

Nikolay Bulychev

TAILOR-MADE BLOCK COPOLYMERS OF POLY (ACRYLIC ACID) AS PIGMENTS SURFACE MODIFICATION AGENTS

N.S. Kurnakov Institute of General and Inorganic Chemistry of Russian Academy of Sciences,
31, Leninsky avenue, 119991 Moscow, Russia; nbulychev@mail.ru

Received: April 17, 2009

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Abstract. The influence of the molecular architecture and the composition of block copolymers on their solid-liquid interface behaviour were investigated in detail. For this purpose, the surface modification of hydrophilic titanium dioxide and hydrophobic copper phthalocyanine pigments in aqueous dispersion by a series of amphiphilic block copolymers has been studied. As pigment stabilizers, amphiphilic copolymers consisting of poly(isobornyl acrylate) (PiBA) and poly(acrylic acid) (PAA) with well-defined molecular structure, controlled molecular weight and narrow polydispersity index have been synthesized by atom transfer radical polymerization (ATRP) using the macro-initiator strategy (to yield block copolymers). The dispersion stability, with and without the use of ultrasonic power, was studied by the electrokinetic sonic amplitude (ESA) method. Data obtained showed that the ultrasonic treatment causes a significant increase of the amount of a polymer adsorbed on the particle surface, which is primarily attributed to the ultrasonically induced activation of the pigment surface.

Keywords: pigment dispersion, block copolymer, amphiphilic copolymers, polymer adsorption, ultrasonic treatment, electrokinetic sonic amplitude method, sedimentation, pigment surface modification.

1. Introduction

In the recent years, aqueous colloidal dispersions of pigments have attracted an increasing interest from both scientific and practical points of view. Amphiphilic polymers have shown to be effective stabilizers of various colloidal dispersions, such as pigments in aqueous media [1-9].

The colloidal stabilization of particulate aqueous dispersions by polymer surfactants is a result of the adsorption of amphiphilic macromolecules on the particle surface: often one block of the amphipolar block copolymer acts as an anchor. Depending on the constitutional characteristics of the block copolymer and the particulate

system, mono- or multi-layers of certain structure and thickness which provide steric and/or electrostatic stabilization, are being formed.

The polymer adsorption on the particle surface itself is a result of specific interactions between structural motifs of the macromolecule and active sites on the particle surface. The chemical structure of the polymeric stabilizers has to be adjusted to the nature (*e.g.* hydrophilicity, charge, *etc.*) of each type of particles. Thus, comparative studies of the adsorption behaviour of polymers and the colloidal stabilization may be used as a sensitive approach to elucidate effects of the variation of the polymer structure on their behaviour at the solid-liquid interface.

It has been shown [7-9] that mechanical, in particular ultrasonic, treatment of aqueous dispersions of pigments in the presence of polymeric stabilizers leads to a significant enhancement of the stability of these dispersions. IR-analysis was used to prove that the thickness and stability of the polymer adsorption layers are increased and improved by the ultrasonification [7]. Parameters (thickness and structure) of polymer adsorption layers affected by the ultrasonic treatment have been investigated [9]. However, the effect of the ultrasonic treatment on the pigment-polymer interaction and structure formation of adsorption layers, especially for tailor-made amphiphilic copolymers, is not fully understood and needs further investigation for elucidating of the observed phenomena.

In the framework of this research, the aim of this paper is a detailed comparative study of the solid-liquid interface behaviour of well-defined amphiphilic polymers of various molecular architecture and different composition. For this reason, amphiphilic block copolymer structures are compared in the present study as stabilizers for aqueous colloidal dispersions of hydrophilic titanium dioxide (TiO₂) and hydrophobic copper phthalocyanine (CuPc) pigments.

Block copolymers have been synthesized via the macroinitiator strategy. First, a given monomer is polymerized to a certain conversion followed by a

purification step [10-16]. Then this polymer, usually carrying a functional end group, is used as a macroinitiator to initiate the polymerization of the second monomer. All synthetic procedure has been described elsewhere in detail [11-13].

As to studying polymer-particle interactions, electrokinetic sonic amplitude (ESA) measurements were shown to be a powerful method [9, 17-22] that provides information about the process of polymer adsorption onto solid particles. The desired information is derived from the dynamic mobility (μ_D) of the dispersed particle. μ_D represents the electrophoretic mobility of a particle in an alternating electric field. When such a field is applied to a colloidal system, it exerts an electric force on the particles, which causes them to move backwards and forwards. This motion generates the ESA signal, which in turn provides information about the particle motion, and thus on characteristics of the particle itself [19-22]. Practically, the applied field is measured directly, and the acoustic impedance of the suspension can be determined by measuring the reflection coefficient of a sound wave at the electrode-colloid boundary.

