

PHASE BEHAVIOR OF CHARGE STABILIZED COLLOID DISPERSION WITH ADDED WATER SOLUBLE POLYMERS*

Jia-xue Liu and Yong-feng Men**

State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry,
Chinese Academy of Sciences, University of Chinese Academy of Sciences, Changchun 130022, China

Abstract Demixing and colloidal crystallization in the mixture of charge stabilized colloidal poly(methyl methacrylate) particles and soluble poly(ethylene oxide) were investigated by means of synchrotron small-angle X-ray scattering (SAXS) technique. Phase diagram of the mixture was obtained based on visual inspection and SAXS results. The phase behavior is determined as a function of the concentration of the polymer as well as the volume fraction of the colloidal particles. The system shows a one phase region when the concentration of the polymer is low, whereas a two-phase region is present when the concentration of the polymer is larger than a critical concentration at certain volume fraction of the colloids. Interestingly, a face centered cubic colloidal crystalline structure was formed under certain conditions, which has been rarely observed in experiments of colloid-polymer mixtures with competing interactions.

Keywords: Colloid-polymer mixture; Phase behavior; Crystallization.

INTRODUCTION

Colloidal dispersions provide a unique opportunity to precisely adapt particle interactions, easily convertible from repulsive to attractive, from short to long range, from spherically symmetric to dipolar or directed interactions^[1] with experimental means. A direct consequence of this fascinating tunability enables researchers to mimic atomic behavior on a conveniently accessible mesoscopic scale. In addition, the stability investigation of colloid is very important in commercial applications such as personal care or food products to help stabilizing the system against sedimentation, thereby precluding phase separation and increasing product shelf life^[2–4].

Scientifically, interaction between colloidal particles with attraction is one of the hot issues because the system shows a rich phase behavior like crystallization, phase separation, reentrant glass transition and gelation. Depletion attraction introduced by adding of polymer in colloidal dispersion is one of the easy ways to introduce attraction into colloidal dispersion. Exclusion of polymer from the region between the closely spaced colloidal particles creates an imbalance in polymer osmotic pressure, which leads to an effective attraction between colloidal particles. Depletion attraction is a result of entropy. The nature of depletion attraction depends on the particle and polymer concentrations and the relative size of the particles and polymer molecules^[5, 6]. Asakura and Oosawa^[7] were the first to identify the depletion mechanism, and they developed a theoretical model for the resulting two-particle interaction. Depletion interaction is the origin of the rich phase behavior displayed by the colloid-polymer mixtures. Thus mixture of colloidal particles and polymer is regarded as a good model to study

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** Corresponding author: Yong-feng Men (门永锋), E-mail: men@ciac.jl.cn

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the complex systems and investigate comprehensively. Mixtures of colloids with hard-sphere potential and ideal non-adsorbing polymer have been investigated experimentally and theoretically. Investigations have shown that for short-range interactions gelation is induced by spinodal decomposition^[8]; the system undergoes a gas-liquid phase separation which is interrupted by the dynamical arrest of the particles in the colloid-rich region, leading to formation of gels. By contrast, for large ranges of the attraction, phase separation can proceed to completion, without being interrupted by dynamic arrest leading to gelation^[9, 10]. However, in the presence of gravitational effects the structure may no longer be capable of sustaining its own weight; instead, it collapses, disrupting the phase separation process^[10] or rupturing the gel that was previously formed^[11–13].

In practice, electrostatic interaction cannot be avoided in most systems, especially in aqueous colloidal dispersion. Contrary to attractive interactions which lead to form ordered phases or condensation, long-ranged repulsions tend to destroy this tendency. Fundamentally the competing mechanism of the two kind interactions leads to more complex structures and phase behaviors^[14]. Colloids with long-range repulsions can form glasses and crystals at lower densities than that in hard sphere system^[15, 16], and by combination with short-range attractions, a cluster fluid may emerges^[14, 17–19] and reentrant glass transition between repulsive glass and attractive glass^[20, 21] can be observed.

