Structure of adsorption layers of amphiphilic copolymers on inorganic or organic particle surfaces

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Summary

The structure of adsorption layers of amphiphilic block and block-like copolymers of poly(isobornyl acrylate) (PiBA) and poly(acrylic acid) (PAA) on the surface of hydrophilic titanium dioxide (TiO_2) and hydrophobic copper phthalocyanine (CuPc) pigments in aqueous dispersion has been studied by the electrokinetic sonic amplitude (ESA) method. The electroacoustic behaviour of the polyelectrolyte block copolymer coated particles could be described in the context of the polymer gel layer theory. The polymer layer around the particles was found to be much thinner for CuPc as compared to TiO_2 substrate. This is attributed to differences in the adsorption mechanism and the composition of the adsorption layer normal to the substrate surface. Adsorption models were established which consider effects of the copolymer structure.

Introduction

Amphiphilic polymers are effective colloidal stabilizers of aqueous dispersions.[1-4] In case of polyelectrolyte-type copolymers, this is due to the formation of adsorption layers of certain morphology providing electrosteric stabilization.[5-7] The interaction and layer formation of polyelectrolyte copolymers on, e.g., TiO$_2$ (hydrophilic) and copper phtalocyanine CuPc (hydrophobic) particles dispersed in aqueous media strongly depend on the composition and structure of the copolymers as it was shown, e.g., with the example of a series of well-defined amphiphilic block and block like-copolymers of isobornyl acrylate (iBA) and acrylic acid (AA) [8].

The employed poly(isobornyl acrylate)-*block*-poly(acrylic acid) block copolymers PiBA$_x$-*b*-PAA$_y$ and poly(isobornyl acrylate)-*block*-poly(acrylic acid-*co*-isobornyl acrylate) block-like copolymers PiBA$_x$-*b*-(PiBA$_y$-*co*-PAA$_z$) differ in the architecture of the hydrophilic block. In case of PiBA$_x$-*b*-PAA$_y$, the hydrophilic PAA block consists of acrylic acid (AA) repeat units only, whereas the hydrophilic PiBA$_y$-*co*-PAA$_z$ block of the block-like copolymer PiBA$_x$-*b*-(PiBA$_y$-*co*-PAA$_z$) contains a relatively low mole fraction of the hydrophobic iBA comonomer in a random sequence. The differences in the constitution of the block and block-like copolymers are illustrated in the schematic chain architectures shown in the captions of Fig. 1 and Fig. 2. For the synthesis and characterization of these tailored copolymers it is referred to the literature [9].

The following of the copolymer adsorption onto the pigments by the electrokinetic sonic amplitude (ESA) method (cf. [10]) revealed pigment specific anchoring of the copolymers, and a sequential adsorption process. [8] (cf. [7]) The ESA signal gives the dynamic mobility µ of the dispersed particle, and, at low frequencies of the applied electrical field, µ is only affected by the surface charge density of the particle, i.e., directly related to the zeta potential [11, 12]. This means that an observed change in the ESA signal upon addition of a (co)polymer directly reflects the altering of the surface charge density as related to the (co)polymer adsorption. As to the graphical illustration of the change of the ESA

signal with the amount of added copolymer to the particle dispersion, it may be advantageous to use the reduced dynamic mobility μ/μ_o, with μ_o representing the dynamic mobility of the non-treated particle, i.e., in the polymer-free dispersion [7]. For theoretical and practical details of this analytical method it is referred to the literature [12-15] and own work [7, 10].

From the investigation of the adsorption of $PiBA_x$-*b*-PAA_y block copolymers, and $PiBA_x$-*b*-($PiBA_y$-*co*-PAA_z) like copolymers on TiO_2 or CuPc particles by the ESA method under constant low frequency, models of the interaction of the copolymers with the pigment surface and the thickness of the resulting polymer adsorption layer as a whole were proposed [8] (cf. [7]). However, insights on the dimensions of the inner structure of the adsorbed polymer layer as related to the copolymer architecture have not been accessible in these experiments. More detailed information about the inner structure and of the thickness of the adsorption layer can only be obtained by means of ESA measurements under variation of the applied alternating electrical field (cf. [12, 16]). This is reported in this communication.

Experimental

Materials and measurements

Titanium dioxide TiO_2 rutile pigment Kronos 2310 with a particle size of 0.3 µm and breadth of particle size distribution of 60 nm, and copper phthalocyanine (CuPc, BASF AG, Ludwigshafen) with a primary particle size of 0.1 µm and a particle size distribution breadth of 15 nm were employed as received. The synthesis and characterization of both the tailored poly(isobornyl acrylate)-*block*-poly(acrylic acid) block copolymers $PiBA_x$-*b*-PAA_y and block-like copolymers $PiBA_x$-*b*-($PiBA_y$-*co*-PAA_z) have already been described elsewhere [8, 9].

