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## INFLUENCE OF NON-ADSORBING POLYMER ON THE FORMATION OF COLLOIDAL CRYSTALS

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### ABSTRACT

We studied the effect of non-adsorbing polymer on the crystallization phenomena of colloidal dispersions. The experiments have been performed on dispersions of monodisperse stearyl silica spheres in cyclohexane to which polystyrene or poly(dimethyl siloxane) was added. For all polymers used the behaviour was roughly similar.

The addition of free polymer has a pronounced effect on the crystallization phenomena. The rate of crystallization increases dramatically. Besides ordering on top of the sediment, it turned out to be possible to induce crystallization throughout the entire sample just around the minimum concentration required for phase separation into a colloid-rich and a polymer-rich phase.

#### 1. Introduction

The phase transitions that occur in a colloidal dispersion depend, like in atomic systems, on the details of the interaction between the colloidal particles. In the case of repulsive interactions a disorder-to-order transition occurs, whereas attractive interactions give rise to gas-liquid and liquid-solid equilibria or fluid-solid transitions. One way to vary the interactions is by changing the solvent quality for example by means of temperature variation. At some temperature the solvent quality is sufficiently poor to destabilize the homogeneous dispersion. The system can then display a reversible phase separation from a single homogeneous dispersed phase to two phases with different concentrations.

Similar phase separations can be induced through the addition of a non-adsorbing polymer to a dispersion. The observed phenomena depend among other things on the molecular weight and

the concentration of the polymer, the size and volume fraction of the silica particles, the stabilizing layer of the particles and the (quality of the) solvent.

Asakura and Oosawa [1,2] showed for the first time, why the addition of (small amounts of) non-adsorbing polymer results in an additional attractive force between the particles when the effective diameter of the polymer exceeds the distance between the colloidal particles. Later more sophisticated theories to describe the attraction were developed [3,4,5]. At sufficiently high polymer concentrations the attraction between the particles can lead to a phase separation into a colloid-rich and a polymer-rich phase. This phenomenon was first observed and recognized as being caused by the above mentioned attraction by Sieglaff [6]. Subsequently this phase separation, that is sometimes referred to as depletion flocculation, was observed in many other experiments [7,8,9,10]. Theories were developed to describe this phase separation into two phases [10,11,12,13]. These theories predict that the minimum concentration of polymer required to induce phase separation decreases with the molecular weight of the polymer [8,10,11], the size and concentration of the particles [8,14] and the quality of the solvent [5] and increases with the length of the stabilizing polymer on the colloidal particles [13]. Furthermore, if the ratio of the size of the colloidal particles relative to that of the polymer molecules exceeds 3, the concentrated phase will be an (ordered) solid. At size ratios below 3 there is a limiting point and liquid-gas coexistence becomes possible, as well as liquid-solid transitions at higher densities [15]. Experimental results, which qualitatively support this theoretical prediction, have been obtained by Vincent et al. [9].

As the presence of non-adsorbing polymer may lead to a fluid-solid transition, it seems reasonable to expect, that this addition also influences the crystallization phenomena. This is indeed observed. An old example of this is the addition of non-adsorbing polymer to a solution of proteins leading to a successful crystallization of proteins, which could not be crystallized with other methods [16]. Also in aqueous dispersions of charge stabilized colloidal particles, addition of polymer can give rise to the formation of crystallites in the colloid-rich lower phase [10,15,17,18,19].

Here we present results on the effect of non-adsorbing polymer on the ordering phenomena of a sterically stabilized silica particle system. In section 2 the materials and methods used in this study are described. In section 3 the results are given. Finally in section 4 the main conclusions are summarized.

## 2. Materials and sample preparation

Samples were prepared by mixing a dispersion of stearyl silica particles in cyclohexane with a solution of a polymer in cyclohexane. The stearyl silica particles consist of silica cores, which were synthesized according to Stöbers method [20] and coated with octadecyl alcohol [21]. It was concluded from extensive experimental work that these particles (nearly perfectly) behave as hard spheres in dispersions of cyclohexane [22]. The hydrodynamic radius  $a$  of the system SCA14(0)STE was 160 nm and the polydispersity  $\sigma$  as measured by electron microscopy was 6%. For the system coded SBM1(1)STE,  $a = 160$  nm and  $\sigma = 6\%$ . The following polymers were used: a polystyrene polymer (PS) and three poly(dimethyl siloxane) polymers (PDMS)

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TABLE 1  
Molecular weight of the polymer

polymer	$M_W$ (g/mole)	$M_W/M_N$
PS	100 000	1.06
PDMS 35K	35 700	1.00
PDMS 70K	69 600	1.08
PDMS150K	152 700	1.11

