

Effectiveness of block copolymers as stabilizers for aqueous titanium dioxide dispersions of a high solid content

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Abstract

Copolymers of 2-(dimethylamino)ethyl methacrylate (DMAEMA) and sodium methacrylate (MANa) have been synthesized and tested as dispersants for the aqueous dispersion of titanium dioxide (80 wt.% solid). The molecular composition of the block copolymers has an effect on the dispersion stability. Triblock copolymers consisting of PMANa outer blocks are unable to stabilize the dispersion. Triblock copolymers of the reverse structure form poorly stable dispersions due to at least partial particle bridging. In the case of non-blocky distribution of the DMAEMA and MANa comonomers in the chains, the stabilization capability is lost. A decrease in the anchoring strength of the diblocks has a deleterious effect on the dispersion stability. Finally, the surface coverage depends on the availability of free copolymer chains (unimers) coexisting with micelles. These trends have been confirmed in a fully formulated paint containing Cu-phthalocyanine pigment.

Keywords: Dispersion stability; Dispersion agent; Titanium dioxide; Block copolymer; Paint

1. Introduction

The production of a large-range of commercially available products, such as coal [1], ore [2], paints [3], printing inks [4], ceramics [5,6], pesticides, pharmaceuticals [7,8] requires the use of well-defined and very stable solid dispersions. For obvious economical reasons, high solid dispersions are by far preferred, although more difficult to be prepared and stabilized. The dispersion stability, that ultimately controls the quality of the final product, is commonly imparted by appropriate dispersants, which actually build up either a steric or an electrostatic barrier against flocculation [9,10]. Aqueous dispersions, which, due to very strong environmental incentives, are nowadays growing fast, need more efficient dispersants, since the stabilization mechanisms that operate in water are sensitive to external parameters, such as water hardness, pH, ionic strength and temperature.

Our research center has reported on the synthesis and properties of poly(4-vinylpyridine-*b*-sodium methacrylate) dispersants [11], which combine advantageously the electrostatic stabilization of low molecular weight ionic surfactants, such as sodium dodecyl sulfate, and the steric stabilization of nonionic surfactants [12-14]. Indeed, these block copolymers that contain a polyelectrolyte component impart very high stability to dispersions through a mechanism, known as electrosteric stabilization [9]. It has been shown that latexes stabilized by polyelectrolyte-containing block copolymers are definitely less sensitive to ionic strength [15] than low molecular weight ionic surfactants and that dispersants based on the aforementioned poly(4VP-*b*-MANa) copolymers outperform poly(4VP-*b*-EO) ones (where EO stands for ethylene oxide) [11].

Our study of poly(4VP-*b*-MANa) copolymers has shown that (1) the molecular composition of the block copolymers has an effect on the amount of copolymer required for imparting a good stability to the slurry rather than on the stability itself, (2) when the two structures of triblock copolymers are compared, triblocks consisting of PMANa outer blocks have a stabilizing efficiency comparable to the diblock copolymers, whereas the reverse structure is much less efficient, (3) in the case of a non-blocky distribution of 4VP and MANa in the copolymer chains, the stabilization effect is lost and (4) a decrease in the anchoring strength of the diblocks has a deleterious effect on the dispersion stability. The purpose of this study is to know whether these guidelines can be considered as general or not. Thus, a series of block copolymers consisting of an anchoring poly(2-(dimethylamino)ethyl methacrylate) block and a stabilizing poly(Na methacrylate) one have been synthesized, while changing the molecular architecture (AB diblocks, ABA and BAB triblocks), and molecular weight and composition in the case of diblocks (Table 1). A tapered block has also been synthesized by anionic polymerization, and a random copolymer of these two comonomers has been prepared by radical polymerization. The former copolymer consists of two main PMANa and PDMAEMA blocks connected to each other through a transient block of regularly changing composition, in contrast to the latter, which is composed of MANa and 2-

(dimethylamino)ethyl methacrylate (DMAEMA) units randomly distributed all along the chains. Actually, *tert*-butyl methacrylate was used as precursor for the Na methacrylate unit, because of well-controlled anionic polymerization and easy hydrolysis into acid, which is then neutralized with sodium hydroxide. For the sake of comparison, the ethyl spacer between the amino and ester functionalities in DMAEMA has been substituted by a propyl spacer. The molecular characteristics of all these block copolymers are listed in Table 1.

Finally, the information collected from the rheological study of TiO₂ dispersions stabilized by PDMAEMA-containing copolymers will be confirmed in fully formulated paints based on a blue organic pigment (Heliogenblue L7101 F) [16].