The advantage of reporting electroacoustic data in terms of dynamic mobility μ_D rather than reporting the raw ESA measurement data is that the dynamic mobility μ_D is a property of the suspension. Unlike the ESA signal, μ_D does not depend on the device geometry, neither on the acoustic properties of the device nor on the strength of the applied electric field.

Earlier studies of the change of μ_D of aqueous TiO_2 dispersions upon addition of amphipolar polyelectrolytes have shown that ESA is a powerful method to reveal the nature of specific polymer-pigment interactions and how this is related to the molecular architecture of the employed polyelectrolytes [21-23]. In these investigations, the saturation concentration (SC), which is defined as the polymer concentration at which the curve obtained by plotting μ_D vs. the polymer concentration reaches a plateau, was used for characterizing and quantifying the pigment-polymer interactions.

2. Experimental

2.1. Materials

Pigments: titanium dioxide rutil pigments Kronos 2310 with particle size 0.3μ and β -copper phthalocyanine (β -CuPc) with primary particle size $0.1 \mu\text{m}$ were chosen.

Materials for synthesis of the PiBA-PAA block copolymers: Isobornyl acrylate (iBA, Aldrich, tech.) was purified by vacuum distillation (394 K/18 mmHg). 1-Ethoxyethyl acrylate (EEA) was synthesized by the acid catalyzed addition reaction of acrylic acid to ethyl vinyl ether as described previously [11-13], and purified by vacuum distillation (303 K/7 mbar). Cu(I)Br (Aldrich,

98 %) was purified by stirring with acetic acid, then by filtering and washing with methanol, and finally by drying in a vacuum oven at 343 K. N,N,N',N'',N'''-pentamethyldiethylenetriamine (PMDETA, Acros, 99+ %) was distilled (358–359 K/12 mmHg). Methyl-2-bromopropionate (MBP, Acros, 99 %) was used as received. Dimethyl 2,6-dibromoheptanedioate (DHD, Aldrich, 97 %). (Trimethylsilyl)diazomethane (2.0M solution in diethyl ether, Aldrich) was used as received. Solvents were purchased from Aldrich (HPLC grade) and used without purification. All other chemicals were used as received.

2.2. Techniques

2.2.1. Synthesis of PiBA-b-PAA block copolymers by ATRP

The synthesis of the PiBA-*b*-PAA block copolymers consists of 3 steps: first, a PiBA macroinitiator is prepared, which is then used in the second step as a macroinitiator for the synthesis of the PiBA-*b*-PEEA block copolymer. In the third step, the PEEA segment is deprotected to PAA to yield the desired PiBA-*b*-PAA block copolymer. A typical synthetic procedure is illustrated for the preparation of sample BP14-7F4:

1) preparation of PiBA macroinitiator (HP14I4): polymerization of iBA by ATRP

A typical polymerization procedure is as follows (HP14I4). A mixture of 0.11361 mol (24.0 ml) of the monomer iBA and $2.8402 \cdot 10^{-4} \text{ mol}$ (0.059 ml) of PMDETA as the ligand was bubbled with N_2 for 1h to remove oxygen. Ethyl acetate as the solvent was also bubbled with N_2 for 1h to remove oxygen and 8 ml (25 vol %) ethyl acetate was added to the reaction flask. Cu(I)Br ($2.8402 \cdot 10^{-4} \text{ mol}$, 0.04074 g) was added and the reaction flask was placed in an oil bath at 363 K. When the reaction mixture reached the desired reaction temperature, the polymerization was started by adding $5.6803 \cdot 10^{-4} \text{ mol}$ (0.063 ml) of methyl-2-bromopropionate as the initiator. Samples were withdrawn periodically to monitor the monomer conversion (by $^1\text{H-NMR}$) and the average molecular weight (by SEC). The reaction was ended by cooling the reaction mixture in liquid nitrogen. The resulting polymer was dissolved in THF and copper was removed by passing the diluted reaction mixture over a column of neutral Al_2O_3 to remove the copper catalyst. After evaporating the excess solvent, the polymer was precipitated in methanol (10-fold excess).

2) preparation of PiBA-*b*-PEEA block copolymer (BP14-7F4): synthesis of PiBA-*b*-PEEA by ATRP

A typical polymerization procedure is as follows (BP14-7F4). The monomer EEA was passed through a small column of basic alumina to remove traces of residual acid. The PiBA macroinitiator (HP14I4, 4.075 g; $38.15 \cdot 10^{-5} \text{ mol}$) was dissolved in the monomer EEA (11 ml; $76.30 \cdot 10^{-3} \text{ mol}$), and oxygen was removed from the mixture by bubbling

with N_2 for 1h. $Cu(I)Br$ (0.165 g ; $1.150 \cdot 10^{-3}\text{ mol}$, 3 eq. relative to initiator) was added under nitrogen atmosphere, and the reaction flask was immersed in an oil bath thermostated at 323 K . Polymerization was started by adding PMDETA (0.360 ml ; $1.725 \cdot 10^{-3}\text{ mol}$) as the ligand. Samples were withdrawn periodically to monitor the monomer conversion (by 1H -NMR) and the average molecular weight (by SEC). The reaction was ended by cooling the reaction mixture in liquid nitrogen. The block copolymer was dissolved in THF, and the copper was removed passing the diluted reaction mixture over a column of neutral Al_2O_3 . Solvent was evaporated, and the polymer was precipitated in cold methanol (10-fold excess).