The weight averaged molecular weight  $M_W$  and the ratio of  $M_W$  and the number averaged molecular weight  $M_N$  of these polymers are collected in table 1. Using the relationships between the molar mass and the mean square end-to-end distance [23] we estimate the radius of gyration to be about 10 nm for the polystyrene polymer and about 10-20 nm for the PDMS polymers. Samples were prepared by mixing a dispersion of stearyl silica in cyclohexane and a solution of a polymer in cyclohexane and subsequently homogenized by sonification and with a vortex mixer. The volume fraction of stearyl silica ranged from 25 to 55 per cent and the concentration of polymer was varied from 0 to 7 g/dm<sup>3</sup>. The mixtures of stearyl silica and polystyrene in cyclohexane were allowed to stand at 34.5 °C (the theta temperature for polystyrene in cyclohexane). The samples with the polymer poly(dimethyl siloxane) were studied at ambient temperature (about 20 °C).

### 3. Results and discussion

All samples were visually inspected for a period of two months. After a period of about one month no significant changes were observed any more. For a fixed concentration three regions can be distinguished with increasing polymer concentration. The course of events in these regions is depicted in fig.1. Without added polymer the particles settle under gravity and a dense sediment is formed within a few days. At this stage no crystallization is apparent. However, after a period of about 1-2 months, large vertically oriented columnar crystallites are formed at the interface of the dense sediment and the clear supernatant. The crystalline region typically reached a height of 1-2 mm. Above the crystalline region a small turbid layer can be observed. At low polymer concentrations (region A in fig. 1) the presence of polymer has little if any effect on the crystallization process. Increasing the polymer concentration (region B in fig. 1) the system phase separates into a colloid-rich and a polymer-rich phase, which becomes visible within a few hours. After a few days crystallization can be observed throughout the entire lower phase. Subsequently the crystallites settle under gravity. At still higher polymer concentration (region C in fig.1) a rapid phase separation into a concentrated colloid-rich phase and a polymer-rich phase occurs. At the interface between the colloid-rich phase and the polymer-rich phase a thin layer (0.5-2 mm) of crystallites is formed after a period ranging from a few hours to a few days. These crystallites are usually smaller than those observed on top of

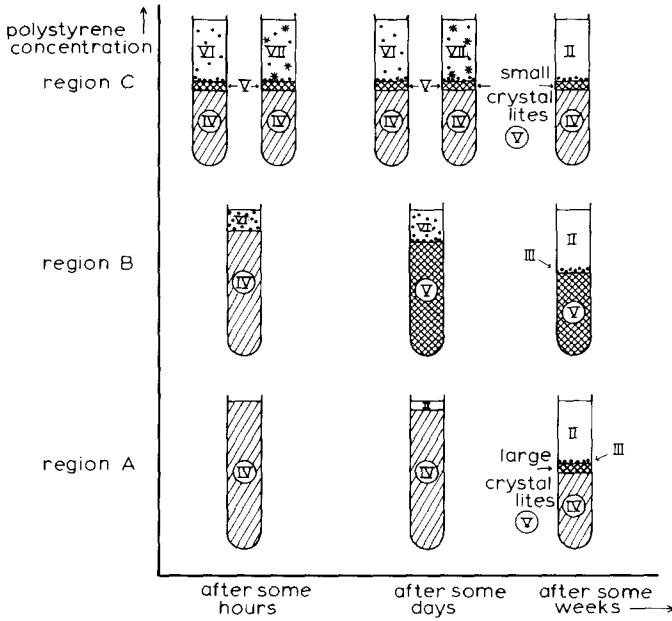


Fig. 1. Crystallization phenomena of dispersions of stearyl silica SCA14(O)STE and polystyrene for different polystyrene concentrations as a function of time. I represents the dilute dispersion, II the solvent, III the turbid layer above the sediment, IV the disordered sediment, V the iridescent (crystalline) sediment, VI a polymer-rich phase, which contains little silica and VII is a dispersion like VI which contains crystallites throughout. Note the differences in the rate of formation of the relatively "clear" upper layer.

