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Application of thermo-responsive poly(methyl vinyl ether) containing copolymers in combination with ultrasonic treatment for pigment surface modification in pigment dispersions

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Abstract

The process of surface modification of hydrophobic organic (copper phthalocyanine (CuPc)) as well as hydrophilic inorganic pigments (titanium dioxide) in aqueous dispersions by employing tailor-made thermo-responsive copolymers and the colloidal stability have been studied as a function of temperature. The pigment surface modification is achieved by conventional adsorption and by thermoprecipitation of amphiphilic methyl vinyl ether (MVE) containing block and graft copolymers, exhibiting a lower critical solution temperature (LCST), with poly(isobutyl vinyl ether) blocks and poly(ethylene oxide) side chains, respectively. The effect of mechanical treatment of the pigment dispersion by ultrasonic power alone or in combination with the LCST property was investigated. The course of the pigment surface coating process was followed by the electrokinetic sonic amplitude (ESA) method. The temperature-controlled sorption of PMVE-*g*-PEO graft copolymers on both inorganic and organic pigment surfaces was investigated. It was found that ultrasonic treatment together with LCST thermoprecipitation is a promising method for the surface modification of pigments with regard to dispersion stability.

Keywords: Polymer; Adsorption; LCST

1. Introduction

In recent years, polymer surfactants have been of increasing interest as stabilizers for particulate systems, especially for emulsions and suspensions. Aqueous colloidal dispersions of pigments are important, ecologically friendly colloidal systems widely used in polygraphic and paint industries. The pigment particles are usually of 20–200 nm diameter and may be quite hydrophobic. In order to achieve a good stabilization in aqueous pigment dispersions, many formulations were proposed [1–8]. Earlier we reported about the role of ultrasonic treatment to obtain highly stable dispersions [7,9]. It was shown that the use of polymer surfactants in combination with ultrasonic action can significantly improve the quality of dispersed systems. However, some aspects concerning pigment–polymer interaction and formation of adsorption layers under mechanical action needed additional elucidation.

The colloidal stabilization of aqueous dispersions with polymer surfactants is believed to be a consequence of adsorption of the amphiphilic macromolecules on the particle surface resulting in mono- or multi-layer of certain structure and

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thickness which provides certain sterical and/or electrostatic stabilization effects. Polymer adsorption from aqueous solution on a particle surface is a result of specific interactions of various active sites on the particle surface with corresponding sites (groups) of the macromolecule. Therefore the chemical structures of the stabilizers are believed to be adjusted to the nature (e.g. hydrophilicity, charge, etc.) of each type of the particles.

Thermo-responsive ‘‘smart’’ polymers exhibiting a lower critical solution temperature (LCST) in aqueous solutions change their hydrophilic–hydrophobic balance when passing through the LCST (they become hydrophobic above LCST). One can expect that this property may result in temperature-controlled sorption and affect the structure of the adsorption layer, and thus allowing colloidal stabilization of aqueous dispersions. In other words, temperature-controlled changes in the hydrophilic–hydrophobic balance of those ‘‘smart’’ polymers can be used to adjust surfactant behavior of the polymer in order to achieve colloidal stabilization effects for various particles without changes of chemical structure or composition of the stabilizer.

As to the study of the interaction of copolymers with the pigment surface, electrokinetic sonic amplitude (ESA) technique [10–17] is a powerful method to obtain insights into adsorption/desorption phenomena [18–21]. Such information can be derived from the dynamic mobility μ_D of the dispersed particle as shortly addressed below.

When an alternating field is applied to a colloidal system, it exerts an electric force on the particles which causes them to move back and force. It is this backwards and forwards motion that generates the ESA signal which in turn provides information about the particle motion and thus on the characteristics of the particles itself. In practice, 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, i.e., electrophoretic mobility of a particle in an alternating electric field rather than reporting the raw ESA measurement data, is that the dynamic mobility is a property of the suspension: so unlike the ESA it does not depend on the device geometry, on the acoustic properties of the device or on the strength of the applied electric field. With the Acoustosizer 2 instrument which is applied in the present study, dynamic mobility μ_D can be determined with an accuracy of $\pm 1\%$.

More specifically, a potential for suspensions of arbitrary concentration is measured from pressure waves generated by the movement of charged particles in the oscillating electric field. The variation of this potential with frequency can be used for determining μ_D of particles. The change of μ_D upon addition of a polymer to the pigment dispersion reflects the formation of thin polymer layers on the particle surface and allows to calculate the zeta-potential as well as the particle size. For fixed low frequencies as applied in this work, μ_D is affected by the surface charge of the particle only [16,18–20]. The study of the change of the dynamic mobility μ_D of aqueous titanium dioxide (TiO_2) dispersion upon addition of amphipolar polyelectrolytes has shown that ESA is a powerful method to reveal the course of polymer–pigment interactions and how this is related to the molecular architecture of the employed polyelectrolytes. For example, Eisenbach et al. reported about the potential of block and graft copolymers based on acrylic acid, styrene and isobutene as polymeric stabilizers for carbon black and TiO_2 dispersions [19–21]. In these studies, the saturation concentration (SC), i.e., the polymer concentration at which the curve obtained by plotting the measured dynamic mobility vs. the polymer concentration reaches a plateau and doesn't change further, was used for characterizing pigment–polymer interactions [18].