Colloidal particles with adding hydrophilic polymer have emerged as suitable candidates to investigate the phase behavior of systems with competing interactions. For example, phase behavior of latex, emulsions^[22–25] or protein systems^[26, 27] with added polyethylene oxide (PEO) have been extensively studied. In this work, we have investigated the phase behavior of the systems of the mixtures of charge stabilized PMMA colloidal dispersion and PEO solution. The phase diagram of the mixtures was obtained by visual observations as well as synchrotron small angle X-ray scattering (SAXS) experiments. It was found that under certain conditions, a phase separation occurred and a rarely observed face centered cubic colloidal crystalline structure was formed in these colloid-polymer mixtures.

EXPERIMENTAL

The colloidal poly(methyl methacrylate) (PMMA) particles were prepared by emulsion polymerization following standard procedure. The system was cleaned through centrifugation-redispersion for several times to obtain a clean colloidal dispersion. The size and the polydispersity of the PMMA particles were obtained *via* analyzing the SAXS results of the system. The radius of the particles is 90 nm with a polydispersity of about 3%. PEO, a nonionic hydrophilic polymer was purchased from Alfa. It has a molecular weight of 1×10^6 g/mol. Its radius of gyration is about 67.7 nm, dependent on the molecular weight M_w in water solution according to experimental findings, $R_g = 0.0215M_w^{0.583 \pm 0.031}$ nm^[28]. A stock colloidal dispersion with volume fraction of 15.06% and a stock polymer solution with concentration of 10 mg/mL were then prepared. Samples were prepared by diluting the stock colloidal dispersion with stock solution of salt and PEO, as well as water. To map out the different phases of the system on the (Φ, c_{PEO}) plane where Φ denotes the volume fraction of PMMA colloids and c_{PEO} the concentration of PEO in the system, we prepared sample series of constant Φ with varying c_{PEO} by vigorous mixing.

Synchrotron SAXS measurements were carried out at beamline BW4 at HASYLAB am DESY, Hamburg, Germany. The energy of the X-ray radiation was 8.979 keV, resulting in a wavelength of 0.13808 nm. The size of the primary X-ray beam at the sample position was 0.4 mm $\times$ 0.4 mm. The sample chamber was fixed onto a translational stage at the beamline. The sample to detector distance was 13841 mm. The effective scattering vector q ($q = (4\pi/\lambda) \sin\theta$, λ is the wavelength, and 2θ is the scattering angle.) at this distance ranges from 0.021 nm⁻¹ to 0.265 nm⁻¹. SAXS patterns were collected with an exposure time of 180 s with a 2D MarCCD detector (2048 $\times$ 2048 pixels, pixel size 79.1 μ m). The SAXS data were calibrated for background scattering and normalized with respect to the primary beam intensity.

RESULTS AND DISCUSSION

The stock colloidal dispersion forms long range ordered structure as indicated by their iridescence arising from the strong electrostatic repulsive interactions. A certain concentration of salt was added during preparing the samples to screen this strong repulsion between particles. PEO couples weakly to sodium dodecyl sulfonate (SDS) molecules in solution which are the surfactant used in the colloidal dispersion synthesizing process. However, the change in conformation of the polymer chains due to the adsorption of surfactant micelles remaining in the aqueous phase is negligible^[29, 30]. PEO is highly soluble in water because of its ability to form weak hydrogen bonds with the lone pair of electrons on the oxygen in its back bone. Therefore, PEO is widely used for fundamental studies of the interactions of nonadsorbing polymers with colloidal particles and the resulting effects on phase behavior^[30, 31] and protein crystallization^[26].

The polymer PEO added into the PMMA colloidal dispersion will introduce the depletion attraction between particles which is an entropic result. The depletion layer surrounding each spherical particle into which the polymer chain cannot penetrate will be overlapped. Thus an effective attraction is reduced due to the imbalance of the osmotic pressure between the bulk solution and the overlap region. Usually, there are three parameters which control the phase behavior of the ideal colloid-polymer mixtures: the ratio of the radius of gyration of the polymer molecules and the radius of the colloidal particles which scales the depletion interaction range; the concentration of the polymer related with the strength of the depletion interaction; and the last but not the least, the volume fraction of the colloidal dispersion. In the current case, we try to find the dependence of the phase behavior on the concentration of the polymer and the volume fraction of the colloidal particles.

