-angle scattering can be used to distinguish between mass and surface fractals in a monodisperse system of scatterers.

The plots of $\ln I(h)$ versus $\ln h$ for PS_{68}-b-$PVBA_{38}$ diblock copolymer in methanol, ethanol and isopropanol solvents have been obtained and shown in Fig.4. The power law behaviour and two kinds of asymptotic slope of these curves are observed, which is expected for "self-similar" or fractal structures. Very similar behaviour is found in other selective solvents, but the exponent α depends largely on the selective solvents, and the results are also given in Table 1, Table 2, and Table 3 for different solvent conditions. These results are clear indication for self-similar structures, which is frequently called fractals. Therefore, the copolymer system consists of two types of fractal systems, the mass fractals and surface fractals. The mass and surface fractal dimensions are common for disordered objects and demonstrate self-similar behaviour, which is understood as a structure that displays the same behaviour and is independent of a length scale. In other words, if two pieces of different sizes are cut from the polymer coil and the smaller one is optically magnified to equal size, then the structures appear indistinguishable.[26] The mass fractal dimension D_m of 2.12–2.47 is the characteristic of a copolymer coil that has an internal structure between a hard sphere (D_m=3.0) and a fully swollen randomly coiled macromolecule in a thermodynamically good solvent (D_m=2.0).[27] That is to say, when the copolymer is in methanol, ethanol and isopropanol, PS_{68}-b-$PVBA_{38}$ diblock copolymer distribution of mass is $M(r) = M_0 r^{2.12-2.47}$, where r is the measured spherical radius, indicating that the mass fractal dimension D_m is a measure of the compactness of the copolymer coils, i.e. the larger the mass fractal dimension D_m, the more compact the structure, the lower the D_m, and the more open the structure is. On the other hand, D_s of 2.79–2.60 is the characteristic of a copolymer coil that has a rather rough surface, indicating that the measured area can be written as $A(r) = A_0(r)^{-0.6--0.79}$, when the copolymer is in methanol, ethanol and isopropanol. It is easy to understand that D_s measures the degree of irregularity or the roughness of the surface. The larger the surface fractal dimension D_s, the rougher the structure is. D_s=2 represents a smooth Euclidean surface, and D_s=3 represents a surface so convoluted that it is space-filling. As can be seen from Table 1, the mass fractal dimension D_m and the average radius gyration $< R_g^2 >^{1/2}$ of the copolymer coils in methanol is lowest and D_s is highest among the three solvents used. At the same time, the highest value of D_m and $< R_g^2 >^{1/2}$ and the lowest value of D_s are achieved in isopropanol (Table 1), indicating that the copolymer micellar aggregates are rather small, open and rough in methanol solvent. From ethanol to isopropanol, the diblock copolymer aggregates become bigger, more compact and smooth.

Table 2. Structure parameters of PS_{56}-b-$PVBA_{48}$ in aqueous solution with different pH.

pH	$< R_g^2 >^{1/2}$/nm	ω	a/nm	ωa/nm	D_m	D_s
5.4	10.96	0.4	16.67	6.67	2.39	2.98
6.9	11.23	0.4	17.08	6.83	2.26	2.82
8.1	11.69	0.4	17.78	7.11	2.18	2.58

Table 3. Structure parameters of PS_{56}-b-$PVBA_{48}$ with and without $CoCl_2$ in ethanol solvent.

Solvent	$< R_g^2 >^{1/2}$/nm	ω	a/nm	ωa/nm	D_m	D_s
ethanol	12.16	0.4	18.50	7.40	2.29	2.70
ethanol+$CoCl_2$	11.72	0.4	17.83	7.13	2.35	2.90

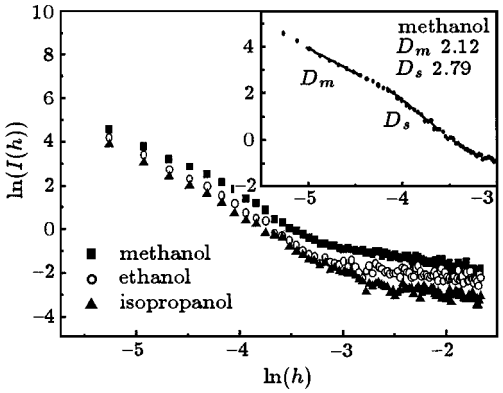


Fig.4. Plots of $\ln(I(h))$ versus $\ln h$ of PS_{68}-b-$PVBA_{38}$ in methanol, ethanol and isopropanol.

