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Stabilization of Carbon Black with Ionic-Hydrophobic Polyelectrolytes

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Summary: The mode of action and efficiency of amphipolar copolymers of different molecular architectures with copolymers consisting of ionic (acrylic acid) and hydrophobic (styrene) constitutional units and sequences (segments, blocks, grafts) as stabilizers of carbon black dispersion are discussed. The pigment-copolymer interactions were investigated by the ESA method as well as lumifuge and rheological measurements. The results indicate that there are distinctive differences in the stabilization behavior depending on the molecular architecture with better results being achieved for block and graft copolymers.

Introduction

The high potential of amphipolar copolymers as stabilizers for particulate systems has been shown in recent years especially as far as emulsions and dispersions are concerned [1, 2]. One promising area of application of copolymers is the stabilization of pigments. Using amphipolar copolyelectrolytes, both electrostatic and steric effects can be combined [3, 4] by the so-called electrosteric stabilization [5, 6]. In order to obtain an optimal stabilization of the particulate system one can take advantage of the variable macromolecular architecture as given in random, block or graft copolymers and different structural elements of ionic, hydrophilic and hydrophobic nature [7]. Despite the wide-spread application of these polymeric stabilizers, the general understanding of the interactions with the pigment surface (thermodynamics and kinetics of the adsorption) as well as their conformation in the adsorption layer is still limited. These interactions are influenced by the nature of the pigment, the matrix as well as the molecular architecture, the charge density and charge distribution within the polymeric stabilizer molecules.

In earlier papers we have reported about the potential of ionic-hydrophobic acrylic acid (AA)-

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styrene (S) based copolymers as polymeric stabilizers and their pigment-polymer interaction in aqueous TiO_2 dispersion. Poly(acrylic acid) (PAA) and poly(styrene-*b*-acrylic acid) block (PS-*b*-PAA) and poly(acrylic acid-*g*-styrene) graft copolymers (PAA-*g*-PS) showed distinct differences in their interactions with the TiO_2 particles. It was found that PAA adsorbs via H-bonding and complexation forming trains at high pH values and coils or loops at lower pH values. Because of the possibility of intermolecular hydrophobic interactions, the amphipolar block and graft copolymers exhibit, in addition to the ionic interactions with the charged particle, so-called "solloid" and bilayer formation on the particle surface; this results in a better stabilization and long time performance as compared to PAA and is indicative of a higher efficiency of the electrosteric in comparison to electrostatic stabilization [8].

In this paper we describe the pigment-polymer interactions and the potential of these amphipolar copolyelectrolytes as stabilizers for aqueous carbon black dispersion. Carbon black is an organic pigment that is increasingly applied in automotive top coats or inks. Carbon black interacts preferably with the hydrophobic segments of a stabilizer [9]. In order to explore the potential of amphipolar copolyelectrolytes as polymeric stabilizers in general and to elucidate how the stabilization of carbon black dispersions [11] is effected by the architecture of the copolymer, well defined acrylic acid (AA)/styrene (S) model copolyelectrolytes with different molecular architecture were synthesized and investigated for the interactions with the particle surface as well as their stabilizing efficiency. The ratio of ionic hydrophilic and hydrophobic constituents was kept constant in order to be able to evaluate the influence of the polymer architecture on the stabilization of pigment dispersions. The structures of the investigated acrylic acid (AA)-styrene (S) macromolecules are shown in Fig. 1.

Experimental

Reagents

Tert-butyl acrylate (TBA), acrylic acid (AA), styrene (S) and *sec*-butyllithium were obtained from Fluka Chemie AG, Switzerland. Other chemicals needed for the synthesis were supplied by Merck, Germany. All chemicals were purified before use as described elsewhere [10]. The used carbon black FW 285 was provided by Degussa, Germany. FW 285 was characterized by an a particle size of d_{50}=11 nm and a specific surface of 350 m^2/g according to BET [11].