After the sample is prepared, the colloid particles begin to aggregate, and a delayed deposit process due to gravity is observed, when the amounts of the polymer solution added are enough in the colloid-polymer mixtures. With different amounts of the polymer solution, the sedimentation velocities of samples are also different though these differences are not significant for the final structure formed by the particles. Sedimentation is finished in about two hours. The observed phenomenon is summarized in Table 1. Table 1 shows the observed results with increasing the concentration of PEO at the volume fraction of the colloidal particles of 4.66%, 7.49% and 11.98%. At the volume fraction 4.66% of the colloidal dispersion, when c_{PEO} is larger than 0.4 mg/mL in the mixtures, one observes sedimentation in several minutes after the samples were prepared. At $c_{\text{PEO}} = 0.6$ mg/mL and $c_{\text{PEO}} = 0.8$ mg/mL, the upper layer of the phase separated system was transparent after the completion of the sedimentation in the systems. When c_{PEO} is larger than 0.8 mg/mL, the upper layers become more and more turbid with increasing the concentration of PEO. At the volume fraction of the colloidal particles of 7.49%, when c_{PEO} is larger than 0.8 mg/mL in the mixtures, delayed sedimentation can be observed. From $c_{\text{PEO}} = 0.8$ mg/mL to $c_{\text{PEO}} = 1.6$ mg/mL, the upper layers of the samples are transparent and become turbid with more polymer. On increasing the colloidal volume fraction to 11.98%, when c_{PEO} is larger than 1.2 mg/mL in the mixtures, one observes sedimentation with transparent upper layers. Turbid upper layers are not observed under the experimental conditions. From the observation, the area with transparent upper layers becomes larger with increasing the volume fraction of the colloidal dispersion. Meanwhile, the concentration of PEO where the sedimentation with transparent upper layers is present also becomes larger. This phenomenon can be understood as follows: On one hand, it might be due to the existence of the adsorbing effect of the polymer PEO onto the colloidal particles, which is supposed to be very weak but still exists. On the other hand, the polymer PEO increases the viscosity of the system, which results in the sedimentation possessing larger clusters or larger gel fractures. We believe that at high concentration of polymers, the sedimentation present with turbid upper layers is also a result of the high viscosity introduced by the polymers.

Table 1. Separation situation and the appearance of upper layer of PMMA colloid and PEO solution mixture systems

Φ	c_{PEO} (mg/mL)	Sediment or not*	Upper layer
4.66%	0	N	—
	0.2	N	—
	0.4	N	—
	0.6	Y	Transparent
	0.8	Y	Transparent
	1.0	Y	Turbid
	1.2	Y	Turbid
	1.4	Y	Turbid
	1.6	Y	Turbid
	1.8	Y	Turbid
	2.0	Y	Turbid
7.49%	0	N	—
	0.2	N	—
	0.4	N	—
	0.6	N	—
	0.8	Y	Transparent
	1.0	Y	Transparent
	1.2	Y	Transparent
	1.6	Y	Transparent
	1.8	Y	Turbid
	2.0	Y	Turbid
11.98%	0	N	—
	0.4	N	—
	0.8	N	—
	1.2	Y	Transparent
	1.6	Y	Transparent
	2.0	Y	Transparent

* “Y” and “N” denote “with” and “without” sedimentation in the samples.