Table 1. Characteristics of the copolymers used

Code	Before hydrolysis	Monomer unit (average n')	Mn (total) ^a	NMR composition (wt.%)	Mw/Mn	CMC (mg/l)
PMANa		64	6900		1.07	-
D _{34H}	DMAEMA- <i>b</i> -tBMA	23-49	10600	34-66	1.1	120
D _{34L}	DMAEMA- <i>b</i> -tBMA	12-26	5600	34-66	1.1	100
D ₁₅	DMAEMA- <i>b</i> -tBMA	16-101	16800	15-85	1.2	120
D ₄₅	DMAEMA- <i>b</i> -tBMA	15-20	5300	45-55	1.1	15
T _{in}	tBMA- <i>b</i> -DMAEMA- <i>b</i> -tBMA	25-23-25	10700	34-66	1.1	115
T _{out}	DMAEMA- <i>b</i> -tBMA- <i>b</i> -DMAEMA	11-49-11	10600	34-66	1.1	150
Rd	DMAEMA/tBMA (radical)		17000 ^b	35-65	1.7	340
Tp	DMAEMA/tBMA (tapered)		7400 ^b	36-64	1.1	75
P ₃₈	DMAEMA- <i>b</i> -tBMA	15-30	6900	38-62	1.1	26

^a Equal to Mn(SEC) of the first sequence divided by the weight percentage of it (NMR analysis). ^b Equal to Mn(SEC).

2. Experimental

2.1. Copolymers synthesis

The block and tapered copolymers were synthesized by living anionic polymerization of *tert*-butyl methacrylate (tBMA) with DMAEMA [17]. The random copolymers were synthesized by radical polymerization under starved conditions [11]. The main molecular characteristics of the copolymers used in this study are listed in Table 1. Finally, the poly(tBMA) block was transformed into polyacid by acid hydrolysis.

2.2. Dispersions preparation

Titanium dioxide, RCL 535 from SCM Chemicals, was of the rutile type. It was precoated with alumina and characterized by a surface area of 12 m²/g and a density of 4.2 g/cm³. To 50 ml of an aqueous solution of copolymer (in demineralized water at pH 9), 200 g of titanium dioxide were added and ground with a dissolver disk at a speed rate of 3700 rpm for 15 min (volume fraction of TiO₂ = 0.48). The copolymer content was changed and referred to as the weight ratio with respect to titanium dioxide (e.g. 1 g dispersant for 200 g TiO₂ is reported as 0.5%).

2.3. Rheological measurements

Dispersion rheology was measured with a Rheotest 2 equipped with a Couette geometry at 25°C. The samples were pre-sheared in the Couette cell at 0.54 s⁻¹ for 20 min. An incremental shear rate sweep (from 0.54 to 1312 s⁻¹ and then back to 0.54 s⁻¹) was carried out in order to monitor the τ vs. $\dot{\gamma}$ curves. Data reported at each shear rate were steady-state values for the upwards scanning. The dispersion was then maintained under shear at 1312 s⁻¹ for 1 min. During the downwards sweep, data were recorded after 5 s of stabilization at the studied shear rate. The Bingham model was used (Eq. (1)).

$$\tau = \tau_{\beta} + \eta_{p1}\dot{\gamma} \quad (1)$$

where τ is the shear stress measured at the shear rate $\dot{\gamma}$. The apparent yield value, τ_{β} , and the plastic viscosity, η_{p1} , were extrapolated from the linear part of the τ vs. $\dot{\gamma}$ curve being, respectively, the origin and the slope.

2.4. Paints

Copolymer of about 7.5 g in the acid form was solubilized in 60 g water. The pH was fixed between 8 and 9 by the addition of 7 g of 2-dimethylaminoethanol. After addition of 0.5 g antifoam agent and 25 g Heliogenblue L7101F, the mill base was ground together with 1.0 mm glass beads with an Eiger Mini Motormill for 1 h. The mill base was left standing overnight before characterization.

The mass tone was prepared by mixing 16 g Heliogenblue mill base with 96 g Neocryl XK62 and 4 g butylglycol. It was characterized after overnight aging. The aged mass tone was added to a white paint in a 90/10 titanium dioxide/colored pigment (wt.%) ratio, and homogenized under stirring. Full characterization was carried out on the paint aged overnight.

Transmissions were measured with a home-built photo-spectrometer equipped with a daylight source (halogen lamp HLX 64625). All paints (mass tone and white reduction) were applied on translucent foil using the K-control coater 101 (RK-Print-Coat Instr.) with a bar of $S = 0.8$ mm, which affords a wet film thickness of 150-175 μm , followed by drying at room temperature (23°C). Gloss was measured at an angle of 20° with a micro-TRI glossmeter (Byk Gardner). Color was characterized with the Ultra Scan from Hunter Lab (ACMP-PC2 software).

3. Results and discussion

In this study, the copolymer concentration range (ca. 5-40 g/l) is far above the critical micelle concentration (CMC, at least 14 times). As it was previously highlighted [11], micelles basically act as more or less stable reservoirs of unimers, which are the actual adsorbed species.