In previous investigations, a variety of block copolymers based on poly(methyl vinyl ether) (PMVE) and poly(isobutyl vinyl ether) (PIBVE) have been already used for the stabilization of copper phthalocyanine (CuPc) and carbon black (CB) aqueous dispersions [22]. PMVE belongs to the class of thermo-responsive polymers and exhibits a lower critical solution temperature (LCST) around 36 °C [24]. The introduction of such a thermo-responsive segment in an otherwise temperature-insensitive poly(vinyl ether) provides an efficient strategy for the design of a new class of amphipolar smart polymer surfactants with stabilization activity that is responsive to environmental conditions.

The investigation of the colloidal stabilizing efficiency of the above mentioned series of PMVE–PIBVE block copolymers for aqueous CuPc and CB dispersions by sedimentation measurements [22] revealed that an optimal block length ratio exists. As to the effect of the block copolymer constitution, i.e., AB 2-block vs. ABA or BAB 3-block copolymer, it was found that BAB are superior to ABA, but there is practically no difference between the BAB 3-block copolymers and AB 2-block copolymers with optimized block length ratio. These tailored surfactants showed stability properties that are even better than those of the commercial Pluronics®.

In order to further elucidate the interaction of the block copolymers with pigment surface, the optimized PMVE-*b*-PIBVE 2-block copolymer and PIBVE-*b*-PMVE-*b*-PIBVE 3-block copolymer were employed for ESA measurements with copper phthalocyanine (CuPc) pigment in aqueous dispersion.

Since it is well known from literature that amphipolar graft copolymers may be advantageous over amphipolar block copolymers [18,20], graft copolymers consisting of PMVE backbone and poly(ethylene oxide) (PEO) grafts were included in our studies for aqueous dispersion of CuPc and also titanium dioxide (TiO_2). Considering the distinct difference of the LCST of PEO (LCST > 100 °C) and PMVE (LCST = 36 °C) [23,24], the PMVE backbone can be considered to represent the less hydrophilic, i.e., the comparatively hydrophobic part in these graft copolymers.

2. Experimental part

2.1. Materials

As pigments, β-copper phthalocyanine (β-CuPc, BASF AG, Ludwigshafen) with primary particle size 0.1 μm and breadth of particle size distribution of 15 nm, and titanium dioxide

Table 1
Overview of the chemical structure, average block lengths, overall number average molecular weight M_n and polydispersities M_w/M_n of the studied methyl vinyl ether (MVE)/isobutyl vinyl ether (IBVE) block copolymers, and cloud point temperature T_{cp} in aqueous solution

Samples[a]		M_n[b]	M_w/M_n[c]	T_{cp}
AB diblock copolymer	$PMVE_{45}$-*b*-$PIBVE_{10}$	3600	1.13	37
ABA triblock copolymer	$PIBVE_{22}$-*b*-$PMVE_{75}$-*b*-$PIBVE_{22}$	8800	1.35	37

[a] The number after the abbreviation of each polymer block indicates the corresponding degree of polymerization.
[b] Determined by ^1H NMR.
[c] Determined by SEC in $CDCl_3$ as solvent with polystyrene standards.

rutile pigment Kronos 2310 with particle size 0.3 μm and breadth of particle size distribution of 60 nm were employed as received.

The AB and ABA block copolymers based on methyl vinyl ether (MVE) and isobutyl vinyl ether (IBVE), and the statistical copolymers (the backbones for the graft copolymers) of MVE with 2-chloroethyl vinyl ether (CEVE) with various molecular weights and narrow polydispersities, were synthesized by "living" cationic polymerization techniques as described elsewhere in Refs. [24] and [25], respectively. The characteristics of the two block copolymers used in this work are given in Table 1.

The poly(methyl vinyl ether)-*graft*-poly(ethylene oxide) (PMVE-*g*-PEO) graft copolymers have been synthesized using a grafting-to method as summarized below; details of the synthesis are given elsewhere [26]. First, P(MVE-*stat*-CEVE) copolymers with primary Cl atoms as reactive functional groups have been prepared by living random cationic copolymerization of MVE and a small amount of CEVE. These chlorine pendant groups were reacted with amino terminated PEO ($M_n = 2000–5000\ g\ mol^{-1}$). Different amounts of PEO were attached to the backbone in order to prepare a variety of graft copolymers. Tables 2 and 3 give an overview of the composition, molecular weight and polydispersity of the starting P(MVE-*stat*-CEVE) employed in the PEO grafting reaction and of the PMVE-*g*-PEO graft copolymers used in this study, the PMVE-*stat*-CEVE representing the backbones of the graft copolymers.