3) deprotection of PiBA-*b*-PEEA to PiBA-*b*-PAA by heating (BP14-7F4WD)

For thermolysis of the PiBA-*b*-PEEA block copolymers, a sample was spread out on a glass surface and heated in an oven at 353 K for 24 h. TGA analysis confirmed total conversion of PiBA-*b*-PEEA to PiBA-*b*-PAA.

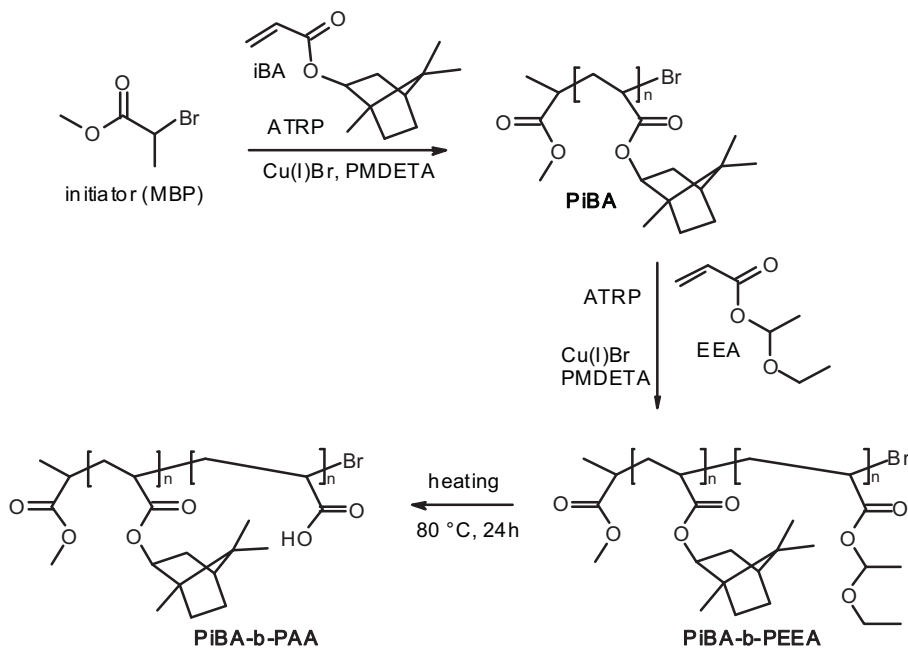


Fig. 1. Diagrammatic representation for the synthesis of PiBA-*b*-PAA block copolymers

Table 1

Summary of the data and results of the synthesis of various PiBA macroinitiators

Entry	Initiator	$[M]_0/[In]_0/[Cu]_0/[ligand]$	Temperature, K	Time, min	Conversion, %	$M_{n,exp}^*$, $g \cdot mol^{-1}$	M_w/M_n	Composition
HP14F4	MBP	100/1/0.5/0.5	363	45	19	3600	1.33	PiBA ₁₇
HP14I3	MBP	200/1/0.5/0.5	363	215	26	10600	1.24	PiBA ₅₁
HP14I4	MBP	200/1/0.5/0.5	363	120	26	10600	1.30	PiBA ₅₁
HP14L1	BHD	200/1	363	60	36	14900	1.17	PiBA ₇₂

* a conversion factor of 1.4 is applied.

Samples BP14-7F3WD and BP14-7I1WD were prepared in the same way. For sample BP7-14-7A1WD (PAA-*b*-PiBA-*b*-PAA triblock copolymer), a PiBA macroinitiator was prepared using a difunctional initiator dimethyl 2,6-dibromoheptanedioate (BHD), further steps being identical.

2.2.2. Characterization

1H NMR spectra were recorded in $CDCl_3$ at room temperature, with a Bruker AM500 or a Bruker Avance 300 spectrometer. SEC analysis was performed on a Waters instrument, using a refractive index detector (2410 Waters), equipped with Waters Styragel 10^3 - 10^4 - 10^5 Å serial columns ($5\text{ }\mu\text{m}$ particle size) at 308 K . Polystyrene standards were used for calibration and $CHCl_3$ as an eluent at a flow rate of 1.5 ml/min . Thermogravimetric analysis (TGA) was performed with a Mettler Toledo TGA/SDTA851e instrument under nitrogen or air atmosphere at a heating rate of $10^\circ/min$ from 298 to 1073 K .