Electrokinetic sonic amplitude (ESA) measurements were carried out with an Acoustosizer 2 Instrument (Colloidal Dynamics, Sydney, Australia). 1 wt.-% aqueous dispersions of TiO_2 of CuPc were employed in the copolymer adsorption studies. Frequency dependent ESA measurements (frequency range 1.0 - 18 MHz

were carried out for the saturation concentration SC (cf. [7]) of added copolymers. At SC, all the added polymer is adsorbed to the pigment surface, i.e., practically none is remaining in solution. For the evaluation of the ESA data according to the polymer gel layer theory [12], the following theoretical parameters were used: dynamic viscosity $\eta = 0.95$ $N \cdot s \cdot m^{-2}$ (viscosity of water at 22 °C), Debye-Hueckel parameter $\kappa = 0.2$ nm^{-1}, drag coefficient $\alpha = 0.02$ $N \cdot s \cdot m^{-2} \cdot nm^{-2}$, and relaxation frequency $\omega_0 = 0.85$ s^{-1}. For details of the experimental protocol and data analysis it is referred to earlier publications [8, 16].

Results and discussion

In agreement with the results reported earlier [8], the structurally similar iBA and AA based block and block-like copolyelectrolytes employed in this work revealed the same adsorption features as reflected from the ESA measurements under constant low frequency. The corresponding dynamic mobility μ vs. polymer concentration curves for aqueous TiO_2 and CuPc dispersions are depicted in Fig. 1 and Fig. 2.

In the case of hydrophilic TiO_2 particles, $PiBA_{17}$-PAA_{72} block copolymer first adsorbs via ionic groups of PAA, forming a layer of more or less immobilized PAA chains in a train-like conformation, with islands of collapsed PiBA blocks on top (cf. [8]). This goes along with an overall decrease in surface hydrophilicity of the particles as reflected in the initial decrease of the ESA signal (dynamic mobility μ) upon addition of copolymer, finally reaching a minimum value. The monolayer covered TiO_2 is subsequently stabilized by further adsorption of copolymer via interactions between the existing surface-immobilized PiBA blocks and PiBA blocks of dissolved block copolymer (cf. [8]) as reflected by an increase of the ESA signal after a minimum value has been passed (see Fig. 1, curve 1), resulting in a bilayer consisting of a PAA anchoring layer, a PiBA interphase, and an outer layer of PAA polyelectrolyte. ([8]; cf. [7])

In case of the $PiBA_{20}$//$PiBA_3$/PAA_{91} block-like copolymer, the initially increasing ESA signal (Fig. 1, curve 2) infers a distinctly different adsorption

mechanism that is related to the conformation and aggregation of single block-like copolymer molecules in aqueous solution. Micelle-like spheres consisting of a core of the collapsed PiBA block covered by loops and tails of PAA segments that are a result of the intramolecular interaction of isolated iBA units of the hydrophilic block with the hydrophobic PiBA core are attached to the TiO_2 surface via a fraction of the carboxylate groups of the micelle like aggregate. In this way, a so-called solloid (cf. [2]) layer is formed. This adsorption process does not cause any decrease in the TiO_2 surface charge density (screening of charges) as in the case of the initial adsorption of block copolymers (see above), but to the contrary increases the zeta potential of the coated particle in comparison to the bare particle.

As to the hydrophobic CuPc pigment, the initial adsorption of copolymer always proceeds via the hydrophobic PiBA block, presumably again in a train-like conformation, with the hydrophilic block reaching into to the aqueous phase. In case of block copolymer adsorption ($PiBA_{51}$-PAA_{30}), the dispersed particle is stabilized by the dangling PAA block, and in case of the block-like copolymer, by loops of PAA segments that are attached to the adsorbed PiBA block by isolated iBA units. The copolymer adsorption results in a pigment hydrophilization, as it is reflected from the increase of the ESA signal from the very beginning of the copolymer addition.

Irrespective of the pigment type or copolymer, an upper limit of the dynamic mobility is observed upon polymer addition, and a so-called polymer saturation concentration SC is defined [7, 8, 10] beyond which no further changes of the dynamic mobility µ is observed.

Further details, and how the observed phenomena were explained by differences in the conformation of the adsorbed copolymers as related to the copolymer architecture have been already discussed elsewhere. [8]

The amount of polymer adsorbed to the pigment surface, and thus the overall thickness of an adsorption layer can be calculated for collapsed coils by relating the saturation concentration values SC as determined from the curves depicted in

Fig. 1 and Fig. 2 to the surface area of the uncoated pigment (cf. [8, 16]). Here the saturation concentration SC is given by the concentration of added copolymer above which the dynamic mobility of the dispersed particle remains more or less constant, i.e. becomes independent of polymer concentration. The significant differences in the thickness of the adsorption layer on TiO_2 and CuPc (Tab. 1) is in full agreement with the previously proposed [8] (and outlined above) adsorption mechanisms: Monolayer formation with hydrophobic PiBA anchor blocks in case of CuPc, and multilayer formation for TiO_2.