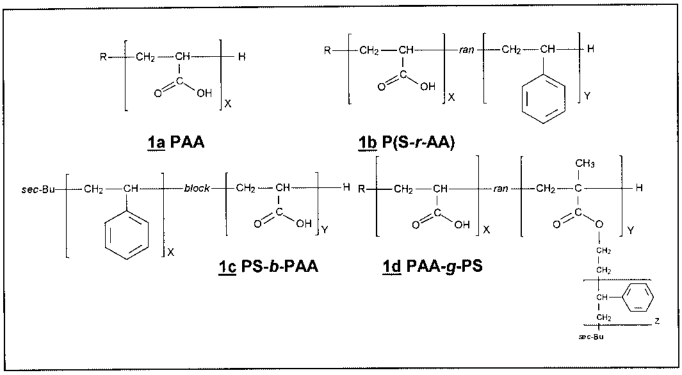

Figure 1. Molecular structure of the investigated poly(acrylic acid) (PAA; 1a), random acrylic acid-styrene copolymer (P(S-*r*-AA); 1b), poly(styrene-*block*-acrylic acid) (PS-*b*-PAA; 1c) and poly(acrylic acid-*graft*-styrene) (PAA-*g*-PS; 1d) (R: benzylmercaptane end group (BnS-))

Co/Polymer Synthesis and Characterization

Poly(acrylic acid) homopolymers (PAA, Fig. 1, 1a). and random acrylic acid-styrene copolymers (P(S-*r*-AA), Fig. 1, 1b) were synthesized by free radical (co)polymerization of acrylic acid (AA), and styrene (S) with AA, respectively, with AIBN as initiator; benzylmercaptane (BnSH) was used as chain transfer agent [12] to control the molecular weight of the homo and copolymers [10]. The access to graft copolyelectrolytes with an ionic PAA backbone and hydrophobic polystyrene (PS) grafts (PAA-*g*-PS, Fig. 1, 1d) is given by the macromonomer technique [13]: The free radical copolymerization of methacryloyl PS macromonomers and *tert*-butyl acrylate (TBA) with AIBN as initiator and BnSH followed by hydrolyzation of the resulting poly(TBA-*g*-PS) intermediate copolymer with hydrochloride acid in dioxane [14] gives the amphipolar AA-S graft copolymers (PAA-*g*-PS). AA-S 2-block copolymers (PS-*b*-PAA, Fig. 1, 1c) were synthesized by sequential anionic polymerization of S and TBA with *sec*-BuLi in THF as described in literature [15] followed by hydrolyzation with hydrochloride acid in dioxane. All block and graft copolymers and the macromonomers as well as the intermediate reaction products were characterized by gel permeation chromatography (GPC) and ^{1}H-NMR. More detailed reports of the synthesis and characterization of these block [16] and graft [17] copolymers are given elsewhere.

Methods

ESA (electrokinetic sonic amplitude) measurements were carried out with an AcoustoSizer™ AZR2, Colloidal Dynamics, Sydney, Australia on 2 % w/w FW 285 carbon black dispersion (pH=8) to obtain the dynamic mobility [18]. The rheology and stability measurements were performed on a 10 % w/w (pH=8) dispersion with a UDS 200 Universal Dynamic Spectrometer, Paar Physica, USA and a Lumifuge 114, L.U.M. GmbH, Germany (3000 rpm). All dispersions were prepared at 23°C according to DIN EN-ISO 8780-2 [19] in water for 2 hours with Zirconox Micro Milling Beads (2.8<Ø<3.3 mm), Jyotti Ceramics, India. More detailed information about ESA and the preparation of dispersions can be found in the literature [10].

Results and Discussion

Copolyelectrolyte Synthesis and Structure

The synthesis route leads to well defined ionic hydrophobic acrylic acid (AA)-styrene (S) copolyelectrolytes with different molecular architectures and nearly the same charge density per macromolecule of about 60 to 70 mole-% AA in the copolyelectrolyte. The characteristic data of the random, block and graft copolymers employed in the investigation of the stabilization behavior are summarized in Table 1.