2.2.3. Pigment stabilization techniques

For the preparation of aqueous pigment dispersions, the pigment was added to water alone or together with the polymer dissolved in THF and dispersing of the pigment was first achieved by means of a laboratory stirrer (700 rpm for 10 min). When ultrasonification was applied, the system was subsequently treated with ultrasound for 2 min with an ultrasonic generator Branson Sonifier B-12 with actual power of 1.5 W/cm².

Colloidal stabilization of the aqueous dispersions was monitored by sedimentation measurements of 1% dispersions of CuPc and TiO₂. The pigment-polymer interaction and the polymer adsorption layer formation were investigated by electrokinetic sonic amplitude (ESA) measurements as described elsewhere [9, 21-23]. The particle size was measured by ESA [21]. Standard optical equipment was used for refractive index measurements.

3. Results and Discussion

3.1. Synthesis of Various PiBA-*b*-PAA Block Copolymers for Pigment Stabilization

PiBA-*b*-PAA block copolymers with various compositions were chosen as polymeric stabilizers for TiO₂ and CuPc aqueous dispersions. The PiBA segment acts as the hydrophobic part, while PAA is the hydrophilic part.

The synthesis of the PiBA-*b*-PAA block copolymers by atom transfer radical polymerization (ATRP) consists of 3 steps (see Fig. 1): first, a PiBA macroinitiator is prepared, which is then used in the second step as a macroinitiator for the synthesis of the PiBA-*b*-PEEA block copolymer. In the third step, the PEEA segment is deprotected to PAA to yield the desired amphiphilic PiBA-*b*-PAA block copolymer. For a detailed discussion about the controlled radical polymerization of PiBA polymers by ATRP, we refer to our previously published papers [11-13].

A summary of the data and results of the synthesis of the various PiBA polymers that are used as macroinitiators for the block copolymerizations is given in Table 1. All polymerizations of iBA were carried out in 25 vol % of ethyl acetate as solvent. All polymerizations were performed with a proper control over the molecular weight, while relatively narrow polydispersities (M_w/M_n) were obtained. Conversions were kept low in order to retain maximal bromine chain end functionality, which is necessary for the synthesis of well-defined block copolymers.

The above synthesized PiBA polymers were used as a macroinitiator to polymerize EEA as the second block. In this way, PiBA-*b*-PEEA block copolymers are obtained with different molecular composition. A summary of the data and results of the synthesis of various PiBA-*b*-PEEA block copolymers is given in Table 2.

A kinetic analysis of the block copolymerization shows the controlled behaviour of the polymerization reaction. The increase of the molecular weight as a function of conversion shows a linear behaviour, while polydispersity decreases during the polymerization reaction (see Fig. 2a). However, the first order kinetic plot shows a deviation from linearity after some time. This is due to partial deprotection of the EEA to acrylic acid that forms a complex with the Cu catalyst, reducing the actual catalyst concentration, and thus lowering the concentration of radicals in the system (see Fig. 2b). In SEC analysis, almost no unreacted macroinitiator could be observed (see Fig. 3). This means that a pure block copolymer is obtained, and proves that the polymerization of iBA (synthesis of the PiBA macroinitiator) under the used polymerization conditions occurs with only minimal loss of bromine end group.

After synthesis, the PiBA-*b*-PEEA block copolymers are converted to the corresponding PiBA-*b*-PAA block copolymers by a heating step. All polymers were spread out on a glass surface and heated in an oven at 353 K for 24h. ¹H NMR and TGA experiments confirmed total

Table 2

Summary of the data and results of the synthesis of various PiBA-*b*-PAA block copolymers

Entry	Initiator	[M] ₀ /[In] ₀ / [Cu] ₀ /[ligand]	Temperature, K	Time, min	Conversion, %	M _{n,exp.} , g·mol ⁻¹	M _w /M _n	Composition*	Composition (after deprotection)
BP14-7F3	HP14I3	200/1/3/4.5	333	160	25	16100	1.35	PiBA ₅₁ -PEEA ₅₆	PiBA ₅₁ -PAA ₅₆
BP14-7F4	HP14I4	200/1/3/4.5	333	80	14	11300	1.32	PiBA ₅₁ -PEEA ₃₀	PiBA ₅₁ -PAA ₃₀
BP14-7I1	HP14F4	150/1/3/4.5	343	245	45	14100	1.22	PiBA ₁₇ -PEEA ₇₂	PiBA ₁₇ -PAA ₇₂
BP7-14-7A1	HP14L1	300/1/3/4.5	343	395	19	15100	1.18	PEEA ₂₅ -PiBA ₇₂ - PEEA ₂₅	PAA ₂₅ -PiBA ₇₂ - PAA ₂₅

* composition was determined from ¹H NMR analysis.