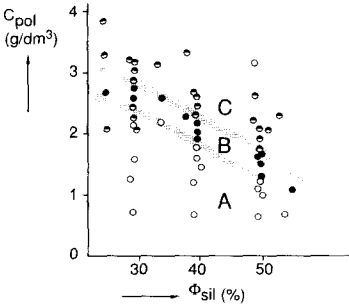
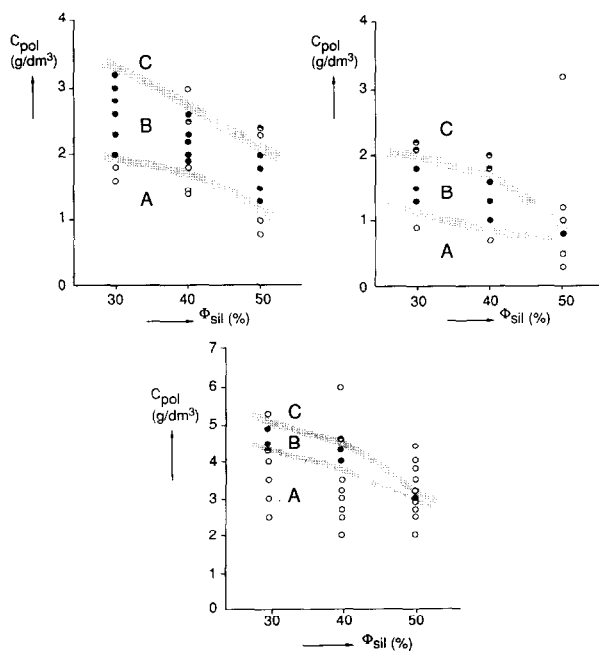


Fig. 2. Crystallization phenomena of dispersions of stearyl silica SCA14(O)STE and polystyrene as a function of their concentration.  $\phi_{sil}$  is the volume fraction of stearyl silica and  $C_{pol}$  is the concentration of polystyrene, o, ◐ and ● denote no crystallization, crystallization on top of the sediment within a week and in the entire sediment, respectively.

the sediment in region A. Remarkably, scattered crystallites may also be observed throughout the polymer-rich phase. Upon further increasing the polymer concentration the layer of crystallites on top of the sediment becomes progressively thinner and eventually disappears.

Samples with different silica concentration show similar behaviour albeit at different polymer concentrations. This is depicted in fig. 2 for polystyrene. Clearly an "optimal band" of polymer concentrations is observed, corresponding to region B, for which crystallization occurs throughout the entire colloid-rich part of the system. Although they are gradual, the transitions between the regions A, B and C occur within a small polymer concentration range indicated by the shaded areas in fig. 2. On going from A to B the thickness of the crystalline layer on top of the colloid-rich part of the system increases and eventually fills the entire lower phase. The same happens on going from C to B.

Fig. 3 shows results of experiments with three poly(dimethyl siloxane) polymers with



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Fig. 3. Crystallization phenomena of dispersions of stearyl silica SMB1(1)STE and poly(dimethyl siloxane). The symbols have the same meaning as in fig. 2. The molecular weights of the polymer are: a. 35700 g/mole, b. 69600 g/mole and c. 152700 g/mole.

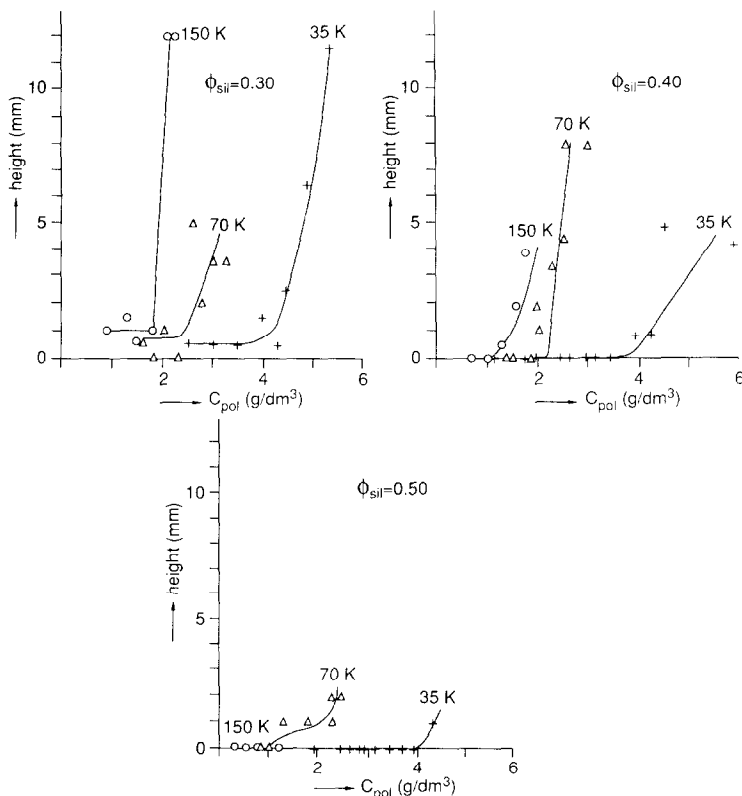


Fig. 4. Height of the relatively clear upper layer after 24 hours as a function of the polymer concentration at various molecular weights of the polymer PDMS and volume fractions of steryl silica SMB1(1)STE.