Table 2
Molecular characteristics of random methyl vinyl ether (MVE)/2-chloroethyl vinyl ether (CEVE) copolymers $P(MVE)_x$-*stat*-$(CEVE)_y$: comonomer composition, number average molecular weight M_n and polydispersity M_w/M_n

Name	MVE units x[a]	CEVE units y[a]	CEVE[a] (mol%)	M_n[b] ($g\ mol^{-1}$)	M_w/M_n
B1	284	5	1.73	32 490	1.17
B2	344	10	2.82	30 290	1.11
B3	320	12	3.61	33 940	1.20
B4	299	17	5.38	30 490	1.18

[a] Determined by ^1H NMR.
[b] Determined by SEC in $CDCl_3$ as solvent with polystyrene standards.

2.2. Techniques

For cloud point temperature (T_{cp}) measurements, a copolymer solution was dissolved in Milli-Q water at the concentration 1 g/L and then put into test tubes and kept at 4 °C for 24 h. The phase transition temperature of the solutions was measured by monitoring the transmittance of a 540 nm red laser through a 3 cm polystyrene cuvette with a heating rate of 0.1 °C/min between 10 and 50 °C. The transmittance was recorded on a UVIKON 810 UV/VIS spectrophotometer.

Colloidal stabilization of the aqueous dispersions was monitored by sedimentation measurements of 1 wt.% dispersions of CuPc and TiO_2. Unlike graft copolymers, block copolymers used for the stabilization of CuPc cannot be dissolved directly in water. Therefore, for the preparation of the aqueous dispersions, the copolymers were predissolved in ethyl acetate as a solution aid (5 wt.%), and then this polymer solution was introduced to the aqueous phase together with the pigment (ethyl acetate/water 1/9 v/v) [22]. This procedure prevents the precipitation of the PMVE–PIBVE block copolymers. The total concentration of block copolymers as well as graft copolymers for sedimentation studies was 0.5 wt.%. After mixing with a laboratory stirrer (700 rpm for 10 min), the system was treated with ultrasound for 2 min with an ultrasonic generator UZDN-2 or Branson Sonifier B-12 with actual power of 1.5 W/cm^2. During ultrasonification, the pigment is being coated with the block copolymer and the ethyl acetate evaporates.

The pigment–polymer interaction was investigated by electrokinetic sonic amplitude (ESA) method. ESA measurements were carried out as described earlier [18]. This analytical

Table 3
Overview of the chemical structure of methyl vinyl ether (MVE)–ethylene oxide (EO) graft copolymers $P[(MVE)_x$-*g*-$(PEO)_n]$ as obtained from $P[(MVE)_x$-*stat*-$(CEVE)_y]$ (Table 2) by grafting-to reaction. Compositions, molecular weight characteristics, and cloud point temperatures (T_{cp}) upon heating (i.e., lower critical solution temperature LCST) for 1 mg/mL aqueous PMVE-*g*-PEO graft copolymer solution

Code	Starting polymer	Initial Cl atoms	PEO			M_n[a] ($g\ mol^{-1}$)	M_w/M_n	T_{cp}
			M_n ($g\ mol^{-1}$)	Number PEO grafts	Content (wt.%)			
G1	B4	17	2000	9	48	44 130	1.22	28
G2	B1	5	5000	3	47	51 700	1.24	35
G3	B2	10	5000	3	41	48 290	1.26	31
G4	B3	12	5000	7	64	52 100	1.32	30
G5	B4	17	5000	13	77	45 520	1.08	27

[a] Determined by SEC in $CDCl_3$ as solvent with polystyrene standards.

technique measures the dynamic mobility which in turn is related to the zeta-potential [10,15,18,20].

Transmission electron microscopic (TEM) investigations were carried out according to the standard procedure. The samples of the pigment dispersions were diluted with distilled water by a factor of 100, then dropped on the TEM grid of 3 mm diameter and dried on air for 1 day. The TEM pictures were taken by using a Jeol 2000 FX device under the voltage of 200 kV.

3. Results and discussion

3.1. Pigment surface modification of CuPc with PMVE-b-PIBVE block copolymers

3.1.1. ESA studies

In our previous work [22] it was found that the sedimentation time of CuPc dispersed in aqueous solution of PMVE–PIBVE block copolymers decreases drastically when the LCST of the block copolymer is exceeded. This was attributed to a coagulation of the surface-modified pigment (adsorbed block copolymer with PIBVE anchor block and PMVE tail(s)) which goes along with the collapse of the PMVE block above the LCST.