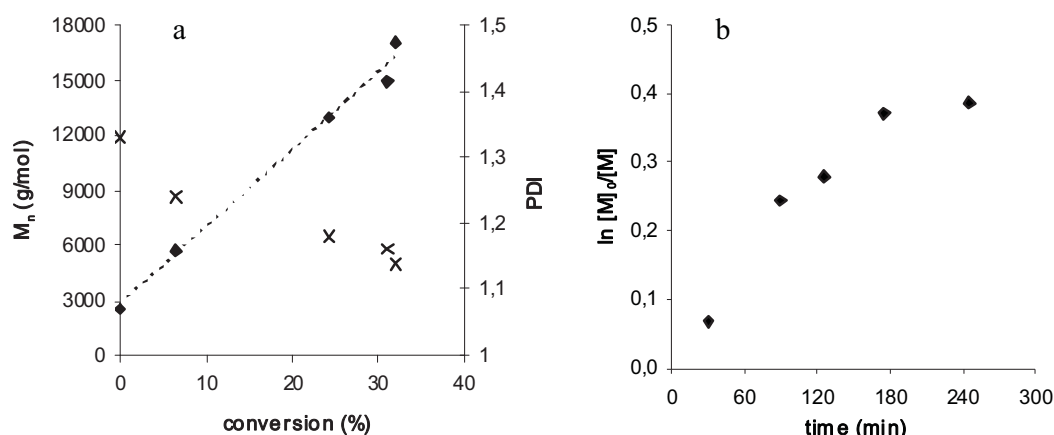


Fig. 2. Evolution of the average molar mass (M_n) and polydispersity (PDI) as a function of conversion of the polymerization of EEA starting from a PiBA macroinitiator [BP14-7I1, Table 2] (dotted line = trend line) (a) and first order kinetic plot (b)

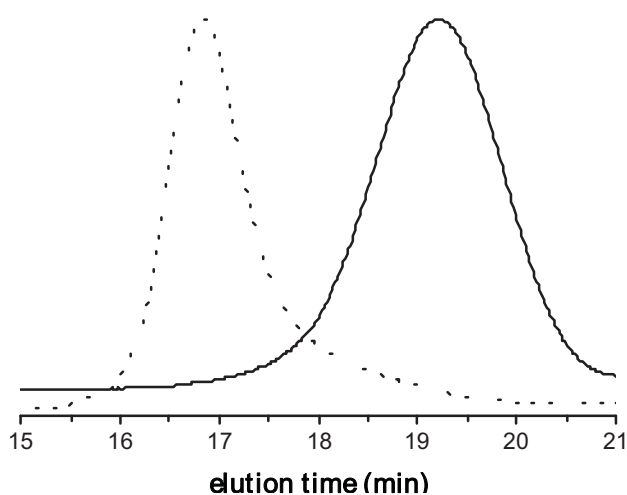


Fig. 3. SEC analysis of PiBA₁₇ macroinitiator (solid line) and the corresponding PiBA₁₇-*b*-PEEA₇₂ block copolymer (dotted line) [BP14-7I1, Table 2]

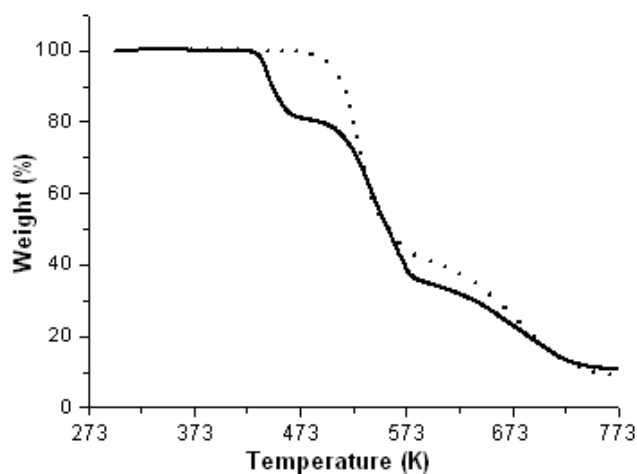


Fig. 4. TGA analysis of PiBA₅₁-*b*-PEEA₅₆ (before deprotection, solid line) and PiBA₅₁-*b*-PAA₅₆ (after deprotection by heating at 353 K for 24 h, dotted line) [BP14-7F3, Table 2]

conversion of PiBA-*b*-PEEA to PiBA-*b*-PAA. A TGA analysis of sample PiBA₅₁-*b*-PEEA₅₆ before and after the heating step is shown in Fig. 4. For the unprotected PiBA₅₁-*b*-PEEA₅₆ sample, TGA analysis reveals a weight decrease at 423 K, which corresponds to the deprotection step to yield PiBA₅₁-*b*-PAA₅₆ with loss of vinyl ether (volatile compound, bp = 306 K).