In a preliminary study [18], the measurement of adsorption isotherms was unsuccessful. Indeed, the complete recovery of the titanium dioxide particles required centrifugation at such a high speed (>15 000 rpm) that micelles of the non-adsorbed copolymer were also sedimented, thus preventing any reliable characterization. In accordance with many research groups [1,5,12-14,19-27], rheology has been chosen as the most appropriate technique for the characterization of high solid dispersions. Rheology is indeed a very efficient tool for studying the stability of dispersions and the dispersant concentration required for the full surface coverage of the solid particles [1,5,21], i.e. the "pigment demand" [3]. The shear rate dependence of the steady-state shear stress of TiO_2 dispersions has been measured in order to learn about the effect of the molecular structure of the polymeric dispersants and the criteria for their design. Four main rheological characteristics of the dispersions have been considered: (i) the viscosity at low shear rate (0.54 s^{-1}), (ii) the apparent yield value (τ_β) (see Eq. (1)), (iii) the hysteresis area and (iv) the plastic viscosity (η_{pl}) (Eq. (1)).

The shear viscosity of dispersions of solid particles is basically influenced by the particle volume fraction [13]. When this volume fraction is close to the maximum packing, a dramatic increase in viscosity occurs. Depending on the type of lattice, the maximum packing for monodisperse spherical particles lies between ca. 0.52 and 0.74 [28]. In this study, the TiO_2 volume fraction has been chosen in this critical region, so that a small change in the dispersion state may have a dramatic effect on the shear viscosity. In this respect, the effective volume fraction must be considered rather than the theoretical one [27-29], since polymer adsorption onto the particle surface results in an increase of the effective particle volume and thus of the viscosity compared to the same dispersion of bare particles. Moreover, in the absence of dispersant, flocculation may occur, which results in a sharp increase in the effective volume fraction and in the final viscosity. Compared to a stable dispersion, flocculation is at the origin of high yield, higher viscosity at low shear rate and large hysteresis [1,5,11-13,19-27]. Indeed, a higher initial stress (yield value) is required for disrupting the flocs in the case of severe flocculation. Under shear, the flocs dissociate, which leads to a sharp drop in viscosity (shear-thinning). As long as some shear is maintained, flocculation remains limited or may be prevented from occurring, which accounts for an important hysteresis.

For being efficient dispersants, block copolymers must be strongly anchored onto the pigment surface. Since TiO_2 used in this study is coated with alumina, amines are expected to adsorb onto alumina by hydrogen bonding with the surface hydroxyl groups and by Lewis acid-base interactions with aluminum, as well. These Lewis acid-base interactions should be the major contribution to the amine anchoring onto alumina-coated TiO_2 [30,31].

3.1. Homopolymer

Since the sodium polymethacrylate (PMANa) block of the polymeric dispersants is known for dispersing properties [2,3,5,6], this polyelectrolyte has been firstly tested [11] and compared to the reference diblock (D_{34H}) (Figs. 1-4). Upon increasing the concentration of PMANa, the shear viscosity of the TiO_2 dispersion dramatically decreases and goes through a minimum. Actually, the adsorption of increasing amounts of polyelectrolyte prevents more efficiently flocs from being formed, until the pigment surface is saturated. This minimum in viscosity is commonly designated as the "pigment demand". The addition of dispersant excess (0.7 wt.%) results in flocculation. As discussed by Napper [9], this polymer excess may contribute to the depletion of the polymer layer in the boundary region between two particles and be responsible for the so-called depletion flocculation [32,33]. This phenomenon does not, however, occur when the polymer anchoring onto the pigment surface is strong enough [11].

Fig. 1. Plot of the viscosity at 0.54 s^{-1} vs. the dispersant/pigment wt/wt.%: (●) PMANa; (■) D_{34H} ; (◆) D_{34L} , πD_{15} .

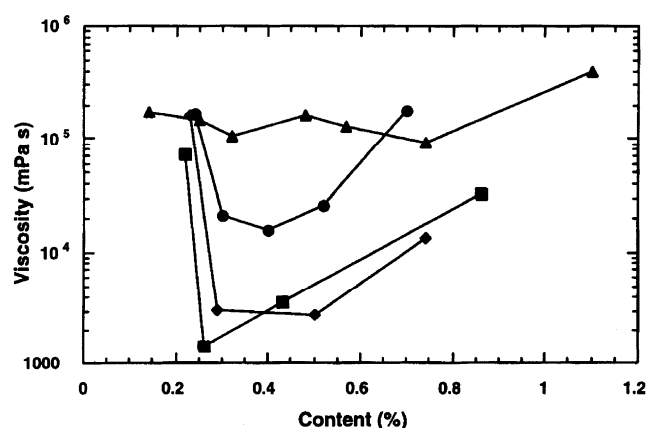
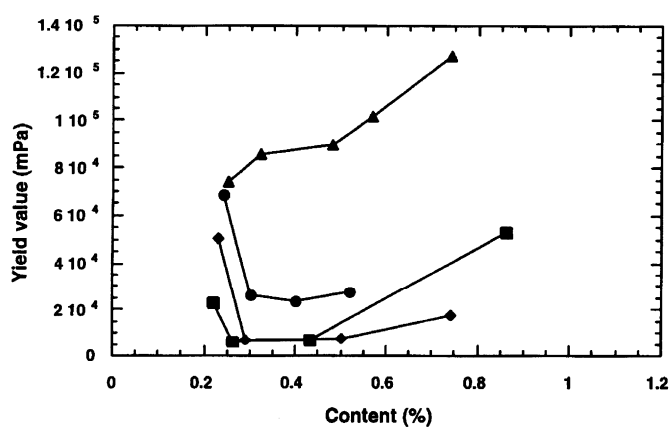