In order to further elucidate the structure of the polymer adsorption layer, ESA measurements under variation of the frequency of the applied alternating electrical field have been carried out. In principle, such data can be used to get detailed information about the structure of adsorption layers, as first shown and theoretically treated for the adsorption of poly(vinyl alcohol) to colloidal silica [12], and was confirmed for the adsorption cellulose based polymers to titanium dioxide and ferrous oxide [16]. According to the polymer gel layer theory [12], it is assumed that the structure of the adsorbed polymer layer consists of an inner layer of polymer molecules adsorbed on the particle surface, and an outer, more permeable layer toward the solution. The inner layer is characterized by a comparatively higher density, and its formation is a direct result of pigment surface - polymer interactions [12,16]. This is schematically depicted in Fig. 3.

The procedure and formula given in literature [12, 16] for the calculation of the thicknesses of the inner (Δ) and outer (δ) polymer layer from frequency dependent measurements of the reduced dynamic mobility μ/μ_o was applied for both TiO_2 and CuPc particles, and block as well as block-like PiBA/PAA copolymers. According to the boundary conditions of the polymer gel layer theory, requiring that no free polymer is left in the solution after the process of polymer adsorption is completed [12], the ESA measurements were carried out for the saturation concentration SC of added copolymers. At SC, all the added polymer is adsorbed to the pigment surface, i.e., practically none is remaining in solution.

The changes of the reduced dynamic mobility (ratio μ/μ_o of the dynamic mobility of polymer-coated to uncoated particle) measured for the frequency range

1.0 - 18 MHz are given by the data points in Fig. 4 and Fig. 5. The averaged thicknesses of the inner (Δ) and outer (δ) adsorption layers (see Fig. 3) as obtained from the analysis of these experimental data according to literature protocols (cf. [16]) are compiled in Table 1.

The μ/μ_o – frequency dependency (solid curves in Figs. 4 and 5) calculated after the polymer gel layer theory by using the averaged layer thickness data of the inner (Δ) and outer (δ) adsorption layers (given in Tab. 1) corresponds well with the experimentally observed change in the reduced dynamic mobility data with frequency of the applied electrical field (data points in Fig. 4 and Fig. 5). This means that the polymer gel layer theory that was originally developed for neutral, i.e., non-ionic polymers can be applied to the adsorption of polyelectrolyte copolymers on hydrophilic as well as hydrophobic surfaces.

The sum of the inner (Δ) and outer (δ) adsorption layer (Tab. 1, columns 4 and 5, respectively) according to the polymer gel layer theory, as obtained by the analysis of the frequency dependent reduced dynamic mobility data, is in good agreement with the values of the thickness of the whole adsorption layer (Tab. 1, column 3) that are based on the polymer saturation concentration (SC) as established independently by the concentration dependency of the ESA signals at constant, low frequency of the applied electrical field (see also Fig. 1 and 2). This is clear evidence for the conclusiveness of the complementary experimental approaches, i.e., frequency independent and frequency dependent ESA measurements.

As already explained above, it is plausible that the initial PiBA-*b*-PAA block copolymer adsorption on TiO_2 particles takes place via anchoring of the PAA block in a train-like conformation, turning the particle surface less hydrophilic because of the hydrophobic PiBA block, as reflected by a decrease in the ESA signal (see Fig. 1). This is followed by a bilayer formation that is driven by hydrophobic interactions of collapsed PiBA of already adsorbed block copolymer with PiBA blocks of still dissolved PiBA-*b*-PAA unimers in order to provide a thermodynamically more favourable ionic hydrophilic outer surface, as reflected by the recovery of the ESA

signal (cf. [7, 8]). The formation and structure of the adsorption layer is sketched in Fig. 6a.

According to this model, the inner, dense adsorption layer as defined by the polymer gel layer theory consists of flatly adsorbed PAA blocks and overlaying islands of collapsed PiBA blocks. Because of the differences in chain length between the long PAA and comparatively short PiBA block, the PAA adsorption layer will not be completely covered by collapsed PiBA. Therefore the zeta potential ξ_Δ at the border between the inner and outer layer (see Fig. 3) will be still partially affected by PAA that is not covered by PiBA. The thickness Δ of this inner adsorption layer (1.6 nm) correlates with the molecular (chain cross-sectional) dimension of the PAA and PiBA chain. The thickness (4.2 nm) of the significantly thicker outer adsorption layer is related to the random flight coil dimensions of dangling PAA blocks as estimated for a PAA chain of about 70 repeat units assuming a characteristic ratio $C_n = 11.3$ [17].

In contrast to this, the adsorption model of block-like copolymers PiBA-b-P(iBA-co-AA) to TiO_2 is based on the adsorption of micelle-like aggregates consisting of the collapsed PiBA block as core and a shell of predominantly loop-like PAA attached to the PiBA core by isolated iBA units of the P(iBA-co-AA) block. Considering the iBA mole content of the P(iBA$_3$-co-AA$_{91}$) block, and the random incorporation of iBA as given by the copolymerization parameters [9], the PAA loops or tails comprise in average about 23 AA units. The aggregates adsorb to the TiO_2 via ionic interactions of the PAA loops and dangling ends. The formation and structure of the adsorption layer is sketched in Fig. 6b.