3.2. Pigment Stabilization Experiments

Data reported in literature [7, 9, 24], show that mechanical, in particular, ultrasonic treatment of aqueous dispersions of pigments in the presence of polymeric stabilizers leads to a significant enhancement of the stability of these dispersions as compared to dispersions prepared

without ultrasonic treatment. It was proven by IR-analysis that the thickness and stability of the polymer adsorption layers were increased and improved by the ultrasonification [7]. Parameters of polymer adsorption layers affected by the ultrasonic treatment were investigated [9]. However, the effect of the ultrasonic treatment on the pigment-polymer interaction and polymer adsorption, especially for novel tailor made amphipolar copolymers is still obscure and needs further investigation for better elucidation of the phenomena observed.

First, sedimentation measurements for TiO₂ and 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 3 and 4.

Table 3

Sedimentation stability of TiO₂ aqueous dispersions stabilized by PiBA-*b*-PAA block copolymers

Polymer	Suspension stability (half-time of the sedimentation, days)	
	Without mechanical treatment	After ultrasonic treatment
PiBA ₇₂	0.2	4
PAA ₂₈	2	10
PiBA ₅₁ - <i>b</i> -PAA ₅₆	2	14
PiBA ₅₁ - <i>b</i> -PAA ₃₀	0.1	1
PiBA ₁₇ - <i>b</i> -PAA ₇₂	3	30
PAA ₂₅ - <i>b</i> -PiBA ₇₂ - <i>b</i> -PAA ₂₅	0.3	7

Table 4

Sedimentation stability of CuPc aqueous dispersions stabilized by PiBA-*b*-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 ₅₁ - <i>b</i> -PAA ₅₆	4	20
PiBA ₅₁ - <i>b</i> -PAA ₃₀	5	45
PiBA ₁₇ - <i>b</i> -PAA ₇₂	0.2	5
PAA ₂₅ - <i>b</i> -PiBA ₇₂ - <i>b</i> -PAA ₂₅	3	14

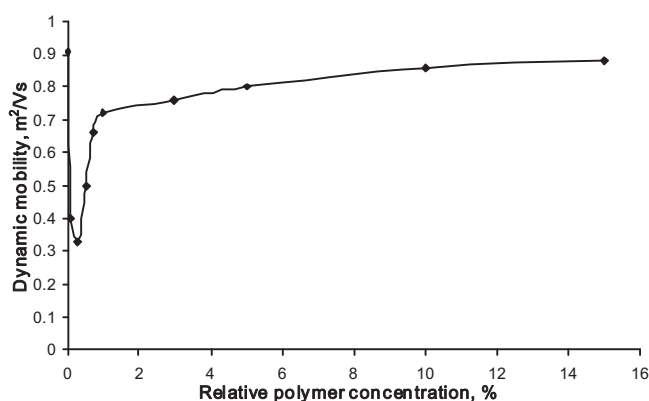


Fig. 5. Dependence of the dynamic mobility on the relative concentration of PiBA₁₇-*b*-PAA₇₂ for 1 wt % TiO₂ aqueous dispersion without ultrasonic treatment

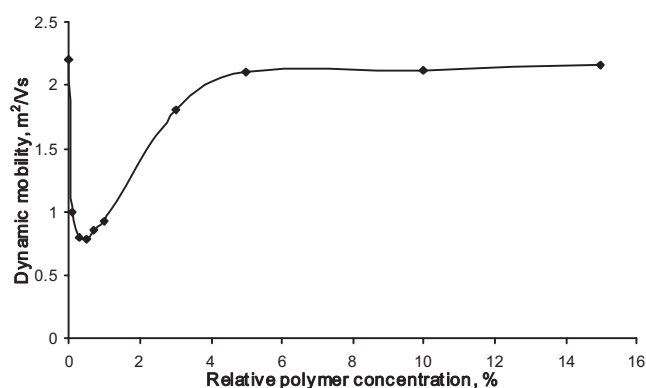


Fig. 6. Dependence of the dynamic mobility on the relative concentration of PiBA₁₇-*b*-PAA₇₂ for 1 wt % TiO₂ aqueous dispersion after ultrasonic treatment

First, as one can see from Tables 3 and 4, all employed copolymers allow to obtain pigment 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 [8]. It could be ascribed to the fact that THF used as a polymer solvent in the present study is known to create micelles with water providing the transport of a polymer to the pigment surface. Second it is evident that, irrespective of the constitution of the copolymer, the ultrasonification substantially improves the dispersion

stability as reflected from the comparison of the sedimentation half times of the non-treated and treated systems. The data also infer that there is an optimal copolymer structure with regard to the block length ratio; this is in accordance with previously discussed constitutional effects [8]. Third, there is a distinct effect of the pigment surface nature on the polymer structure acting as the best stabilizer: for hydrophilic TiO₂ dispersions, PiBA₁₇-*b*-PAA₇₂ with long PAA block showed good stabilization, for hydrophobic CuPc, PiBA₅₁-*b*-PAA₃₀ with the ratio PiBA/PAA ~ 2 revealed the best result.