Fig. 2. Plot of the yield value vs. the dispersant/pigment wt/wt.%: (●) PMANa; (■) D_{34H} ; (◆) D_{34L} , πD_{15} .



It must be mentioned that the dispersion containing 0.7wt.% PMANa, partly flocculates and breaks down in the Couette cell at intermediate shear rates ($>2.3\text{ s}^{-1}$). This explains why only the low shear rate viscosity has been measured and not the complete rheological behavior.

Weak polyacids, such as poly(methacrylic acid), are not fully neutralized. Their degree of neutralization, α , actually depends on the pH and concentration, as well. At pH 9, α is of the order of 0.9 [34,35]. PMANa may thus be considered as a copolymer of methacrylic acid and sodium methacrylate. The former groups may anchor onto solid particles by hydrogen bonding and the latter ones by electrostatic interactions with an oppositely charged surface. At pH 9, the alumina surface is close to neutrality [5,12], so that anchoring should primarily occur by hydrogen bonding [2]. The polyelectrolyte is more likely adsorbed with a loop-train conformation, in such a way that loops of PMANa protrude into the bulk solution and provide the solid particles with an electrosteric stabilization. In the extreme situation where only one chain end of the polyelectrolyte would be anchored to the solid surface, the thickness of the protective barrier (length of the stretched chains) would be ca. 16 nm (0.25 nm per monomer [36]). This thickness should be smaller by a factor of at least two or three, as result of the ca. 10% anchoring units and the loop-train conformation. This situation may explain the limited dispersion efficiency of polyelectrolytes, which cannot prevent flocculation from occurring even when the particle surface

is completely covered.

Fig. 3. Plot of the hysteresis area vs. the dispersant/pigment wt/wt.%. (●) PMANa; (■) D_{34H} ; (◆) D_{34L} , πD_{15} .

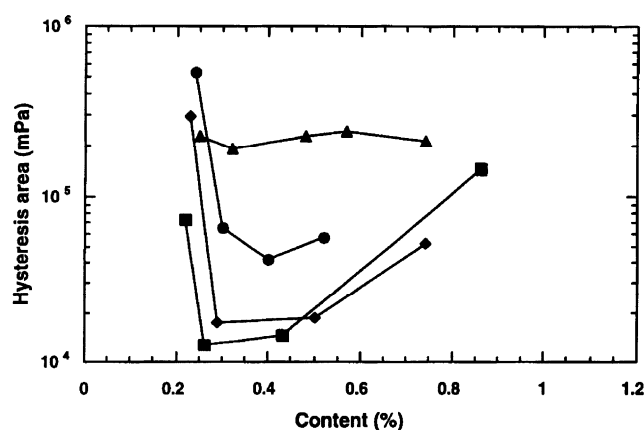
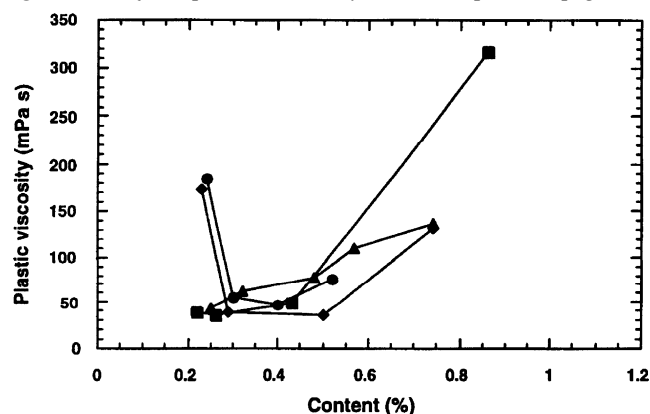


Fig. 4. Plot of the plastic viscosity vs. the dispersant/pigment wt/wt.%. (●) PMANa; (■) D_{34H} ; (◆) D_{34L} , πD_{15} .



In the case of the diblock copolymer D_{34H} , a rapid drop in viscosity is followed by a substantial increase upon increasing concentration (Fig. 1). Compared to PMANa, the minimum in viscosity is much lower, which is the signature of a better stabilization [1,3,5,21]. This improved stabilization is confirmed by a strong reduction in hysteresis (Fig. 3).