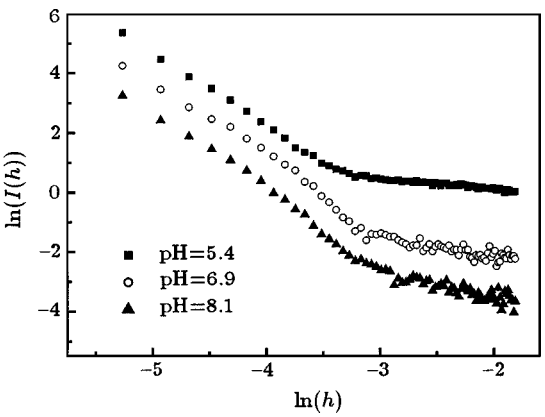


Fig.5. Plots of $\ln(I(h))$ versus $\ln h$ in solvent with different pH for PS_{56}-b-$PVBA_{48}$ solutions.

The aggregation behaviour of the diblock copolymer changes with the pH value in aqueous solutions, as shown in Table 2 and Fig.5. Table 2 shows the structural parameters of PS_{56}-b-$PVBA_{48}$ in aqueous solution of different pH. The fractal dimensions D_m and D_s decrease with increasing pH, as shown in Fig.5, indicating the expansion of copolymer micellar aggregations to a rather open and smooth disc form with increasing pH in aqueous solution. At a higher pH, the PVBA block is negatively charged, and the aggregates expand due to prevailing negative ion repulsion. Adding a polar salt in solvents can also influence the copolymer aggregation behaviour obviously. Figure 6 shows the $\ln(I(h))$ versus $\ln h$ of PS_{56}-b-$PVBA_{48}$ in ethanol solvents with and without the presence of $CoCl_2$, the results are summarized in Table 3. D_m and D_s increase with the change in solvent, representing the shrinkage of copolymer micellar aggregations to a rather small, compact and rough disc form in the course of adding $CoCl_2$ in ethanol solvent. The solvent power of the solvent is reduced and the PS_{56}-b-$PVBA_{48}$ chain shrinks due to the complexing reaction of the polar salt with the carboxyl group in the solvent. The micellar behaviour of the diblock copolymer shows a similar dependence on the nature of the solution at the above three processes. However, the dependence of the micellar behaviour on the nature of the solution for the two processes could be very different. The differences of these three processes indicate that the diblock copolymer aggregation behaviour in the selective solvent is influenced noticeably by the nature of the solvent.

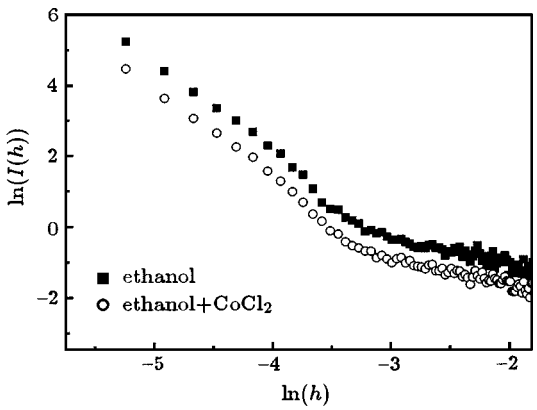


Fig.6. Plots of $\ln(I(h))$ versus $\ln h$ of PS_{56}-b-$PVBA_{48}$ in ethanol with and without $CoCl_2$.

4. Conclusion

The above SAXS study reveals some striking features: (1) The approximate shape of the micellar aggregations is just like flat disc with $\omega = 0.4$ in the selective solvents. (2) Power law behaviour is found for the scattering intensity $I(h)$ as a function of the scattering vector for different PS_m-b-$PVBA_n$ copolymers in different solvents. (3) The copolymer micella in methanol has the lowest fractal dimension D_m and average radius gyration $< R_g^2 >^{1/2}$ and highest D_s among the three solvents used. At the same time, the maximum of D_m and $< R_g^2 >^{1/2}$ and the minimum of D_s are achieved in isopropanol, indicating that the copolymer micellar aggregates are rather small, open and rough in methanol. From ethanol to isopropanol, the diblock copolymer aggregates become bigger, more compact and smooth. (4) The value of $< R_g^2 >^{1/2}$ increases with increasing pH in aqueous solutions. This indicates that the PS_m-b-$PVBA_n$ micelle experience expanding in the course of increasing pH in aqueous solutions. The fractal dimensions D_m and D_s decrease with increasing pH in aqueous solutions, indicating the expansion of copolymer micelle to a more open and smooth disc form with increasing pH in aqueous solutions. (5) $< R_g^2 >^{1/2}$ decreases

with the addition of $CoCl_2$ in ethanol solvents, D_m and D_s increase with the change in solvent, indicating the shrinkage of copolymer micelle to a smaller, more compact and rough disc form in the course of adding $CoCl_2$ in ethanol solvents.

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