These AB and ABA block copolymers of MVE (A) and IBVE (B) (PMVE-*b*-PIBVE and PIBVE-*b*-PMVE-*b*-PIBVE) are amphiphilic below the LCST and become quite hydrophobic above the LCST; this is a consequence of the collapse of the PMVE block above the LCST. In order to further explore the pigment–polymer interaction and the observed sedimentation phenomena, ESA method was applied. The change in the dynamic mobility which is proportional to a change in the zeta-potential reflects adsorption phenomena of copolymers on the pigment surface [18,20]. Therefore ESA measurements were carried out below and above the LCST of selected block copolymers. The composition and molecular properties of the block copolymers used for this study are given in Table 1.

First, aqueous dispersions of CuPc stabilized by $PMVE_{45}$-*b*-$PIBVE_{10}$ and $PIBVE_{22}$-*b*-$PMVE_{75}$-*b*-$PIBVE_{22}$, which are the best colloidal stabilizers at room temperature [22], were studied by ESA measurements. Figs. 1 and 2 represent the change of the dynamic mobility of surface-modified CuPc dispersion with increasing amount of AB (Fig. 1) and BAB (Fig. 2) block copolymers added to the system for the surface modification.

As one can see, the pigment–polymer suspensions, stabilized by di- and triblock PMVE containing copolymers give a phenomenologically quite similarly shaped curve for the change of the dynamic mobility μ_D with increasing polymer concentration without (curve 1) and with applied thermoprecipitation (curve 2). Without thermoprecipitation, the saturation of surface layer seems to be reached already at 5% for the $PMVE_{45}$-*b*-$PIBVE_{10}$ and at 3% for the $PIBVE_{22}$-*b*-$PMVE_{75}$-*b*-$PIBVE_{22}$ in relation to the pigment. In this context it is interesting to note that, although the saturation concentration observed for the 2- and 3-block copolymer differs by about a factor of 1.5 (the AB block copolymers being less adsorbed than the BAB 3-block copolymers), the dynamic mobilities μ_D differ by about a factor of 8. This observation is surprising in view of the quite similar sedimentation stability of both types of copolymers [22]. It means that the diblock copolymers which form hydrophilic PMVE tails when adsorbed with the hydrophobic PIBVE anchor block to the CuPc pigment surface are much more effective in pigment stabilization than the BAB copolymers exhibiting PMVE loops [22].

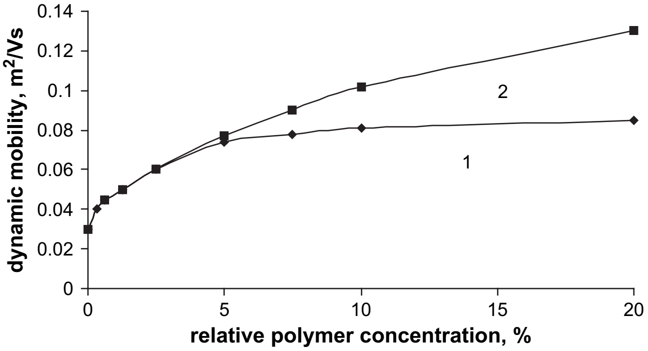

Fig. 1. Dependence of dynamic mobility of surface treated CuPc on the relative concentration of $PMVE_{55}$-*b*-$PIBVE_{10}$ in aqueous dispersion in combination with ultrasonic treatment for pigment surface modification: conventional procedure (curve 1) and LCST thermoprecipitation method (curve 2).

As PMVE is known to exhibit a LCST in aqueous solutions [23], it was interesting to study the creation of a surface layer by the so-called ''LCST thermoprecipitation method'', in combination with ultrasonic treatment, which may increase the thickness of the layers and thus the stabilization of the dispersion in comparison to the polymer deposition below LCST. The LCST technique alone has already been shown to be quite efficient in pigment surface modification [27].

In this work, the procedure of dispersion preparation was slightly changed. First, in constant temperature experiments (below the LCST), the isothermal condition during the ultrasonic treatment is maintained by water cooling. In comparative experiments carried out without cooling, the heat generated by

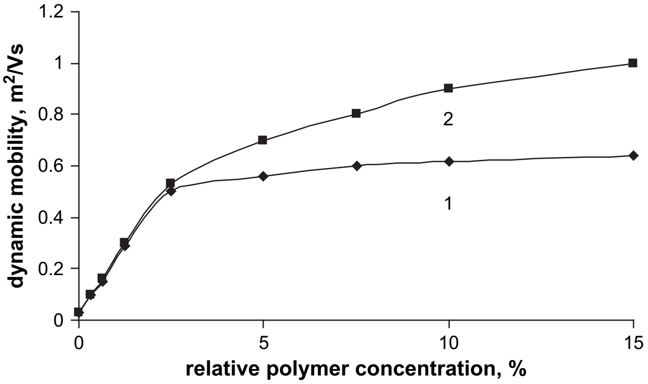

Fig. 2. Dependence of dynamic mobility of surface treated CuPc on the relative concentration of $PIBVE_{22}$-*b*-$PMVE_{75}$-*b*-$PIBVE_{22}$ in aqueous dispersion in combination with ultrasonic treatment for pigment surface modification: conventional procedure (curve 1) and LCST thermoprecipitation method (curve 2).

the ultrasonic treatment caused the temperature of the system to rise up to 45–50 °C. As this temperature is above the LCST of PMVE, the PMVE–PIBVE block copolymers which are hydrophilic (dissolved PMVE-block coils) become hydrophobic in the collapsed coil state and are completely precipitated on the particle surface. This change in hydrophilicity towards a more hydrophobic character of polymer layers results in fast coagulation of the dispersion due to the hydrophobic interaction.