The apparent yield stress, which is a measure of strength and number of flocs [33], is reduced but not completely suppressed by the diblock D_{34H} (Fig. 2). Although some residual flocculation has to be considered, most of the apparent yield stress more likely results from the long-range electrosteric repulsion of the stabilizing layers [20,23,27,29,37]. Indeed, interaction and overlap of the electrical double layer of particles cause electroviscous effects, which tend to increase the effective excluded volume and thus the rheological parameters of stable dispersions.

The diblock D_{34H} would anchor onto the alumina-coated titanium dioxide through the PDMAEMA block, which can interact with alumina through hydrogen bonding and Lewis acid-base interactions as was shown in the case of poly(4-vinylpyridine) [11]. The PMANa block is expected to protrude in the aqueous bulk. Assuming the complete stretching of the polyMANa chains and a length of 0.25 nm [36] for the monomer unit, a layer thickness of ca. 12nm may be calculated, which is much larger than the ca. 5 nm thickness, which is usually recommended in order to overcome the Van der Waals attraction [9,21].

An increase in viscosity, less marked than with poly-MANa, is observed at higher diblock concentration. The question is to know whether a depletion flocculation occurs or not. The excess of dispersant compared to the minimum (ca. 0.26 wt.%) is ca. 0.6wt.% (24g/l), i.e. 200-fold the CMC. At this concentration, micelles formed by the dispersant excess might have a meaningful effect on the water viscosity, and account for the increase in viscosity with concentration of the diblock. The more or less pronounced increase in the rheological parameters could also result from the formation of a micellar network in the bulk. The plastic viscosity tends to corroborate this hypothesis (Fig. 4). At high shear rates, the flocs are broken down into smaller units, which are likely very

similar for all the dispersions. Then, the viscosity is controlled by the hydrodynamic interactions, that result from the applied shear. So, the plastic viscosity only depends on the viscosity of the liquid phase and on the effective volume fraction of the solid particles [1,33,38] which would be constant in this case. Therefore, the increase in the dispersion viscosity at higher diblock concentrations would basically reflect a more viscous dispersion phase rather than a depletion flocculation. In order to support this hypothesis, D_{34H} has been replaced by D_{34L} , which has the same composition, but a molecular weight reduced by half. This reduction in molecular weight expectedly results in a lower plastic viscosity (Fig. 4). The reduction of the thickening of the bulk by the micelles is also reflected mainly in the hysteresis and the apparent yield stress (Figs. 2 and 3), which tend to increase to a lesser extent upon increasing the copolymer concentration. It is, therefore, unlikely that the increase of the rheological parameters at higher copolymer concentrations is due to flocculation. Indeed, in this case, substitution of D_{34L} , with twice a thinner protective polyelectrolyte shell, for D_{34H} should result in higher hysteresis and apparent yield stress in contrast to what is actually observed.

3.2. Influence of the copolymer composition

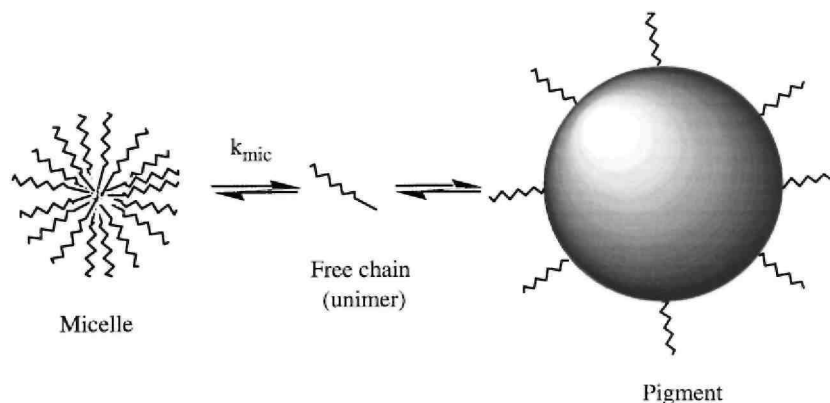
Diblocks with different DMAEMA contents, i.e. 15, 34 and 45 wt.%, have been studied. The best content is 34 wt.% of DMAEMA, since the best stability is then observed (Figs. 1-4). Lower DMAEMA content results in higher viscosity, whereas larger content leads to dispersions too viscous for being measured. Previous studies run in non-selective solvents [21,39-42] have also highlighted the effect of the diblock composition on the surface coverage and the dispersion stability, but not as dramatically as in the present study.