The resulting solloid monolayer can be divided into an inner adsorption layer of thickness Δ consisting of immobilized PAA that is ionically bond to the TiO_2 surface, and the overlaying PiBA layer, and an outer layer of PAA loops and tails of thickness δ. The thicker inner layer as compared to the case of block copolymer adsorption may be associated to both the comparatively large volume of the aggregate's core consisting of a collapsed PiBA block, and steric restrictions in the interaction of relatively short PAA loops of the P(iBA$_3$-co-AA$_{91}$) block of the block-like copolymer in comparison to the much longer PAA block of the PiBA$_{17}$-b-PAA$_{72}$

block copolymer. Accordingly, the much thinner outer adsorption layer in case of the block-like copolymers is related to restrictions in the permeability of the comparatively shorter PAA loops (average of 23 AA repeat units) of the P(iBA-*co*-AA) block that are less mobile than the only single tethered, and much longer PAA block (72 AA repeat units) of PiBA-*b*-PAA. This view is supported by a rough estimate of the differences in the end-to-end distance between a PAA_{73} block and a PAA_{23} loop, using the same characteristic ratio as above.

As already elucidated above, the adsorption model of block and block-like copolymers to the hydrophobic CuPc does not only significantly differ from the adsorption of copolymers on TiO_2, but is quite similar for both block and block-like copolymers. The anchoring of the copolymers on the CuPc surface is given by the hydrophobic PiBA block in a presumably train-like fashion, and the CuPc coating consists of a monolayer only (cf. [8]). This means that the adsorption process of PiBA chains to the CuPc surface involves a decoiling of the globular, collapsed conformation of the PiBA block of the copolymers in aqueous solution. The formation and structure of the adsorption layer according to the polymer gel layer theory is sketched in Fig. 6c.

The inner, dense adsorption layer is comparatively thin and consists of flatly adsorbed PiBA blocks. This is in accordance with the determined thickness Δ (Tab. 1, column 4) which corresponds to the geometrical dimension of the isobornyl residue. The even thinner outer layer (Tab. 1, column 5: thickness δ), which consists of dangling PAA ends in case of block copolymers, and of PAA loops in case of block-like copolymers, is explained by the fact that the PiBA block is not only much longer but also larger in volume than the PAA or P(iBA-*co*-AA) block., respectively. As a consequence, only a fraction of the inner PiBA adsorption layer (see Fig. 3: zeta potential ξ_Δ) is shielded by the mobile PAA, meaning that the shear plane (see Fig.3, zeta potential $\xi_{\Delta+\delta}$ at the polymer layer surface), in average, is not that much shifted. This explanation is in agreement with the differences of the thickness of the outer adsorption layer of the block and block-like copolymer coating on the CuPc particle: the permeable "outer layer" is expected to be thinner for the in average 6 AA repeat units comprising loops of the

P(iBA$_5$-*co*-AA$_{39}$) block of the block-like copolymer as compared to the 30 AA repeat units long PAA block of the PiBA$_{51}$-*b*-PAA$_{30}$ block copolymer.

Conclusion

New insights into the adsorption mechanism of amphipolar copolyelectrolytes on hydrophilic or hydrophobic particles dispersed in aqueous media, and on the layer structure formation, were obtained by electrokinetic sonic amplitude (ESA) measurements and analysis of the electroacoustic data on the basis of the polymer gel layer theory. It was established that the polymer gel layer theory can be applied to polyelectrolytes, and it was found that both the surface characteristics of the dispersed (pigment) particles and the architecture of the iBA/AA comonomer based copolymers distinctly affected not only the copolymer – particle interaction but also the thickness and structure of the coating layer formed around the particles.

In particular, the data revealed that particles with hydrophobic surface such as the CuPc pigment are covered for both the block and block-like copolymers by a relatively thin copolymer monolayer, with the hydrophobic PiBA blocks acting as anchor and the PAA blocks as electrosteric stabilizing moieties. In terms of the polymer gel layer theory, the PiBA blocks form the inner dense layer, and the PAA blocks represent the outer, permeable region of the adsorbed layer. Contrarily, different adsorption mechanisms of block and block-like copolymers were observed for the hydrophilic TiO$_2$ pigment.

In case of block copolymers, the inorganic pigment is covered by a multilayer: PAA of a first adsorption layer of block copolymer act as anchor blocks, an interphase layer consisting of interpenetrating PiBA blocks of this first and a second copolymer absorption layer follows, and PAA polyelectrolyte blocks of the second adsorption layer form an outer shell layer. For block-like copolymers, a solloid monolayer is formed, with some of the PAA loops acting as anchor, and some as electrosteric stabilizing moieties. Here, according to the polymer gel layer theory, the PAA anchor block layer together with the PiBA core of the solloids

correspond to the dense inner layer, and the remaining PAA loops and short dangling ends represent the permeable outer layer.

