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COMPARATIVE STUDY OF THE POLYDIMETHYLSILOXANE MONOLAYER WITH STYRENE AND POLYSTYRENE

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SUMMARY: Polydimethylsiloxane (PDS) and it mixtures with styrene and polystyrene (PSt) are able to form stable monolayers at the liquid-gas interfaces in contrast to pure styrene or PSt. The surface pressure - molecular area isotherms of PDS monolayers have two regions at low and high pressures with pronounced transition plateau in between. The area per PDS molecule in the liquid-expanded state is about 1.60 nm^2 (at 5 mN/m) that can be explained by twisting of polymer chain into the helical conformation. The area per PDS molecule in the liquid-condensed state is about 0.48 nm^2 (at 20 mN/m) that can be explained by PDS reorientation in the helical conformation from the horizontal to the vertical position with respect to the air-water interface. The addition of styrene in the PDS monolayer drastically changes the π-A isotherms (no transition plateau) with area increase from 0.47 till 2.70 nm^2 per PDS with the increasing of polymer concentration from 1 to 10 mass %. In contrast, there are only small quantitative changes in the isotherms in the presence of PSt in the PDS monolayer. Thus, the formation of the polymer adsorption layers at the interface has been studied, modeling the initial and final step of the styrene polymerization in emulsion.

Introduction

Emulsion polymerization is one of the most important methods for preparation of the polysterene latexes with desirable properties. Polydimethylsiloxane (PDS) and sodium alkylsylfonate (trade mark E-30) have been found among the best stabilizers and emulsifiers for preparation of the stable polymer dispersions (latexes) with narrow particle distributions$^{1,2)}$. A high stability of these polymer dispersions is due to the formation of stable interfacial layer from polymer and surfactant molecules on the surface of polymer particles.

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Some monolayer studies have been fulfilled for PDMS and relative polymers in order to understand their orientation at the interfaces, especially their conformational changes by monolayer compression[3-5]. PDS shows a series of conformational transitions at the air-water interface by monolayer compression: flat two-dimentional coils – compressed highly-packed coils – helixes - highly-packed helixes[3-5]. These transitions are possible due to the specific and non-specific interactions of PDS polymeric chains with water. The substitution of methyl group in polydimethylsiloxane onto ethyl (PDES), propyl (PDPS) or fatty alkyl (PMAS) groups leads to the decrease in the stability of their monolayers. As was shown in the work[3], PDES, PDPS and PMAS form a thin films with the thickness 5.5, 5.8 and 4.8 nm, respectively.

By surface pressures higher than equilibrium pressure of molecular spreading the two-dimentinal monolayers is forming three-dimentional phase (monolayer collapse). A novel class of polysiloxanes (cyclo-linear) shows a sequence of monolayer collapses by forming organized multilayers at the air-water interface[5]. These effects are observed as pronounced plateaus in the surface pressure – molecular area isotherms by collapse pressures. The film thickness in each of these cases is proportional to the thickness of one monolayer. The authors[5] are concluded that such mechnaism of the organized monolayer collapses is particular for the polymers, which are able to form mesophases.

The aim of the work is the comparative study of the both stabilizer factors (polymeric and surfactant) on polymer monolayers and latexes.

Experimental part

α-(Carboxyethyl)-ω-(threemethylsiloxy)polydimethylsiloxane (PDS) with the general formular:

$$HOOC\text{-}CH_2\text{-}CH_2\text{-}Si(CH)_2\text{-}[\text{-}O\text{-}Si(CH)_2]_n\text{-}O\text{-}Si(CH)_3\,,$$

where n=7-9,

was generously donated by Prof. A.A.Zhdanov (INEOS RAS) and described in the work[6].

Sodium alkylsylfonate (trade mark E30) was made by Leina-Werke (Germany). E30 is the mixture of some fatty alkylsylfonate with the general formular:

$R\text{-}SO_3Na$, where R is $-C_{15}H_{31}$ as the average value between $-C_{12}H_{25}$ and $-C_{18}H_{37}$.

Styrene (St) was washed from stabilizer and prurified by double distillation according to the traditional scheme[7)]. Polystyrene (PSt) was prepared by emulsion polymerization of styrene at the ratio monomer:water=1:9 (but without emulsifier) at 80°C with potassium persulfate (as initiator) at concentration of 33.6 mM (1 mass. % to styrene) in order to obtain the sulfo-groups at the end of polymer chains.