For a colloid-polymer mixture system, depletion interaction will drive the system to aggregate or form crystalline structure to gain more entropy. SAXS technique is a useful means to obtain such information. Figure 1 presents the integrated SAXS intensity distribution of the mixtures shown in the table. At very low concentration of PEO in the colloidal dispersion, due to the weak attractive interaction, colloid particles cannot overcome the electrostatic repulsive interaction between particles to aggregate together. Consequently, the intensity distribution of SAXS in this region shows scattering behavior of dispersed spheres. With the increasing of the concentration of the polymer PEO, the particles aggregate together. In Fig. 1(a), one finds diffraction peaks originating from a face centered cubic (FCC) structure super-imposed onto the scattering intensity from the colloidal spheres at certain conditions. One should pay attention to that, at the polymer concentration between 0.6 mg/mL to 1.0 mg/mL where no colloidal crystallization occurred though sedimentation was observed, the scattering intensity distribution at small q range of the samples does not show the sign of aggregation of the colloidal particles. When the polymer concentration is larger than 1.4 mg/mL, the scattering intensity of the systems also shows no sign of aggregation of the colloidal particles. It is well known that there is a cluster phase before gel formation in the mixture system with competing interaction. In the mixtures, when the concentration of PEO is large enough, the particles can joint together and form finite clusters due to depletion attraction interaction. These clusters grow up and finally sediment under the force of gravity. With the increasing of the concentration of the polymer, the attractive interaction increases. At a suitable scale of the attraction, the colloids crystallize under the competing interactions between attraction and repulsion. If the concentration of the polymer increases further, the system tends to form gel due to the strong attraction. But because of the effect of the gravity, the gel will fracture during the forming process, and finally the colloidal particles are sediment as

fractures. The mechanism is different for these two situations, so that the structures after sedimentation are different. However, the structure information is not observed in SAXS measurements because of the existence of the strong repulsion. In our system, though the colloidal particles aggregate due to the depletion interaction induced by adding polymer PEO into the colloidal dispersion, the strong electrostatic repulsion makes the particles stay apart from each other. The position of the diffraction peaks originated from an FCC colloidal crystalline structure indicates that the distance between the centers of the particles is 192 nm which is 12 nm larger than the diameter of the colloidal particles.

