Exploration of Amphipolar Copolymer Adsorption on the Hydrophobic Surface

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Abstract: The data on thicknesses of the adsorbed polymer layer as obtained for the CuPc pigment dispersions under conditions of ultrasonic treatment in comparison to the systems without ultrasonic treatment are reported. The thicker adsorption layers observed for the ultrasonically treated systems confirm that an activation of the pigment surface occurs by the action of ultrasonic power.

Keywords: adsorption, ultrasound, pigments, polymers.

I. INTRODUCTION

In recent years, aqueous colloidal dispersions of particles have been of increasing interest from scientific as well as practical points of view. In order to achieve stable aqueous particle dispersions, many approaches were proposed [1-10]. Earlier we reported about the effect of mechanical and ultrasonic action for obtaining highly stable dispersions [7,9]. It was shown, that using of surface active polymers in combination with mechanical treatment can significantly enhance the quality of dispersions. However, some specific aspects of the particle-polymer interaction and structure of forming adsorption layers, especially under mechanical, i.e., ultrasonification still have not yet been studied in detail.

Electrokinetic sonic amplitude (ESA) studies have been demonstrated to be very convenient and powerful method that is able to provide the information about the process of polymers adsorption [7] and was employed in this study. Specially synthesized tailor-made PiBA-PAA block copolymers were used as stabilizers of aqueous dispersions of hydrophobic pigment CuPc. The polymer layers created on the particle surfaces in the absence and presence of mechanical (ultrasonic) action were investigated.

II. EXPERIMENTAL PART

Materials

As particles, β-copper phthalocyanine (β-CuPc) (primary particle size 0.1 μm) has been chosen.

The PiBA-PAA block copolymers of various well-defined structure, molecular weight and narrow polydispersity, were synthesized by controlled radical polymerization as described [3].

Techniques

For the preparation of aqueous dispersions, particles were added to water alone or together with the polymer dissolved in THF and dispersion of particles was first obtained by means of the laboratory stirrer (700 rpm for 10 min). When ultrasonic treatment was applied, the system was subsequently affected with ultrasound (for 2 min) with the ultrasonic generator Branson Sonifier B-12 with actual power of 1.5 W/cm^2.

Stabilization of the aqueous dispersions was studied by sedimentation measurements of 1 % wt. dispersions of CuPc. The particle-polymer interaction and the formation of polymer adsorption layer were examined by electrokinetic sonic amplitude (ESA) measurements as described in literature [7]. The size of particles was measured by ESA [7]. Standard optical equipment was used for refractive index measurements.

III. RESULTS AND DISCUSSION

Data reported in literature [11-16], showed that ultrasonic treatment of aqueous dispersions of particles in the presence of polymer stabilizers is leading to a significant improvement of the stability of such dispersions in comparison with dispersions prepared without ultrasonic action. It has been proven by IR-analysis that the firmness and stability of the adsorption layers of polymer were increased and improved by the ultrasonic action. Parameters of polymer adsorption layers obtained by the ultrasonic action were investigated [7]. However, the effect of the ultrasonic action on the particle-polymer interaction and adsorption of polymers, especially for original tailor-made amphiphilic copolymers is still not clear and needs further investigation for better understanding of the phenomena observed.Initially, sedimentation measurements for CuPc aqueous dispersions stabilized by a series of tailor-made amphipolar copolymers containing PiBA and PAA segments in the presence and absence of ultrasonic treatment have been carried out. These data are presented in Table 1.

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Table 1: Stability of CuPc aqueous dispersions with PiBA-PAA block copolymers.

Polymer	Suspension stability (half-time of the sedimentation, days)	
	Without mechanical treatment	After ultrasonic treatment
$PiBA_{72}$	3	10
PAA_{28}	0.3	2
$PiBA_{53} - PAA_{49}$	4	20
$PiBA_{53} - PAA_{26}$	5	45
$PiBA_{17} - PAA_{97}$	0.2	5
$PAA_{17} - PiBA_{72} - PAA_{17}$	3	14

First, as one can see from Table 1, all employed copolymers allow to obtain particle dispersions even in the absence of ultrasonic action while recent data on the application of PMVE containing block copolymers showed the impossibility to obtain dispersions without mechanical treatment [3]. It could be ascribed to that fact that THF used in the present study is known to create micelles with water and so provide the transport of a polymer to the particle surface. Secondly, irrespective of the composition of the copolymer, the ultrasonic action substantially enhances the dispersion stability as it is seen from the comparison of the sedimentation stability of the non-treated and treated systems. The data also show that an optimal copolymer structure exists with regard to the blocks length ratio; this fact is in accordance with previously reported constitutional effects [3]. Third, there is a pronounced effect of the particle surface nature on the polymer structure revealing the best stabilization: for hydrophobic CuPc, $PiBA_{53} - PAA_{26}$ with the ratio PiBA/PAA $\sim$ 2 revealed the best result.