Acknowledgements

Literature

[1] D.H. Napper, Polymeric Stabilization of Colloidal dispersions, Academic Press, New York **1983**

[2] P. Somasundaran, S. Krishnakumar. Colloids Surf. A **1997**, *123*, 491.

[3] K. Holmberg, B. Jöhnsson, B. Kronberg, B Lindman, Surfactants and Polymers in Aqueous Solution, 2nd edition, J. Wiley & Sons, Chichester 2003.

[4] D.J. Cartridge, *Polymers Paint Color J.* **1994**, *184*, 10

[5] J.P. Kaczmarski, M.-R. Tang, J.E. Glass, R.J. Buchacek, *Progr. Org. Coat.* **1997**, *30*, 15

[6] N.G. Hoogeveen, M. Cohen Stuart, G.J. Fleer, *J. Colloid Interface Sci.* **1996**, *182,* 133

[7] C. Schaller, T. Schauer, K. Dirnberger, C.D. Eisenbach, *Eur. Phys. J. E* **2001**, *6*, 365

[8] N. Bulychev, W. Van Camp, B. Dervaux, Y. Kirilina, K. Dirnberger, T. Schauer, V. Zubov, F. E. Du Prez, C. D. Eisenbach, *Macromol. Chem. Phys.* **2009**, *210*, 287

[9] B. Dervaux, W. Van Camp, L. Van Renterghem, F. E. Du Prez, *J. Polym. Sci.: Part A: Polym. Chem.* **2008**, *46*, 1649.

[10] C.D. Eisenbach, C. Schaller, T. Schauer, K. Dirnberger, ACS Symposium Series 881, *Particle Sizing and Characterization,* American Chemical Society, **2004**, p. 215

[11] R.W. O'Brien, *J. Fluid. Mech.* **1988**, *190*, 71.

[12] M.L. Carasso, W.N. Rowlands, R.W. O'Brien, *J. Colloid Interface Sci.* **1997**, *193*, 200

[13] M. Loewenberg, R.W. O'Brien, *J. Colloid Interface Sci.* **1992**, *150*.

[14] P.F. Rider, R.W. O'Brien, *J. Fluid. Mech.* **1993**, *257*, 607.

[15] R.W. O'Brien, D.W. Cannon, W.N. Rowlands, *J. Colloid Interface Sci.* **1995**, *173,* 406

[16] N. Bulychev, K. Dirnberger, I.A. Arutunov, P. Kopold, T. Schauer, V. Zubov, C.D. Eisenbach, *Progr. Org. Coat.* **2008**, *62*, 299.

[17] M. Kurata, Y. Tsunashima, in *Polymer Handbook*, J. Brandrup and E.H. Immergut, editors, Wiley-Interscience, New York **1989**, p. VII/34

Table 1: Saturation concentration SC of $PiBA_x$-b-PAA_y block or block-like $PiBA_x$-b-($PiBA_y$-co-PAA_z) copolymers adsorbed to the surface of TiO_2 and CuPc particles, total thicknesses d of the copolymer adsorption layer, and thicknessΔ of the inner as well as thickness δ of the outer adsorption layer of the copolymers.

| System	Saturation concentration SC[a], wt.-%	Thickness d of the total adsorption layer[b], nm	Thickness (Δ) of the inner adsorption layer[c], nm	Thickness (δ) of the outer adsorption layer[c], nm
TiO_2 + $PiBA_{17}$-b-PAA_{72}	1,0	5,5	1,6	4,2
TiO_2 + $PiBA_{20}$-b-$P(iBA_3$-co-$PAA_{91})$	3,0	3,6	2,3	1,2
CuPc + $PiBA_{51}$-b-PAA_{30}	0,5	1	0,6	0,5
CuPc + $PiBA_{45}$-b-$P(iBA_5$-co-$PAA_{39})$	0,7	0,8	0,6	0,3