Table 2: Rate of exchange between the micelles and the unimers [43]

Code	CMC (mg/l)	$k_{mic} 10^3 (s^{-1})$
D34H	120	2.43 ± 0.17
D45	15	1.48 ± 0.01
T_{in}	115	0.50 ± 0.11
T_{out}	150	1.28 ± 0.03
P38	26	1.35 ± 0.10

In a selective solvent (water) for the polyelectrolyte block, the copolymer forms micelles, which may be viewed as more or less stable reservoirs of unimers. In the presence of the pigment, the unimers are not only in equilibrium with micelles but also with species adsorbed onto the pigment surface (Scheme 1). Therefore, at constant content, the capability of diblock copolymers to stabilize TiO_2 dispersions will depend on the relative position of these two equilibria.

Scheme 1.



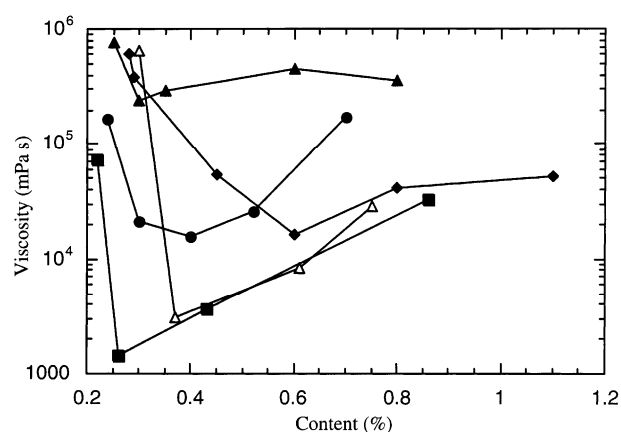
D45 is unable to impart stability to the pigment dispersion. This observation is consistent with a very low CMC combined with a slow rate of exchange for the unimers between the micelles (K_{mic} , see Table 2) [43]. The length of the polyelectrolyte block which is comparable to that of D_{34L} (an efficient stabilizer) has nothing to do with the disappointing behavior of D45. The rheological properties of D_{15} (Figs. 1-4) show that this diblock is less efficient than PMANa in stabilizing the dispersion. Indeed, a shorter anchoring block results in a weaker anchoring. In addition, Qiu et al. [44] have theoretically predicted that diblock copolymers with longer soluble blocks preferentially form self-assemblies with a higher curvature because of the excluded volume interaction of

the soluble segments. So they will tend to remain in micelles rather than to be adsorbed onto solid particles of larger size (i.e. of smaller curvature). The best performances are exhibited by D34 independently of the molecular weight (5600 or 10600) at constant composition (34 wt.% polyDMAEMA) and CMC. This situation is in contrast to the behavior of the poly(4-vinylpyridine-*b*-Na methacrylate) diblocks that proved to be good dispersants in a large range of composition (19-30 wt.% 4VP). Merely the amount of diblock required to reach ca., the same minimum in viscosity was increased by a factor of 2 when the 4VP content was increased in the mentioned limits [11]. A better anchoring of poly4VP compared to polyDMAEMA onto the pigment surface might explain the more complex behavior of the diblocks under consideration in this study.

3.3. Influence of the molecular architecture

No stable dispersion is observed in the presence of the poly(MANa-*b*-DMAEMA-*b*-MANa) copolymer, T_{in} . The CMC, which is comparable to D34H (Table 1) and the thickness of the electrosteric barrier (PMANa block of ca. the same length as D_{34L}) are not good reasons for this failure. However, the exchange rate between micelles and unimers is about five times slower compared to D_{34H} (Table 2). The unstability of the dispersion could therefore be partly related to the slow release of the unimers. This observation is in contrast with the efficiency of the poly(MANa-*b*-4VP-*b*-MANa) copolymer to impart stability to dispersed TiO_2 particles. This efficiency was comparable to the poly(MANa-*b*-4VP) diblock counterpart [11]. The stronger anchoring strength of 4VP compared to DMAEMA seems accordingly to be confirmed.

Fig. 5. Plot of the viscosity at $0.54\ s^{-1}$ vs. the dispersant/pigment (wt/wt.%): (●) PMANa; (■) D_{34H} ; (◆) T_{out} ; (▲) R_d ; (△) T_p .



In the case of the reverse structure for the triblock copolymer, T_{out} , the TiO_2 dispersion is less stable and more dispersant is required compared to D_{34H} (Figs. 5-8). It must be noted that the stability of the TiO_2 dispersion is lost when maintained for a few minutes under high shear. Adsorption on the pigment surface can occur either through one of the two outer PDMAEMA blocks or through each of them simultaneously. In the latter case, the PMANa central block has to bend, which results in an additional entropic penalty that has to be compensated by the adsorption enthalpy. If only one PDMAEMA block is adsorbed, the second one will have to protrude into the bulk solution and to adsorb possibly onto a second pigment particle, so leading to flocculation [45]. In view of the poor stabilization of the pigment dispersion by T_{out} , part of the copolymer chains might be adsorbed on more than one pigment particle. Since the poly(4VP-*b*-MANa-*b*-4VP) copolymer proved to be good dispersant, the two outer blocks were more likely adsorbed onto the same pigment particle so avoiding the particle bridging. This observation is again in favor of the stronger anchoring of 4VP, which allows to compensate the bending of the PMANa block. The poorer anchoring of DMAEMA is also reflected by the detrimental effect of high shear rates on the dispersion stability. Indeed, as result of the bending of part of the PMANa block, desorption of one of the two adsorbed PDMAEMA blocks occurs under high shear and leads to shear induced flocculation, which is not observed in the case of poly 4VP outer blocks.