ESA studies of aqueous dispersions of CuPc, stabilized by block copolymers of PiBA-PAA, allow to give quantitative information about the process of adsorption of polymers as reflected first from the dependence of the value of the dynamic mobility μ on the relative polymer concentration [7] as shown in Fig. 1 and 2, and second from the comparing this dependency for systems without and with ultrasonic treatment.
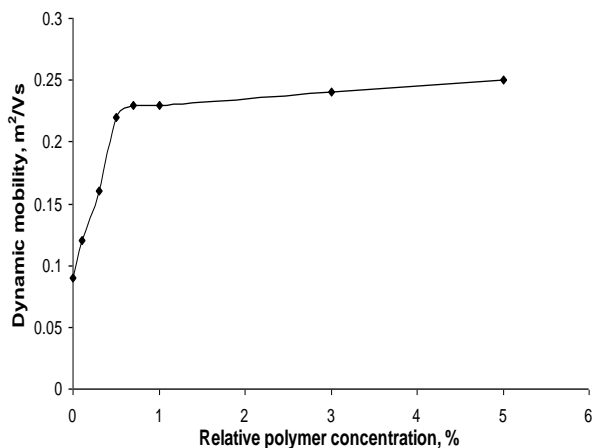

Fig. 1:Dependence of the dynamic mobility value on the relative concentration of $PiBA_{53} - PAA_{26}$ for 1 wt.-% CuPc aqueous dispersion before ultrasonic treatment.
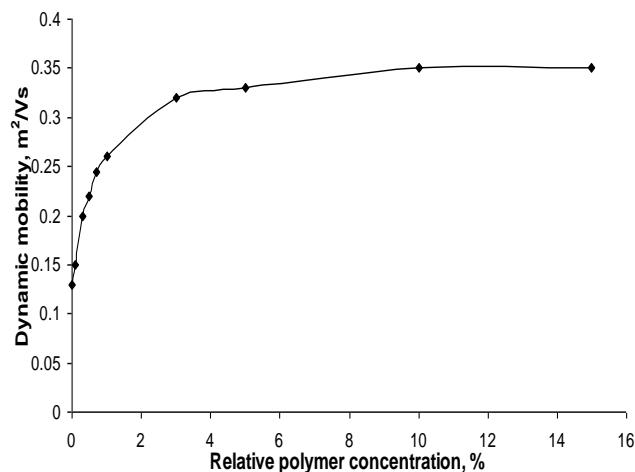

Fig. 2: Dependence of the dynamic mobility value on the relative concentration of $PiBA_{53} - PAA_{26}$ for 1 wt.-% CuPc aqueous dispersion upon the ultrasonic treatment.

Comparing the saturation concentration values before and after ultrasonic treatment, we can see that the amount of polymers adsorbed on the surface significantly increases when ultrasonic treatment is applied. In this view it has to be considered that the ultrasonification gives a finer dispersion by the decreasing the particle size, and, consequently leading to an increase of the surface area value prone to polymer deposition. Thus, both the rise in the total surface area of the particles in dispersions and a possible activation induced ultrasonically of the particle surface value must be considered as being responsible for the obtained effects.

In order to get some quantitative data about the polymer adsorption as revealed from the ESA data, and to correlate the amount of polymer adsorbed with the dispersing conditions, calculations of the surface area of the pristine pigment particle and of the polymer coated particle were done for both the systems without and with ultrasonic treatment and related to the amount of adsorbed polymer.

In these calculations a spherical shape of the pigment particle was assumed, and that the maximum polymer adsorption is indicated by the saturation concentration SC; this saturation concentration is reached when the dynamic mobility vs. relative polymer concentration curve (Fig. 1 – 2) becomes more or less parallel to the abscissa and doesn't change much for increasing polymer concentration [7].

First, the total surface area S_{tot} of the particles with surface area S_{part} is obtained from the measured average particle diameter d_{part} and the particle number in the dispersion. Since the saturation concentration SC as obtained by ESA measurements corresponds to the total mass of amphiphilic polymer that is adsorbed on the dispersed particles, the increased particle diameter (due to the adsorbed polymer) and thus the thickness of the polymer adsorption layer can be calculated as well. For the background and the equations on which the calculations of the data compiled in Table 2 are based it is referred to the literature [7].

Table 2:Effect of ultrasonic treatment on the particle diameter d_{part}, and effect of ultrasonic treatment on the increase of the particle surface area (S_{tot}) as well as on the saturation concentration (SC) of added amphipolar copolymer as expressed by the corresponding S_{tot} and SC ratio; the indexes 1 and 2 refer to the non-treated (1) and ultrasonically treated (2) sample.

System	Averaged particle diameter d_{part} in μm.		Ratio between particle surface area with and without ultrasonic treatment $S_{tot\,2}/S_{tot\,1}$	Ratio between saturation concentration with and without ultrasonic treatment SC_2/SC_1
	Without ultrasonic treatment	After ultrasonic treatment		
CuPc + PiBA$_{53}$ – PAA$_{26}$	0,8	0,3	2,7	6

Whereas the particle surface area S_{tot} increases upon ultrasonic treatment by about a factor of 2 (minimum) and up to a factor of about 2,7 (see column 4 of Table 2), the saturation concentrations SC as derived from the experimental curves Fig. 1 – 2 is 5 to 6 times higher for the ultrasonically treated systems as compared to the non-treated systems (see column 5 of Table 2); in other words, the SC ratio is about three times larger than the S_{tot} ratio (compare columns 4 and 5 in Table 2). This fact shows that the amount of polymer adsorbed per unit of the particle surface after ultrasonic treatment is higher as compared to non-treated samples.

Table 3:Thicknesses d of the adsorption layer of the amphipolar copolymer on TiO$_2$ and CuPc surface for ultrasonically treated and non-treated dispersions as calculated from the saturation concentration SC values obtained from the ESA studies (see Table 3).

System	Thickness d of the adsorption layer without ultrasonic treatment, nm.	Thickness d of the adsorption layer after ultrasonic treatment, nm.	Ratio between the thicknesses of treated and non-treated samples
CuPc + PiBA$_{53}$ – PAA$_{26}$	1	2,3	2,3

IV. CONCLUSION

Obviously the ultrasonic action not only increases the value of particle surface area by creating a more fine dispersion but also activates the particle surface leading to an definitely higher polymer adsorption as compared to the non-treated samples. The thicker adsorption layers observed for the ultrasonically treated systems confirm that an activation of the pigment surface occurs by the action of ultrasonic power.

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