The thickness of the deposited layers indeed increases due to thermoprecipitation (Figs. 1 and 2, curve 2); a saturation concentration could not be established, which is ascribed to the fact that all block copolymers added to the solution precipitate on the particle surface. Thus, an increasing amount of block copolymers results in thicker deposited layers, as is reflected by the higher values of dynamic mobility. In other words, this procedure gives the possibility to create surface polymer layers with controlled thickness.

3.1.2. Transmission electron microscopic (TEM) studies

In order to visualize the surface modification of the pigments in aqueous dispersion by treatment with ultrasound in the presence of polymers exhibiting LCST behavior, the aqueous dispersions were investigated by transmission electron microscopy (TEM). The pictures of CuPc particles stabilized by di- and triblock PMVE copolymers after mechanical (ultrasonic) treatment below LCST are depicted in Fig. 3.

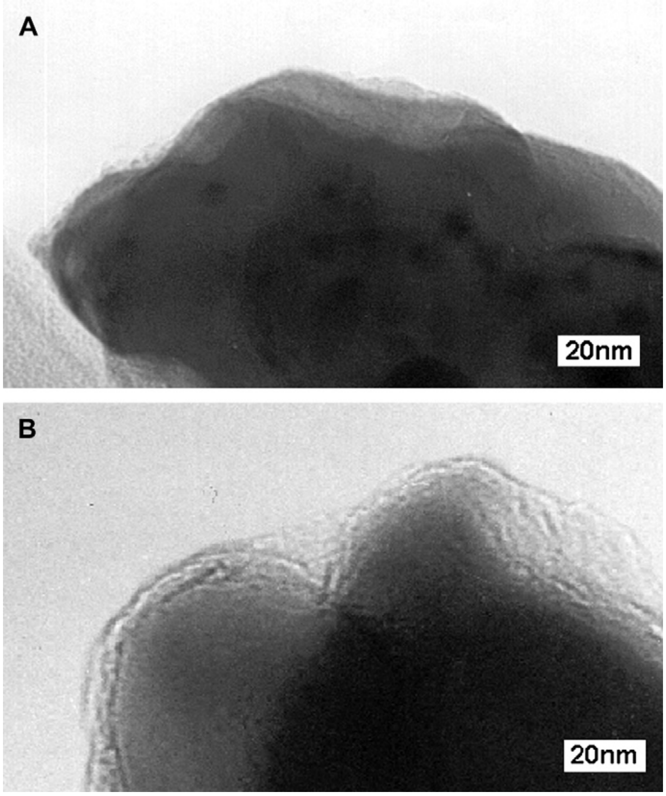

Fig. 3. TEM pictures of CuPc particle in aqueous dispersion stabilized by the (A) PMVE$_{45}$-*b*-PIBVE$_{10}$ and (B) PMVE$_{22}$-*b*-PIBVE$_{75}$-*b*-PMVE$_{22}$ after ultrasonic treatment below LCST.

One can identify the polymer layers as the corona (grey zones) created by di- and triblock PMVE copolymers. The thickness of these layers is limited by the amount of polymer, which can be deposited on the particle surface up to saturation of polymer layer. The excess of the polymer will apparently create aggregates and will not precipitate on the particles. As also seen from Fig. 3, the thickness of the polymer layer created by triblock copolymer is a little bit higher as compared to the layer in the presence of the diblock copolymer. This is in agreement with the difference between the absolute values of dynamic mobility obtained by ESA measurements (curves 1 in Figs. 1 and 2).

The TEM pictures of CuPc particles, as covered by PMVE$_{45}$-*b*-PIBVE$_{10}$ according to the thermoprecipitation technique are given in Fig. 4.