different molecular weight (see table 1). The phase behaviour of these systems is roughly similar to the phenomena described for the polystyrene polymer. Here again an "optimal band" of fully crystallizing samples is observed. However the observation of crystallites on top of the sediment (region C in fig. 1) is less pronounced than in dispersions with the polymer polystyrene. Furthermore smaller concentrations of poly(dimethyl siloxane) than of polystyrene with similar molecular weight were needed to induce crystallization. This is expected since the size of a PDMS polymer will be larger than the size of a PS polymer of similar molecular weight [23]. Therefore PDMS is expected to be more effective in inducing phase separation and crystallization.

To illustrate the interaction between the phase separation process into a colloid-rich and a polymer-rich phase and the crystallization phenomena more quantitatively, we define a limiting concentration, below which the system is stable. Due to sedimentation of the colloidal particles under gravity a sediment is slowly formed, giving rise to a clear upper layer of polymer solution. Above the limiting concentration the system is destabilized and a phase separation into

a lower, turbid colloid-rich phase and an upper, relatively clear polymer-rich phase occurs. Due to this phase separation process the upper layer grows much faster than due to sedimentation only. Experimentally we have defined the limiting concentration as the lowest concentration, where the formation of the upper layer after 24 hours can not be merely ascribed to sedimentation. In fig. 4 the height of the (relatively) clear upper layer of a silica dispersion containing various amounts of PDMS after 24 hours is given. The limiting concentration for poly(dimethyl siloxane) at different silica concentrations and molecular weights of polymer, as obtained from fig. 4 as the points, where the height rises sharply, are given in table 2. The limiting concentrations are in accordance with rough estimates based on data of De Hek and Vrij [8] and Vincent et al. [9]. At constant silica concentration, the limiting concentration decreases with increasing molecular weight of the polymer. It can also be extracted from table 2 that the limiting concentrations are almost the same as the (lowest) polymer concentration, where crystallization is observed throughout the entire lower phase. A comparison with the experiments on the effect of polymer on the crystallization phenomena of dilute suspensions of charge stabilized latex particles shows that there are similarities and differences with our results. Sperry [10] and Yoshimure et al. [18] also observed that crystallites could be formed around the polymer concentration at which phase separation occurs and Patel and Russel [15] and Gast et al. [19] observed rapidly formed (within 2 weeks) iridescence at polymer concentrations near the onset of the polymer induced phase separation. At higher polymer concentrations Patel and Russel [15] also saw crystallites after periods of time up to 6-8 months. Kose and Hachisu [17] found that crystallization occurs in a "band" of polymer concentrations. However, their "band" is much broader than the one we observed for sterically stabilized particles. Furthermore, they did not observe crystallites on top of the sediment.

#### 4. Conclusions

The crystallization phenomena of stearyl silica in cyclohexane, a system which crystallizes on top of the sediment after a long time (months), are strongly influenced by the addition of

TABLE 2.

Limiting concentrations  $c_{lim}$  and minimal concentration, where crystallization was observed throughout the entire sediment,  $c_{crys}$  of PDMS at different volume fractions of stearyl silica SBM1(1)STE  $\phi_{sil}$ . 35K, 70K and 150K denote the molecular weights of the polymer (see table 1).

$\phi_{sil}$	$c_{crys}$ (g/dm <sup>3</sup> )			$c_{lim}$ (g/dm <sup>3</sup> )		
	35K	70K	150K	35K	70K	150K
0.30	4.5	2.0	1.3	4.0	2.3	1.8
0.40	4.0	1.9	1.0	3.9	2.2	1.2
0.50	3.0	1.3	0.8	4.1	2.3	

polymer. The polymers polystyrene and poly(dimethyl siloxane) appear to have similar effects. In both cases an "optimal band" of silica and polymer concentrations can be observed, where crystallization throughout the entire concentrated phase can be observed within a short time (days). This band is situated around the limiting concentration for phase separation. The PDMS polymer is more effective in inducing crystallization than the PS polymer with a similar molecular weight. Likewise an increase of the molecular weight of the PDMS polymer leads to crystallization at lower polymer concentrations.

Crystallization in the silica samples is found to occur only throughout the entire colloid-rich part, if the dispersion is initially destabilized by the polymer, possibly resulting in a spinodal decomposition. Subsequently the polymers may also enhance the crystallization kinetics in the colloid-rich phase. The idea of spinodal decomposition may be tested with light scattering experiments. If spinodal decomposition plays a role, one expects to see a peak at small light scattering angles.

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