Fig. 6. Plot of the yield value vs. the dispersant/pigment (wt/wt.%): (●) PMANa; (■) D_{34H} ; (◆) T_{out} ; (Δ) T_p .

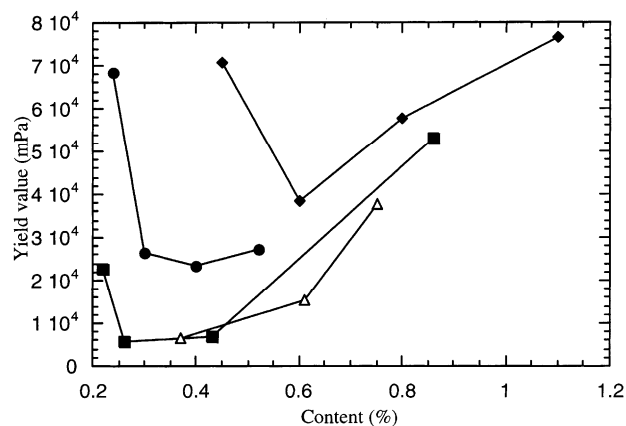


Fig. 7. Plot of the hysteresis area vs. the dispersant/pigment (wt/wt.%): (●) PMANa; (■) D_{34H} ; (◆) T_{out} ; (Δ) T_p .

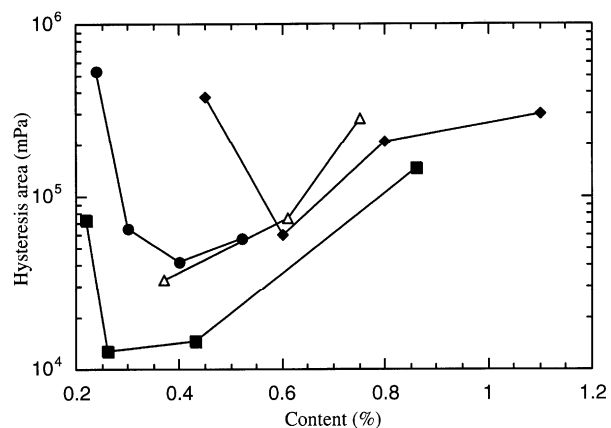
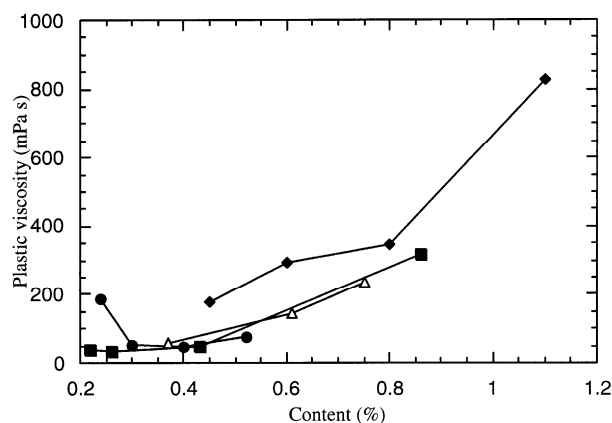


Fig. 8. Plot of the plastic viscosity vs. the dispersant/pigment (wt/wt.%): (●) PMANa; (■) D_{34H} ; (◆) T_{out} ; (Δ) T_p .



3.4. Influence of the copolymer blockiness

A random copolymer (Rd) has been synthesized by radical polymerization of the comonomers mixture. In contrast to all the other copolymers studied, whose the aminated moieties were essentially neutral at pH 9, about 50% of the randomly distributed DMAEMA co-units are expected to be protonated (pK_a close to 9) [46], which prevents their interaction with the pigment surface. Moreover, the random distribution of the comonomers increases the acidity of the methacrylic acid units, which are more extensively neutralized and thus less available for adsorption. As expected, the dispersion stability is so poor that only the viscosity at low shear rate could be measured (Fig. 5). Once again, random copolymer of 4VP and MANa was as efficient as PMANa in providing

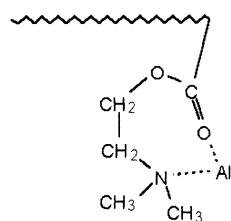
the dispersion with stability. The superiority of 4VP containing random copolymer over the DMAEMA counterpart has to be found in the non-protonation of the 4VP units at pH 9 and a higher anchoring strength.