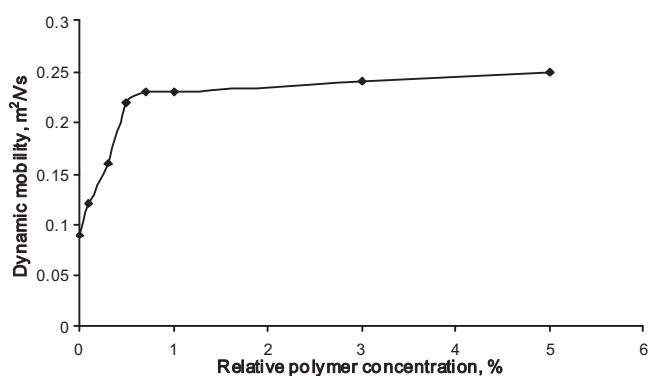


Fig. 7. Dependence of the dynamic mobility on the relative concentration of $\text{PiBA}_{51}\text{-}b\text{-PAA}_{30}$ for 1 wt % CuPc aqueous dispersion without ultrasonic treatment

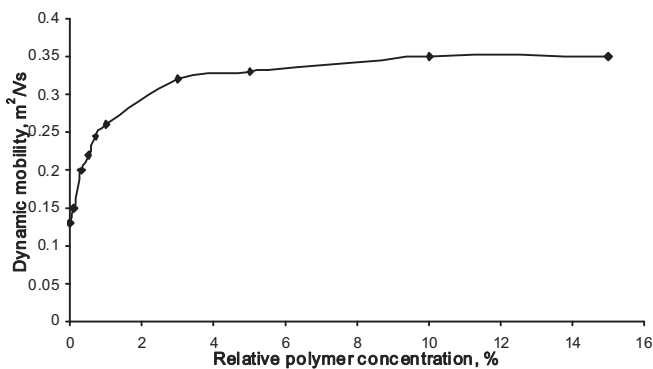


Fig. 8. Dependence of the dynamic mobility on the relative concentration of $\text{PiBA}_{51}\text{-}b\text{-PAA}_{30}$ for 1 wt % CuPc aqueous dispersion after ultrasonic treatment

ESA measurements of aqueous dispersions of TiO_2 and CuPc, stabilized by block copolymers of $\text{PiBA}\text{-}b\text{-PAA}$, give quantitative information about the process of adsorption of polymers as reflected first from the dependence of the dynamic mobility μ on the relative polymer concentration [21-23] as shown in Figs. 5 and 6, and second – from the comparison of this dependency for systems without and with ultrasonic treatment.

As one can see from the comparison of Figs. 5 and 6, ultrasonic treatment has a distinct effect on the behaviour of the particulate pigment-polymer suspension. Without ultrasonic action, the formation of a polymeric adsorption layer on the pigment surface seems to be reached at 1 wt % $\text{PiBA}_{17}\text{-}b\text{-PAA}_{72}$ in relation to the pigment concentration (saturation concentration as indicated by the unchanged dynamic mobility with further increase of polymer concentration). In the presence of ultrasonic action, first the initial dynamic mobility of the pristine TiO_2 is much higher, and the saturation concentration of polymer is only reached at about 5 %. Further addition of polymer does not affect the dynamic mobility. The decrease of the dynamic mobility after addition of small amounts of a polymer is in agreement with the data obtained for $\text{PS}\text{-}b\text{-PAA}$ block copolymers [21].

Obviously the ultrasonic action not only increases the pigment surface by creating more fine dispersion but also activates the pigment surface leading to an ultimately higher polymer adsorption in comparison to the non-treated samples. Similar results were obtained for CuPc aqueous dispersions as can be seen from Figs. 7 and 8.

Comparing the values of saturation concentration without and after ultrasonic treatment, one can infer that the amount of polymer adsorbed on the particle surface significantly increases when ultrasonification is applied. In this context it has to be considered that the ultrasonic treatment leads to a finer dispersion by decreasing the particle size, and, consequently leading to an increase of the surface area prone to polymer deposition. Thus both

the increase in the total surface area of the dispersed particles and a possible ultrasonically induced activation of the particle surface must be considered as being responsible for the observed effects.

In order to get some quantitative information 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 of the systems without and with ultrasonic treatment and related to the amount of adsorbed polymer.

In these calculations it was assumed that the pigment particle has spherical shape, 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 (Figs. 5–8) becomes more or less parallel to the abscissa and does not change much for increasing polymer concentration [21].

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 for calculations of the data compiled in Table 5 it is referred to the previously published paper [9].