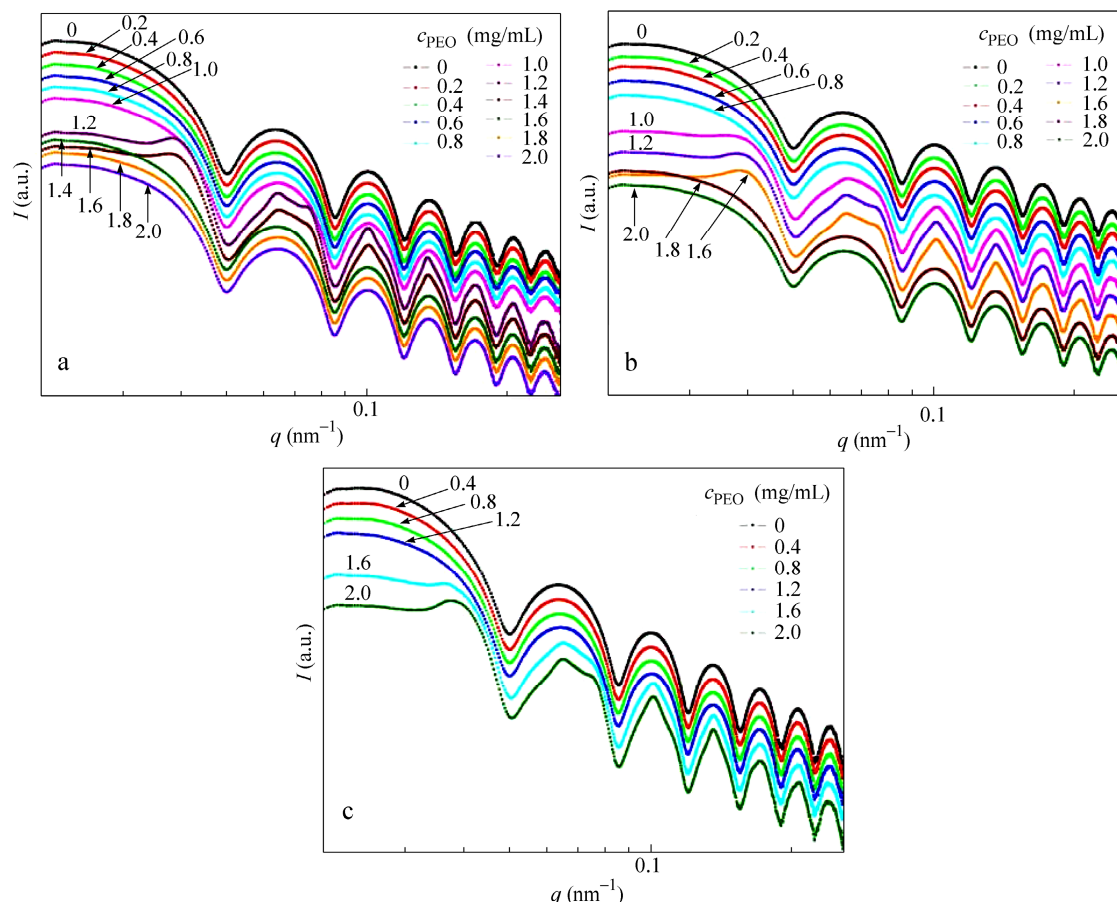


Fig. 1 Integrated 1D SAXS intensity distributions of mixtures of PMMA colloid-polymer (PEO) with different volume fractions of colloidal particles: (a) 4.66%, (b) 7.49% and (c) 11.98%. The PEO concentration c_{PEO} of the mixtures is given inserted table of each figure. Curves are shifted vertically for the sake of clarity.

At higher volume fraction of the colloidal dispersion, same phenomenon was observed (see Fig. 1b). On the volume fraction of the colloidal dispersion 7.49%, colloidal crystals are present at concentrations of the polymer of 1.0, 1.2, and 1.6 mg/mL. At smaller or larger concentrations of the polymer, no obvious change in the scattering intensity distribution was observed though. The scattering intensity distribution curves at 11.98% volume fraction of the colloidal dispersion are shown in Fig. 1(c). It is obvious that colloidal crystallization occurs at higher concentrations of the polymer from 1.6 mg/mL to 2.0 mg/mL. In the concentration range of the polymer investigated, no gel formation was observed.

The phase behavior of the colloid-polymer mixtures as a function of Φ and c_{PEO} according to the visual inspection and the scattering results is shown in Fig. 2. In the region of the system we investigated, the phase diagram can be divided into three regions: one-phase, two-phase and crystalline regions. In one-phase region, the

polymer concentration is low, so that no phase separation takes place. The mixtures with sedimentation are regarded as in two phase region. Aggregates are formed from single particles followed by growth of the clusters or gel formation. The clusters are not crystalline, but they are dense. At high volume fractions of the colloid, a crystalline region is identified within the two-phase region by SAXS measurements.

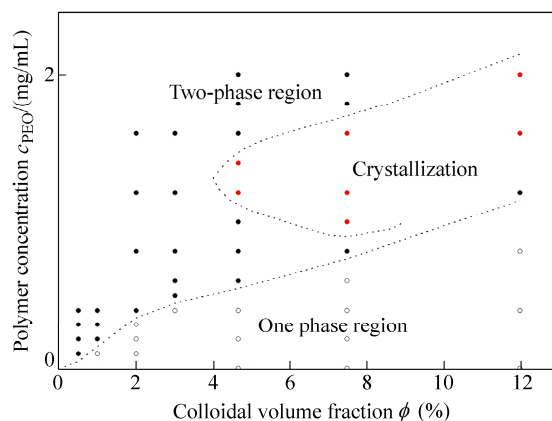


Fig. 2 The phase behavior of (PMMA) colloid-polymer (PEO) mixtures. The dotted lines in the phase diagram are guides for the eye. One-phase systems are indicated by open circles, two-phase systems by filled squares and crystallization by filled circles.

CONCLUSIONS

Systems of charge stabilized PMMA colloids and water soluble polymer PEO mixtures with competing attraction due to depletion and repulsion from colloidal surface charges exhibit interesting phase behavior. Depending on the volume fraction of colloidal particles and concentration of water soluble polymer, the system shows either homogenous one phase or phase separated structures. Upon phase separation, the particles leave their initial homogeneous, random phase by forming a condensed phase. A slow restructuring in morphology of the colloidal network takes place leading to loss of some structural integrity, and eventually collapse of the structure due to gravity. A sub-region where colloidal crystallization was observed was found within the two phase region.

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