First, it can be deducted from Fig. 4A that thermoprecipitation of the block copolymer, which becomes more hydrophobic above the LCST, leads to a significant coagulation of the dispersion. The particles are strongly aggregated with an aggregate size of 5–10 μm. Secondly, the polymer layer is much thicker in comparison to the layer thickness resulting from systems prepared below LCST (Fig. 4B). After decreasing the temperature below the LCST, the block copolymer becomes amphiphilic and partial desorption of the polymer is

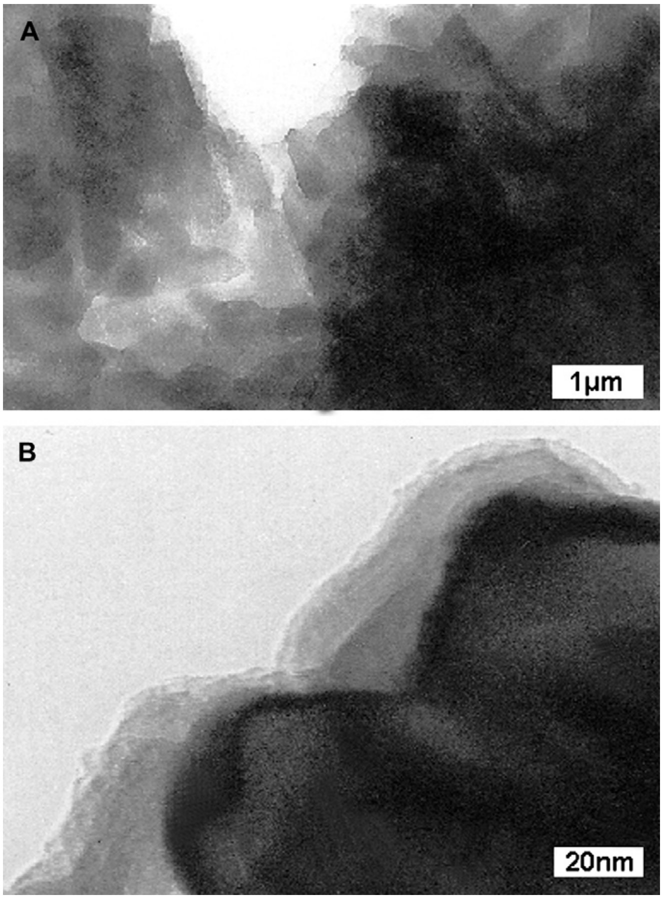

Fig. 4. TEM pictures of CuPc particle surface modified with the PMVE$_{45}$-*b*-PIBVE$_{10}$ in aqueous dispersion after ultrasonic treatment in combination with the thermoprecipitation technique: (A) coagulated dispersion and (B) close-up of a particle surface coating layer.

observed, i.e., the system can be redispersed. In order to retain the thickness of the adsorption layer, one can consider a system in which the polymer can be crosslinked to prevent the desorption process as has been proposed earlier already [27].

3.2. Pigment surface modification with PMVE-g-PEO graft copolymers

3.2.1. Sedimentation studies

In addition to the amphiphilic PMVE–PIBVE block copolymers, a family of graft copolymers consisting of PMVE backbones and PEO grafts were studied as well. Since PMVE–PIBVE graft copolymers are not accessible by known synthetic procedures, the PMVE-*g*-PEO graft copolymers (Table 3) were employed in our comparative studies of block vs. graft copolymers. These graft copolymers can be synthesized by a grafting-to technique starting from an readily available vinyl ether copolymer carrying functional chlorine side groups (Table 2) that can be converted into PEO grafts by reaction with monofunctional PEO. The block and graft copolymers have in common the PMVE part. However, whereas the PMVE block represents the hydrophilic part in the case of the PMVE–PIBVE block copolymers, it is the PMVE backbone which represents the less hydrophilic, i.e., comparatively hydrophobic part in the PMVE-*g*-PEO graft copolymers.

These PMVE-*g*-PEO graft copolymers are hydrophilic below the LCST and become amphiphilic above the LCST of the PMVE-*g*-PEO, the thermoprecipitation (LCST phenomenon) mainly being related to the PMVE backbone. As it was already observed earlier [24,25], the cloud point temperature of the graft copolymers does not change significantly when the PMVE/PEO weight ratio is varied. There is a tendency that the cloud point temperature decreases with increasing graft number, and also with increasing content of remaining chlorine groups (between 35 and 27 °C, Table 3). In aqueous dispersions, hydrophilic pigments (e.g. TiO_2) are known to require hydrophilic surfactants for stabilization whereas hydrophobic pigments such as CuPc require amphiphilic polymers to achieve stabilization. This opens a perspective to use these PMVE-*g*-PEO graft copolymers as universal smart surfactants for surface modification of both polar inorganic and non-polar organic pigments by taking advantage of the temperature-controlled sorption.

The stabilizing activity of the series of PMVE-*g*-PEO polymers in TiO_2 and CuPc aqueous dispersions was investigated at different temperatures. The results are given in Table 4. The half-time of the sedimentation, i.e., the period of time which is necessary for the border between colored and transparent zones in sedimentation measurements to reach 50% of the test-tube height, was chosen as a measure of the stabilization activity.