The comparison of the experimentally measured diameter d_{part} of the polymer coated particles which were obtained by application of ultrasonification (column 3 in Table 5) and without ultrasonification (column 2 in Table 5) shows that smaller particles resulted from the ultrasonification; this was to be expected since ultrasonic

Table 5

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 amphiphilic 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}), μm		Ratio between particle surface area with and without ultrasonic treatment (S_{tot2}/S_{tot1})	Ratio between saturation concentration with and without ultrasonic treatment (SC_2/SC_1)
	Without ultrasonic treatment	After ultrasonic treatment		
TiO ₂ + PiBA ₁₇ - <i>b</i> -PAA ₇₂	1.2	0.6	2	5
CuPc + PiBA ₅₁ - <i>b</i> -PAA ₃₀	0.8	0.3	2.7	6

Table 6

Thicknesses d of the adsorption layer of the amphipolar copolymer on TiO₂ and CuPc surface for ultrasonically treated and non-treated dispersions as calculated on the basis of the saturation concentration SC obtained from the ESA measurements (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
TiO ₂ + PiBA ₁₇ - <i>b</i> -PAA ₇₂	5.5	13.6	3.2
CuPc + PiBA ₅₁ - <i>b</i> -PAA ₃₀	1	2.3	2.3

treatment is known to cause a breaking of agglomerates/aggregates present in pigment slurries.

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 5), the saturation concentrations SC as derived from the experimental curves Figs. 5–8 is 5 to 6 times higher for the ultrasonically treated systems as compared to the non-treated systems (see column 5 of Table 5); in other words, the SC ratio is about three times larger than the S_{tot} ratio (compare columns 4 and 5 in Table 5). This indicates that the amount of polymer adsorbed per unit of the particle surface after ultrasonic treatment is higher as compared to non-treated samples.

The thicknesses of the adsorbed polymer layer as obtained for the TiO₂ and CuPc pigment dispersions under conditions of ultrasonic treatment in comparison to the systems without ultrasonic treatment are compiled in Table 6. Thicker adsorption layers observed for the ultrasonically treated systems confirm that an activation of the pigment surface occurs by the action of ultrasonic power.

A general conclusion that can be drawn from the data compiled in Table 5 and Table 6 is that increase of the thickness of the polymer adsorption layers upon ultrasonic treatment is confirmed from both the information obtained from the ESA measurements and from the calculations of the particle surface.

In particular, the data allow to conclude that ultrasonic treatment of aqueous inorganic pigment dispersions is a powerful method for pigment surface

modification leading first to an activation of the pigment surface; as a consequence, improvement of the pigment-polymer interaction is achieved, which results in the creation of polymer adsorption layers of high thickness.

4. Conclusions

Poly(isobornyl acrylate)-*b*-poly(acrylic acid) were synthesized in a controlled way by ATRP by employing the 1-ethoxyethyl protecting group strategy. Next, these block copolymers were used in pigment stabilization experiments. It was possible to stabilize hydrophobic as well as hydrophilic dispersion. ESA measurements were performed in order to give quantitative information about the process of adsorption of polymers. Increase of the thickness of the polymer adsorption layers upon ultrasonic treatment is confirmed from both the information obtained from the ESA measurements and from the calculations of the particle surface.

Acknowledgements

The author expresses his thanks to the research group of Prof. F.E. Du Prez (University of Ghent, Belgium) for donation of PiBA-*b*-PAA copolymers and to the research group of Prof. Claus D. Eisenbach (University of Stuttgart, Germany) for valuable help in experimental studies.

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СИНТЕТИЧНІ БЛОЧНІ КОПОЛІМЕРИ АКРИЛОВОЇ КИСЛОТИ ЯК РЕАГЕНТИ ДЛЯ МОДИФІКУВАННЯ ПОВЕРХНІ ПІГМЕНТІВ

Анотація. Детально досліджено вплив молекулярної архітектури і складу блочних кополімерів на їх поведінку на границі розподілу фаз. Вивчено процес модифікації поверхні гідрофільного пігменту діоксиду титану і гідрофобного пігменту фталоціаніна міді у водному середовищі за допомогою ряду амфифільних блочних кополімерів. Як стабілізатори використані амфифільні блочні кополімери, які складаються з поліізоборнілакрилату і поліакрилової кислоти з добре охарактеризованою молекулярною структурою, контрольованою молекулярною масою та вузьким молекулярно-масовим розподілом, синтезовані радикальною полімеризацією з переносом атому з використанням макроініціатора (для одержання блочних кополімерів). Методом електрокінетичної звукової амплітуди вивчені властивості дисперсних систем у відсутності та за наявності ультразвукового впливу. Одержані результати вказують на суттєве збільшення кількості адсорбованого полімеру після ультразвукової обробки, що пояснюється активацією поверхні частинок пігменту.

Ключові слова: дисперсні системи пігментів, блочні кополімери, амфифільні кополімери, адсорбція полімеру, ультразвуковий вплив, метод електрокінетичної звукової амплітуди, седиментація, модифікація поверхні пігментів.