Table 1. Copolymer constitution as determined by ^{1}H-NMR and SEC experiments: comonomer composition and molecular weight of the PS block and graft ($M_{n,PS}$) and the copolymer

Copolymer	Type [a]	f_{AA} [b]	$M_{n,PS}$ (PD) [c]	M_n (PD) [d]	Comp. (GD) [e]
PAA	linear	100	-	2400 (1.62)	2000
P(S-*r*-AA)	linear	63	-	1300 (1.94)	-
PS-*b*-PAA	2-block	68	4880 (1.24)	8200 (1.56)	4800-*b*-6000
PAA-*g*-PS-*Y*	*Y*-graft	70	2190 (1.05)	6500 (1.56)	2700-*g*-1600 (0.8)
PAA-*g*-PS-*H*	*H*-graft	65	2190 (1.05)	8300 (1.61)	4300-*g*-3200 (1.6)

a) Molecular architecture

b) Acrylic acid comonomer mole-fraction f_{AA} in copolymer as obtained from ^{1}H-NMR analysis

c) Number average molecular weight $M_{n,PS}$ (polydispersity PD) of PS block or graft as determined by SEC analysis based on PS

d) Number average molecular weight Mn (polydispersity PD) of copolymer as determined by SEC analysis based on PS calibration

e) Molecular composition (number average Mn-*b*/*g*-Mn) and PS graft density (GD) as calculated from $M_{n,PS}$ and f_{AA}; GD represents the average number of grafts per individual macromolecule

As far as the polymer adsorption to carbon black is concerned which in the case of the AA-S copolymers occurs preferably by hydrophobic-hydrophobic interactions between the hydrophobic styrene units and the hydrophobic carbon black surface, PAA can be regarded as a linear ionic-hydrophilic homopolymer with only one hydrophobic benzylmercaptane (BnS-) anchor group at the end [20]. P(S-*r*-AA) exhibits a random distribution of the hydrophobic styrene anchor groups within the stabilizer macromolecule. The block copolymers consist of one polystyrene (PS) anchor block and one ionic poly(acrylic acid) (PAA) stabilizing block (2-block). The structure of the given graft copolymer depends on the graft density (GD): E. g. PAA-*g*-PS-*Y* with GD=0.8 can be considered to consist of 3-star macromolecules (*Y*-shape) since in average 4 out of 5 macromolecules contain one hydrophobic anchor graft and two electrosterically stabilizing blocks; in contrast to this, PAA-*g*-PS-*H* with GD=1.6 can be described as a graft copolymer mixture of *Y*-shape (corresponding GD=1) and gemini structure (*H*-shape corresponding to GD=2; 2 anchor and 2 stabilizing blocks) macromolecules .

Carbon Black-Copolyelectrolyte Interactions

The electrokinetic sonic amplitude (ESA) technique [21] can be used for determining the dynamic mobility μ (electrophoretic mobility in an alternating electric field) and the zeta potential as well as the size of uncoated particles [22]. Furthermore ESA is a suitable method for the investigation of pigment-polymer interaction of non-ionic polymers [23] and (co)polyelectrolytes [24, 25, 26].

As it has been demonstrated in earlier studies, the ESA method is a fast and useful tool for the in-situ investigation of adsorption/desorption phenomena [27]. The variation of the dynamic mobility μ with polymer concentration at low frequencies is only a consequence of a change of the surface charge of the pigment particles caused by the deposition of polymer on the particle surface; thus such curves can be regarded as quasi adsorption isotherms [10]. For normalization reasons and better elucidation of the pigment-polymer interactions it is advantageous to introduce the reduced dynamic mobility μ/μ_0 which relates μ of the polymer containing system to μ_0 of the pure pigment dispersion [18].

The change of the reduced dynamic mobility μ/μ_0 with time is shown in Fig. 2 for the different (co)polyelectrolytes. The particle surface charge increases due to polymer adsorption until a plateau is reached after about 15 min. The obtained reduced mobility curves are indicative of a fast physisorption of the copolyelectrolytes on the pigment surface driven by van der Waals forces or electrostatic interactions [28].

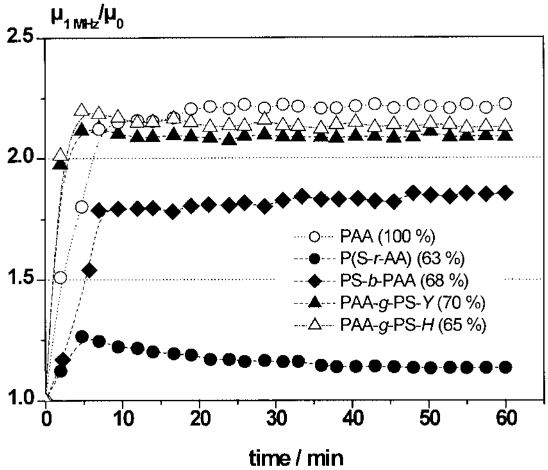

Figure 2. Reduced dynamic mobility μ/μ_0 from ESA measurements for aqueous carbon black dispersions (2 % w/w, pH=8) as a function of time after addition of (co)polyelectrolytes (10 % w/w relative to carbon black mass) with different molecular architecture; the figures in brackets give the mole-% AA in the macromolecule