Table 4
Sedimentation stability of TiO_2 and CuPc aqueous dispersions with various PMVE-*g*-PEO graft copolymers (cf. Table 3) as a function of thermal history, i.e., without (below LCST) and with (above LCST) graft copolymer thermoprecipitation

Code	Number of PEO graft/M_n	Number of Cl in the graft	Half-time of sedimentation $\tau/2$			
			20 °C (below LCST)		50 °C (above LCST)	
			TiO_2 (days)	CuPc	TiO_2	CuPc (days)
G1	9/2000	8	5	10–15 min	30–40 min	7
G2	3/5000	2	30			18
G3	3/5000	7	30			20
G4	7/5000	5	25			23
G5	13/5000	5	25			20

Below the LCST, all graft copolymers are hydrophilic; thus, with exception of G1 they act as efficient stabilizers of TiO_2 aqueous dispersions, the PEO grafts acting as anchors to the TiO_2 surface (Table 4, column 4). After increasing the temperature above the LCST, the dispersion stability is extremely reduced (Table 4, column 6). This goes along with a fast coagulation and precipitation of particles of the size of about 7–8 μm. This can be explained by the agglomeration of formerly single TiO_2 particles covered with a graft copolymer monolayer: PMVE backbones collapsing when exceeding the LCST now act as "sticky bridges" between several TiO_2 particles due to the hydrophobic interaction. It is interesting that subsequent cooling below the LCST in combination with ultrasonic action allows to redisperse the system. The stability of the obtained dispersions is comparable to that of non-heated samples. This means that the agglomerates were broken by the action of ultrasonic power and that the PMVE backbone returned to the expanded coil conformation of a dissolved chain.

The poor colloidal stabilization observed for the G1 graft copolymer, carrying only comparatively low molecular weight PEO grafts, is attributed to the weak adsorption of the short PEO chains on the TiO_2 particles; the data indicate that PEO adsorption is improved for higher molecular weight PEO. It is concluded that PEO side chains of the copolymer are responsible for the pigment–polymer interaction causing adsorption of PEO grafts on the pigment particles' surface whereas the PMVE backbone allows for steric stabilization.

In the case of CuPc aqueous dispersions, just the opposite stabilization behavior is observed: below the LCST, only poor, i.e., almost no stabilization effect of the graft copolymers is observed (Table 4, column 5). It is only above the LCST that all graft copolymers act as stabilizers of CuPc aqueous dispersions. This can be explained by the fact that all-hydrophilic graft copolymers below the LCST only weakly interact with CuPc; above LCST, the now collapsed PMVE backbone has become relatively hydrophobic as compared to the expanded coil in aqueous solution (below LCST). Therefore adsorption onto the hydrophobic CuPc surface takes place, while PEO grafts are exposed to the aqueous phase, thus providing the dispersion stability. Lowering the temperatures causes solvation of PMVE backbones, regenerating hydrophilicity and desorption from the CuPc surface. Again, the best results are obtained for the graft copolymers with the longer PEO grafts (5000 vs. 2000).

3.2.2. Electrokinetic sonic amplitude (ESA) measurements

The adsorption of the PMVE-*g*-PEO copolymers on the TiO_2 and the CuPc surface was exemplarily investigated by

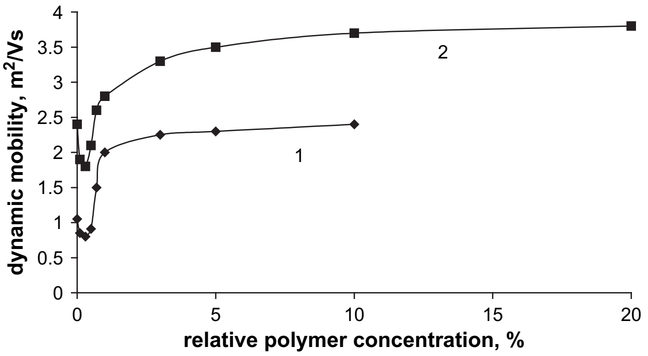

Fig. 5. Dependence of the dynamic mobility on the relative relative concentration of PMVE-*g*-PEO (G3) for TiO_2 aqueous dispersion without (curve 1) and after (curve 2) ultrasonic treatment (at 20 °C).

the ESA method. The change of the dynamic mobility with increasing concentration of added graft copolymers without and with ultrasonic treatment is shown in Fig. 5 (TiO_2 pigment) and Fig. 6 (CuPc pigment).

From Fig. 5, it is evident that phenomenologically similar, but regarding the quantity of the dynamic mobility quite different curves are obtained for ultrasonically non-treated and treated dispersions. Without ultrasonic action, saturation of the surface adsorption layer seems to be reached at 1% of PMVE-*g*-PEO in relation to the employed TiO_2 pigment. After ultrasonification, initial dynamic mobility of the TiO_2 is much higher, and saturation concentration of polymer is only reached at about 5%.