[a]Obtained from reduced dynamic mobility μ/μ_0 vs. polymer concentration curves Fig. 1 and Fig. 2.
[b]Calculated on the basis of the saturation concentration SC (cf. [7]).
[c]Calculated from the frequency dependent ESA data (Fig. 4 and Fig. 5) according to the polymer gel layer theory (cf. [12, 16]).
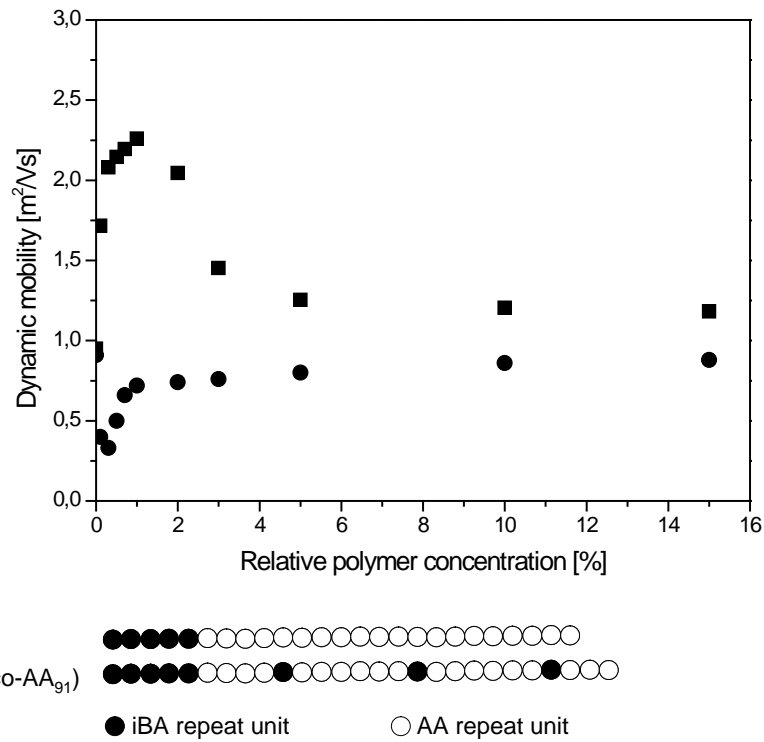
Figure 1. Dependence of the dynamic mobility μ on the relative (to TiO_2) polymer concentration of block copolymer $PiBA_{17}$-*b*-PAA_{72} (●) and block-like copolymer $PiBA_{20}$-*b*-P(iBA_3-*co*-PAA_{91}) (■) for 1 wt.-% TiO_2 aqueous dispersion
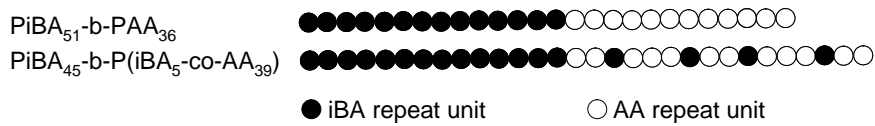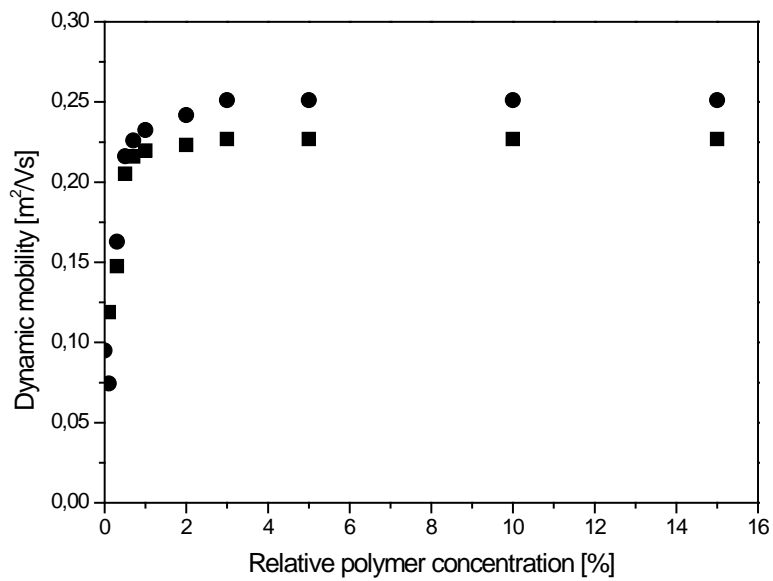