For an inorganic pigment like TiO_2 it has been shown that the surface charge of the fully coated particles depends primarily on the carboxylic group content of the polymeric stabilizer [24]. This has been explained by successive adsorption steps of the copolyelectrolyte on the pigment beginning with the anchoring of the copolymer via the ionic carboxylic groups followed by a bilayer formation. However, in the case of carbon black, the distinct difference in the μ/μ_0 plateau value between the random copolymer P(S-*r*-AA), the 2-block copolymer PS-*b*-PAA and the graft copolymers PAA-*g*-PS-*Y/H*, all having nearly the same AA comonomer content, reveals effects of the polymer architecture on the electrostatic behavior of the coated carbon black (Fig. 2). The main reason for the effects of the copolymer structure on the dynamic mobility μ of the coated carbon black as compared to the coated TiO_2 (cf. [8, 25]) may be the different mechanism of anchoring of the amphipolar copolymer on the pigment surface: Whereas for the TiO_2-pigment the ionic carboxylic comonomer sequences interact with the pigment surface, in the case of carbon black it is the hydrophobic polystyrene sequence that acts as the anchor. The interaction of the organic pigment with the hydrophobic styrene units of these stabilizers results in a mono-layer adsorption and not a "solloid" and bilayer formation like on TiO_2 [8].

Assuming the PS units as anchors, the difference in the plateau value of the reduced dynamic mobility μ/μ_0 observed for the various copolyelectrolytes could be explained by the chain conformation of the adsorbed macromolecule: A more flat conformation is suggested for the P(S-*r*-AA) with trains and loops (see Fig. 3, conformation A) as already found for hydrophobically modified polyelectrolytes on TiO_2 [26]; this is contrasted by a more stretched brush conformation of the fully dissociated PAA sequences of the homopolymer and the block and graft copolymers resulting in a highly charged particle surface (see Fig. 3, conformation B). A comparative schematic illustration of the proposed adsorption behavior of the polymeric stabilizers is given in Fig. 3.

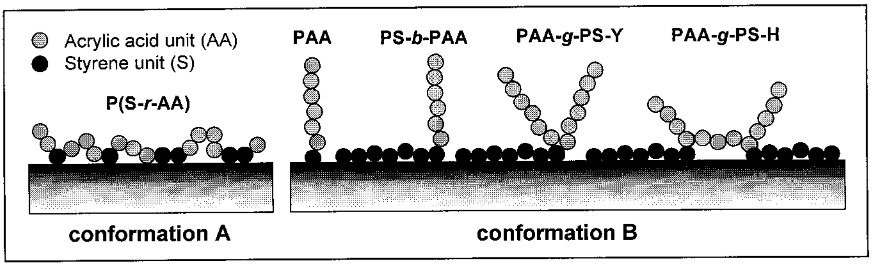

Figure 3. Adsorption behavior and conformation of ionic-hydrophobic stabilizers with different molecular architectures on the carbon black surface

Stabilization Effects of the Amphipolar Copolyelectrolytes on Carbon Black Dispersions

The viscosity of aqueous carbon black dispersions containing the polyelectrolytes was investigated to get further information about the dispersion stabilizing properties. Fig. 4 shows the viscosity behavior of carbon black in the presence of the different stabilizers, indicating the important role of the stabilizer architecture on the rheological properties of the dispersion. The viscosity of the linear homopolymer (PAA) and the random copolymer (P(S-*r*-AA)) is significantly higher as compared to the block and graft copolymers especially at lower shear rates. The lower viscosity of the carbon black dispersion with the block and graft copolyelectrolytes is indicative for well dispersed particles in the media what is a necessary condition for most applications.