Monolayers of surface-active substances, monomers and polymers were prepared and studied on a commercial film balance (NIMA-NFT, UK-FRG). The samples of PDS or E30 (100 μl from 10 mM solutions in chloroform) were spread on distilled water at 20°C between moving and measuring barriers. The prepared monolayers were compressed by moving barrier with constant speed of about 1 cm^2/s and the isotherms of surface pressure (π) - molecular area (A) were recorded.

Mixtures of PDS or E30 with monomer (styrene) or polymer (polystyrene), modeling the initial and final stages of the styrene polymerization in emulsion, were prepared by the following procedures:

1) PDS was dissolved in 7 mg/ml styrene solution in chloroform in the amount sufficient for obtaining solution with concentration from 1 to 10 mass % (calculated on styrene).

2) 1 ml of PDS solution in chloroform (from 1 to 6 mass %) was mixed with 1 ml of PSt solution in chloroform (in concentration 1.6 mg/ml).

After 30 min. relaxation these mixtures were used for monolayer preparations.

Results and Discussion

In order to model a formation of the polymer adsorption layers at the surface of latex particles, the corresponding two-component systems in monolayers at the air-water interface have been prepared and studied. The best stabilizers for preparation of the polymer latexes with narrow particle distributions, such as polydimethylsiloxane and sodium alkylsylfonate, have been investigated in the mixtures with monomer (styrene) or polymer (polystyrene), modeling the initial and final stages of the styrene polymerization in emulsion.

It has been found that polydimethylsiloxane can form stable monolayers at the liquid-gas interfaces (Figs. 1 and 2). In contrast, pure E30 can not form such monolayers,

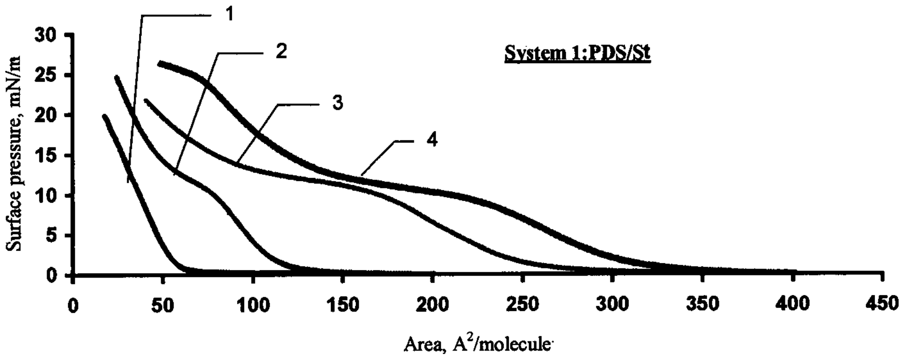

Fig.1. Surface pressure - molecular area isoterms for mixed monolayers of PDS/St at the following PDS concentration in chloroform (mass. % to St): curve - 1 (1), 2 (4), 3 (6), 4 (10).

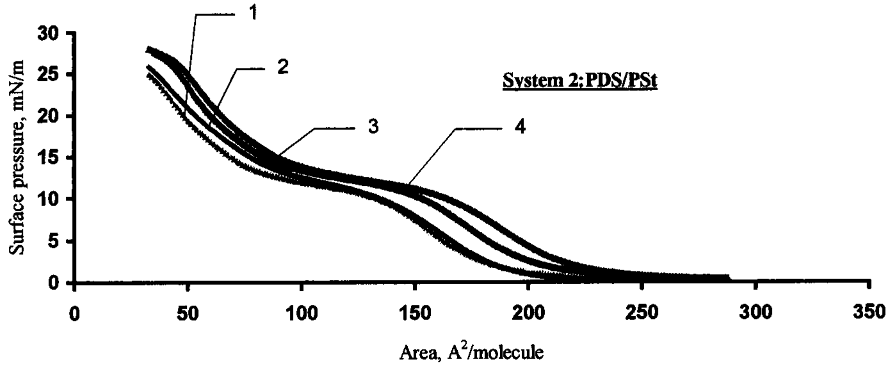

Fig.2. Surface pressure - molecular area isotherms for mixed monolayers of PDS/PSt at the following PDS concentrations in chloroform (mass. %): curve 1-pure PDS, 2 (2), 3 (4), 4 (6).