Figure 2. Dependence of the dynamic mobility µ on the relative (to CuPc) polymer concentration of block copolymer PiBA$_{51}$-*b*-PAA$_{36}$ (●) and block-like copolymer PiBA$_{45}$-*b*-P(iBA$_5$-*co*-PAA$_{39}$) (■) for 1 wt.-% CuPC aqueous dispersion
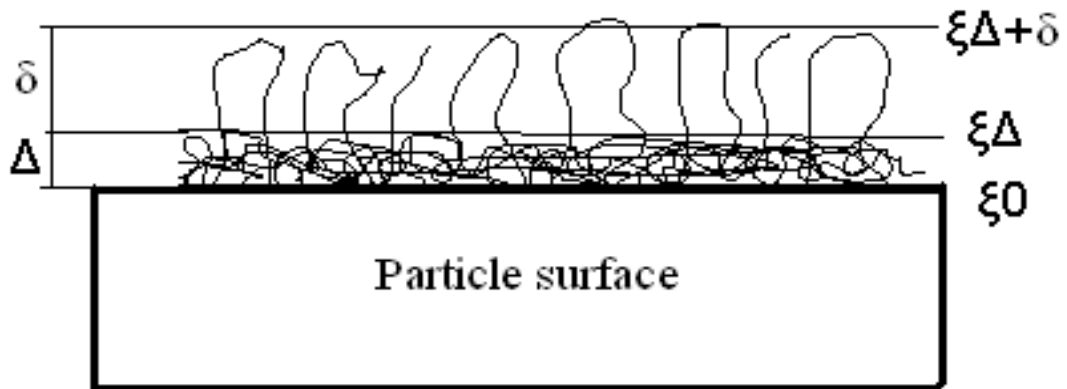
Figure 3. Shear plane displacement caused by the adsorbed layer of a polymer on the particle surface (after [12]).
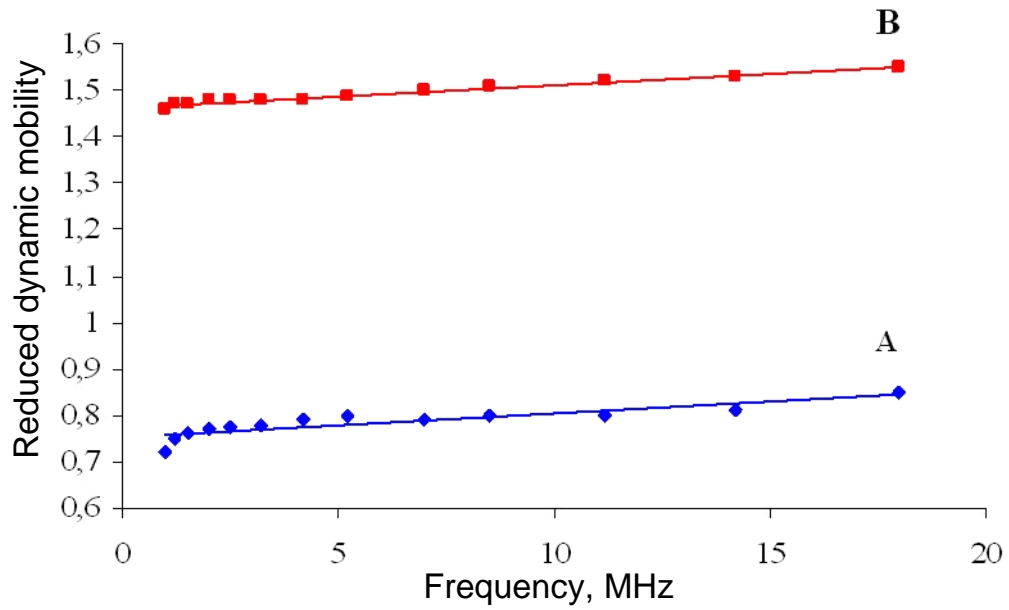**Δ** – thickness of the inner, dense adsorption layer.
δ – thickness of the outer, more permeable layer.
**ξ0** – zeta potential of the pristine surface.
ξΔ – zeta potential at the border between the inner and outer layer.
ξΔ+δ – zeta potential at the polymer layer surface.