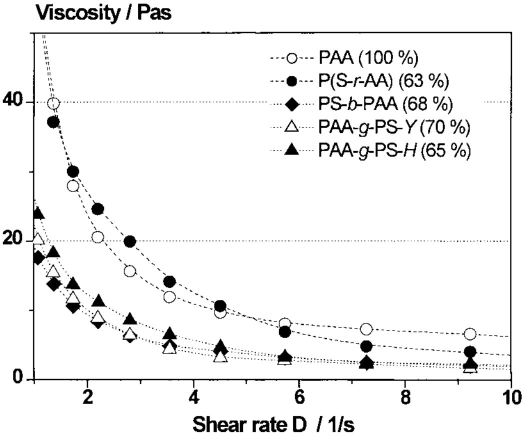

Figure 4. Viscosity of aqueous carbon black dispersions (10 % w/w, pH=8) in the presence of ionic-hydrophobic stabilizers with different molecular architectures (10 wt-% relative to carbon black mass); the figures in brackets give the mole-% AA in the macromolecule

The stabilization effect of the carbon black dispersions by the pigment surface modification with the amphipolar copolyelectrolytes and the correlation to the viscosity was investigated by the sediment volume method. From lumifuge measurements a relative sediment volume is obtained, giving information about the dispersity of the dispersion and its stabilization [29]. The results of the stabilization measurements and the viscosity at a shear rate of 1 (~3000 rpm in the lumifuge [30]) of the different dispersions are shown in Fig. 5.

From the comparison of the viscosity and the sedimentation data in Fig. 5 it is obvious that there is a good agreement between the viscosity and the sediment volume of the dispersion. For all polymeric stabilizers tested the block and graft structures provide a better performance, and the data infer that the graft structure is somewhat favorable over the block structure.

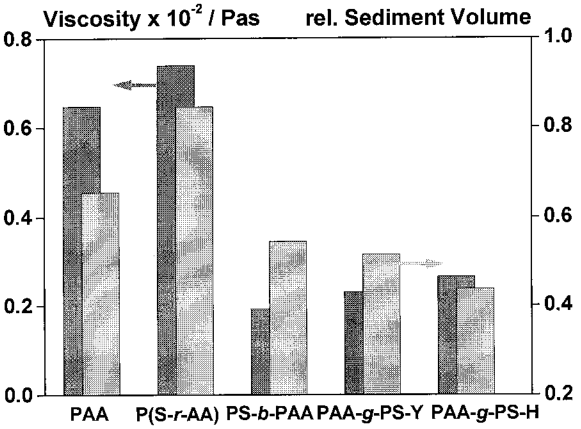

Figure 5. Viscosity (shear rate 1) and relative sediment volume of aqueous carbon black dispersions (10 % w/w, pH=8) in the presence of ionic-hydrophobic stabilizers with different molecular architectures (10 wt-% relative to carbon black mass)

This is another indication of the high efficiency of the electrosteric stabilization by a charged PAA brush and the better performance of styrene anchor blocks as compared to the mono-functionalized PAA or the random distribution within the stabilizer. Therefore it is possible to perform a tailored synthesis of copolyelectrolytes of the graft type with optimal stabilizing properties for organic as well as inorganic pigments dispersions.

Conclusion

The comparative investigation of poly(acrylic acid) and various acrylic acid-styrene based copolyelectrolytes of different polymer architectures showed distinct differences in their interactions with the carbon black dispersion. The pigment-polymer interactions as established by ESA measurements and the stabilizing properties of these stabilizers as quantified by viscosity and sedimentation measurements are strongly influenced by the charge distribution along the macromolecule and the polymer architecture but not the charge density; this is in contrast to the results obtained with TiO_2 pigments where the overall charge density (acrylic comonomer content) played an important role (cf. [8, 25]). Another difference between carbon black and TiO_2 is that "solloid" and bilayer formation occurs on TiO_2 whereas a monolayer is formed on carbon black with styrene-units as anchors. The rheology and sedimentation measurements revealed a better long time performance for block and graft copolymers as compared to poly(acrylic acid) and the random copolymer with somewhat better results for the graft structure.

In summary, these results are a further indication of the high efficiency of the electrosteric stabilization of pigment dispersions by block and graft copolyelectrolytes. By taking advantages of tailored copolymer structures and pigment-specific interactions with particular portions of the copolyelectrolytes, efficient stabilization for organic as well as inorganic pigment dispersions are accessible.

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