The differences in the initial values of the dynamic mobility and its increased level when ultrasonic power was applied can be attributed to mechanical activation of the surface by ultrasonic treatment. The initial decrease of the dynamic mobility upon addition of small amounts of graft copolymers is indicative of a lowering of the surface charge density by the adsorption of the first polymer chains on the charged TiO_2 surface, a phenomenon which has already been discussed in detail elsewhere [26]. The recovery and significant increase of the dynamic mobility, even exceeding the value of the pristine pigment, are attributed to the increasingly steric stabilization effect of further adsorbed graft copolymer; it may be assumed that electrosteric effects that result from proton–ether oxygen interaction have to be considered as well.

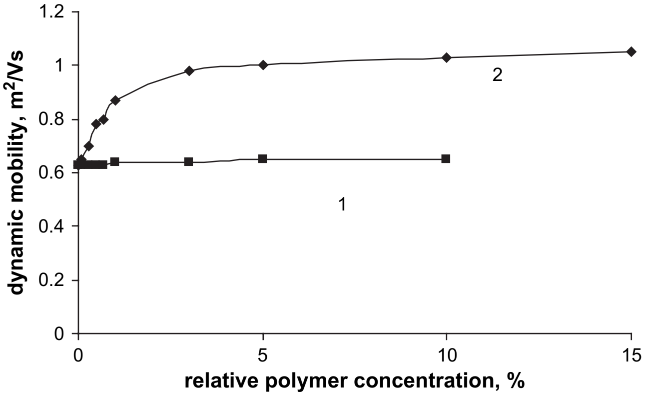

Fig. 6. Dependence of the dynamic mobility on the relative concentration of PMVE-*g*-PEO (G3) for CuPc aqueous dispersion after ultrasonic treatment at 20 °C (curve 1) and at about 50 °C (curve 2).

As already described above, a fast coagulation of the TiO_2 dispersion was observed after exceeding the LCST of PMVE (Table 4). This was attributed to the formation of agglomerates of formerly individual, surface-modified particles by the temperature induced hydrophobic interaction of collapsed PMVE backbones. ESA examinations of such coagulated dispersions gave the same dynamic mobility values as obtained for the starting dispersion prior to the temperature rise. This means that the fast sedimentation of the mechanically treated, surface-modified TiO_2 dispersions is a consequence of a bridging flocculation, and not related to a copolymer desorption. This is also a further proof of the earlier statement that TiO_2–polymer interaction at room temperature is apparently due to the adsorption of the PEO chains, while the PMVE backbones are preferably reaching into the aqueous media.

In the case of CuPc, ESA measurements proved the absence of adsorption below the LCST, as it is seen from the unchanged dynamic mobility values upon addition of copolymer (Fig. 6, curve 1); this is reasonable because one can expect that the all-hydrophilic copolymer (below LCST) does not interact with the hydrophobic CuPc surface. However, as shown from the increase in the dynamic mobility of the aqueous dispersions at temperature above LCST, the PMVE-*g*-PEO graft copolymer is able to adsorb on the CuPc surface; saturation of the adsorption layer is reached at about 3%. The collapsed, and thus comparatively hydrophobic PMVE acts as anchor of the amphiphilic copolymer above LCST, resulting in an effective stabilization of the CuPc dispersion. After decreasing the temperature, the values of dynamic mobility are similar to those for pure CuPc which indicates that desorption has occurred.

4. Conclusions

Block copolymers containing hydrophilic PMVE and hydrophobic PIBVE blocks have been investigated as temperature-controlled stabilizers of CuPc aqueous dispersions. Ultrasonic treatment of the pigment systems dispersed in the aqueous block copolymer solution not only enhances the dispersion stability but also influences the pigment–polymer interaction. For creating thick polymer layers on the particle surfaces it was observed that the precipitation of especially PIBVE polymer segments on the particle surface by exceeding the LCST is much more efficient than the adsorption (isothermal deposition) below the LCST. This is because the solution is depleted of block copolymer precipitating onto the already polymer-coated pigment surface (PIBVE anchors and PMVE tails) when going from the single-phase to the two-phase aqueous block copolymer solution.

Whereas PMVE–PIBVE block copolymers are well suited for the stabilization of aqueous dispersions of hydrophobic pigments such as CuPc, PMVE-*g*-PEO graft copolymers can be employed for the stabilization of CuPc as well as for pigments with hydrophilic surface such as TiO_2. It was shown that, depending on the temperature, these graft copolymers can be adsorbed on both hydrophilic and hydrophobic pigment surfaces. Below the LCST, the affinity of the PEO to the charged TiO_2 surface results in dispersions sterically stabilized by the PMVE backbones, the PEO acting as anchor to the pigment surface. When a dispersion of the hydrophobic CuPc in the aqueous graft copolymer solution is heated above the LCST, the collapsed PMVE acts as anchor to the CuPc, the dissolved PEO coils being responsible for the dispersion stabilization; below LCST, the otherwise all-hydrophilic graft copolymer does not interact with the hydrophobic CuPc. This gives a possibility to use these PMVE graft copolymers as universal smart surfactants for surface modification of both polar inorganic and non-polar organic pigments, and for temperature-controlled interaction.

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