because of the high solubility of sodium alkylsylfonate in water. The π-A isotherms of PDS have two regions at low (liquid-expanded state) and high (liquid-condensed state) pressures with pronounced transition in between (in the region of π=10.0-12.5 mN/m and A=1.30-1.00 nm^2 per PDS molecule) (Figs. 1 and 2). For quantitative characterization and further comparison of the obtained monolayers, the areas per PDS at 5 and 20 mN/m (about the middle of each state) have been chosen. In the case of pure PDS monolayer (Fig. 2, curve 1) the mean area per PDS molecule in the liquid-expanded state is about 1.60 nm^2 (at 5 mN/m) that is almost 1.5 times lower than those calculated for the possible "completely stretched" conformation of PDS molecule at the interface. That can be explained by twisting of polymer chain into the helical conformation, as was proposed earlier in the work$^{3)}$. The mean area per PDS molecule in the liquid-condensed state is about 0.48 nm^2 (at 20 mN/m) that is almost three times lower than those for the liquid-expanded state (Fig. 2, curve 1). Taking into consideration also the pronounced transition between these two state, such a small value of molecular area can be explained by PDS reorientation in the helical conformation from the horizontal to the vertical position with respect to the air-water interface. The possibility of such reorientation was shown in our previous studies on monolayers of various natural and synthetic polymers$^{8)}$. It is important that the monolayer parameters are remain the same by PDS spreading at the interface in the concentration range of 1-6 mass % of polymer (in the initial chloroform solution). This is an additional evidence of stability of the helical conformation of PDS in monolayer.

The addition of styrene in the PDS solution (system 1) drastically changes the π-A isotherm character of the mixed monolayers (Fig. 1). For example, no transition plateau and very small area per molecule (0.47 nm^2) have been found (Fig. 1, curve 1) at low PDS concentrations (1 % in styrene). This can be explained by high degree of PDS folding in the mixed monolayer with styrene, because of high solubility of PDS in styrene and hydrophobic interactions. Because of the high correlation between this value and the mean area per PDS molecule in the liquid-condensed state for pure PDS monolayer (0.48 nm^2), the same vertical orientation of the PDS helical conformation can be also suggested. The pronounced transition plateau and high area per polymer (till 2.70 nm^2) have been observed by increasing of PDS concentration till 8-10 mass % in styrene (Fig. 1, curve 4). This effect is due to the unfolding of PDS at high concentration in the mixed monolayer with styrene (till "completely stretched" conformation of PDS molecule at the interface), because of the increasing ability of hydrophilic interactions of the amphiphilic PDS molecule with aquesous subphase as compared to the hydrophobic interactions with styrene. These models of the adsorption layers are relative to the initial stages of the styrene polymerization in emulsion in the presence of PDS at the corresponding concentrations.

In contrast, the addition of polystyrene in the PDS solution (system 2) did not change essentially the character of π-A isotherm for the mixed monolayers (Fig. 2). For example, π-A isotherms for pure PDS monolayer (Fig. 1, curve 1) and for the mixed monolayer with polystyrene at 2 % PDS concentration (Fig. 1, curve 2) are almost the same. Only small shift of the whole isotherm (with the same pronounced transition plateau) have been found for the mixed PDS-PSt monolayers to higher molecular areas with increasing PDS concentration to 4 and 6 % (Fig. 1, curves 3 and 4, respectively). This can be explained by immiscibility (no interactions) of PDS with polystyrene at all studied PDS concentrations. According to the values of PDS area in the presence of PSt, the conformation of PDS is the same (helix) as for pure PDS monolayers. This model of the adsorption layer, where PDS is located completely at the interface due to immiscibility with polystyrene, is relative to the final stage of the polymer layer formation in the emulsion polymerization of styrene.

In order to estimate the influence of the well-known surfactant (E30) on the emulsion polymerization of styrene, it mixtures with monomer, polystyrene and PDS have been studied. The addition of E30 in the styrene (system 3) or polystyrene solutions (system 4) did not allow us to prepare stable monolayers that correlates with the monolayer properties of the individuale components. Thus, these systems are not useful for our model studies and the presence of only E30 is not sufficient stabilizing factor for monomer-polymer mixtures. But the low stability of the mixed PDS-E30 monolayers (system 5) has been a great surprise to us, because of the high stability of the individual PDS monolayer. The only conclusion can be made that E30 and PDS are strongly interacting with formation of particular complexes, which are easily solubilizing in the aqueous subphase by monolayer compression.

Thus, the key role of PDS as stabilizing factor for styrene and polystyrene interfacial layers have been shown. In contrast, the same influence of E30, known from the styrene emulsion polymerization[1,2], can be realized only through interaction with PDS (i.e. indirectly). That is why, our further research will be concentrated on the study of PDS and surfactant simultaneous influence on the monomer-polymer monolayers (in multicomponent systems) in order to approach the real structure of the interfacial polymer layers at the surface of latex particles.

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