Figure 4: Dependence of the reduced dynamic mobility μ/μ_0 on the frequency of the applied alternating electric field for aqueous TiO_2 dispersions stabilized by copolymers at saturation concentration SC. Points: experimental data; solid line: calculated theoretical curve. **A:** block copolymer $PiBA_{17}$-*b*-PAA_{72}; **B:** block-like copolymer $PiBA_{20}$-*b*-P(iBA_3-*co*-PAA_{91}).
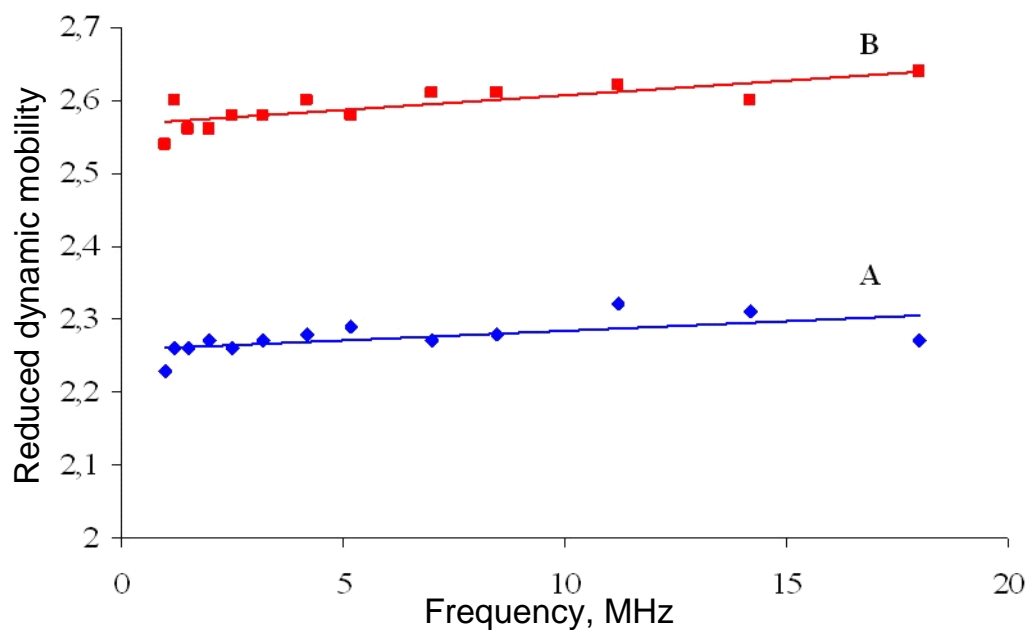
Figure 5: Dependence of the reduced dynamic mobility μ/μ_0 on the frequency of the applied alternating electric field for aqueous CuPc dispersions stabilized by copolymers at saturation concentration SC. Points: experimental data; solid line: calculated theoretical curve. **A:** block copolymer $PiBA_{51}$-b-PAA_{30}; **B:** block-like copolymer $PiBA_{45}$-b-$P(iBA_5$-co-$PAA_{39})$.
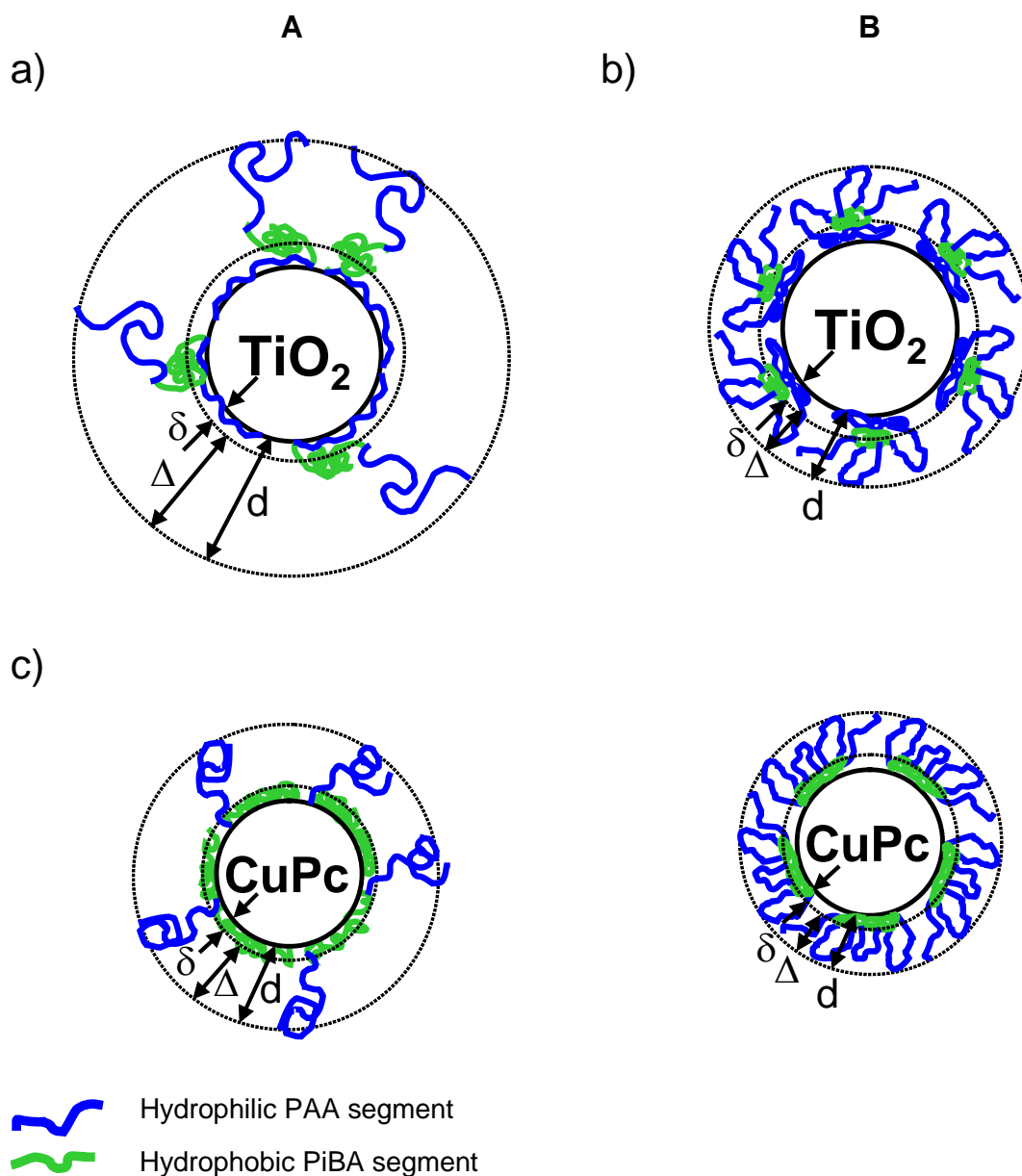
Fig. 6: Schematic representation of the assumed structure of adsorption layers formed by isobornyl acrylate (iBA) / acrylic acid (AA) based block and block-like copolymers:

A: Adsorption model for block copolymers $PiBA_x$-b-PAA_y.

B: Adsorption model for block-like copolymers $PiBA_x$-b-$(PiBA_y$-co-$PAA_z)$.

Δ: thickness of inner adsorption layer; **δ:** thickness of outer adsorption layer; **d:** total thickness of the adsorption layer (see Table 1).