In order to confirm that some blockiness is desirable, as previously highlighted by the 4VP/MANa copolymers [11], DMAEMA and tBMA have been mixed together and then anionically copolymerized. According to the reactivity ratios, $r_{\text{tBMA}} = 0.04 \pm 0.07$ and $r_{\text{DMAEMA}} = 1.3 \pm 0.4$ [17], the hydrolyzed copolymer may be viewed as a tapered copolymer consisting of two main PMANa and PDMAEMA blocks connected to each other through a transient block of a regularly changing composition. Compared to $D_{34\text{H}}$, the minimum in the rheological properties is shifted toward higher concentrations, ca. one and half times higher (Figs. 5-8). Except for the hysteresis, which tends to be higher for Tp, these two copolymers provide the TiO_2 dispersion with a comparable stability.

3.5. Influence of the anchoring block

The previous study showed that 2VP isomer was as efficient anchoring unit as 4VP [11]. Very surprisingly, the position of the nitrogen atom did not influence significantly the adsorption of polyvinylpyridine-containing copolymers. In order to evaluate further the impact of a slight modification of the structure of the anchoring unit on the dispersion stability of diblocks, DMAEMA was replaced by 3-(dimethylamino)propylmethacrylate. This substitution led to the complete loss of stability of the dispersions in possible relation to a much lower CMC (Table 1) and slower exchange rate of the unimers (Table 2). As a result, less unimers would be made available for adsorption. Moreover, the anchoring strength is expected to be low compared to DMAEMA. Indeed, DMAEMA tends to form a "chelate" with Al on the pigment surface (Scheme 2) in contrast to DMAPMA, which does not [47]. The structure of the DMAEMA unit is also at the origin of a lower pK_a , i.e. 8.4 vs. 8.9 for DMAPMA. Therefore, the pK_a of poly(DMAPMA) is expected to be ca. 0.5 unit higher than the pK_a of PDMAEMA (i.e. 8), so leading to the more extended protonation of the DMAPMA block at the expense of its anchoring capacity.

Scheme 2.



If the ethyl spacer between the amine and the ester moiety of DMAEMA is substituted by an isopropyl one instead of the aforementioned propyl spacer, stable dispersions are again observed as it will be reported elsewhere.

3.6. Paints

The requirement for blockiness that was concluded from the study of the model titanium dioxide dispersion has been further evaluated in a fully formulated paint based on Helio-genblue L7101 F (Cu-phthalocyanine pigment) [16]. These paints have been compared to a state-of-the-art reference, made available by Akzo Nobel (see Table 3).

Table 3: Characteristics of the copolymers used in the paints

Code	Before hydrolysis	Mn (total)	NMR composition (wt.%)	Mw/Mn
DMAD	DMAEMA- <i>b</i> -tBMA	11000 ^a	36-64	1.05
TMAD	DMAEMA/tBMA (tapered)	10500 ^b	36-64	1.05
RMAD	DMAEMA/tBMA (radical)	10000 ^b	34-66	1.9

^a Equal to $Mn(\text{SEC})$ of first sequence divided by the weight percentage of it (NMR analysis). ^b Equal to $Mn(\text{SEC})$.

While substituting alumina-coated titanium dioxide by another type of pigment, the chance of success for a stable dispersion by PDMAEMA-containing copolymers will depend on the occurrence of specific interactions

between the anchoring block and the pigment surface. In the case of a Cu-phthalocyanine pigment, stable dispersions are expected to be formed, since the PDMAEMA anchoring block can strongly interact with the pigment surface by complexation of the copper cations along the edges of the crystalline structure [48].

In agreement with the results reported for titanium dioxide, the random copolymer (RMAD) cannot provide the dispersion with stability during the milling process, so that no color characteristic was measured. In contrast, the pure diblock copolymer (DMAD) is at the origin of color characteristics as good as the reference formulation (Table 4). The tapered diblock (TMAD) gives also excellent properties, although slightly inferior to those ones shown in the presence of the pure diblock.

Table 4: Characteristics of the mill base, mass tone and white reduction

Mill base	transmission (%)	Mass tone, gloss	White reduction		
			dL	dC	Gloss
Reference	29	80	0	0	71
DMAD	32	76	0.7	-0.4	68
TMAD	31	82	2.1	-1.0	68
RMAD	No stable dispersion				

These observations confirm the trends reported for dispersions of titanium dioxide. Therefore, these trends should not be specific for a pigment as long as strong interactions between the anchoring block and the pigment occur. It should be mentioned that these copolymers provide the dispersions with very low viscosity, about one-fiftieth compared to the reference. Further improvement could occur at higher pigment loading, as result of increased dispersion shear viscosity and accordingly of better transfer of the mechanical energy to the aggregated pigment particles.

4. Conclusion

Block copolymers containing a stabilizing polyelectrolyte block and an anchoring polyaminated block (polyDMAEMA and poly4VP) have been observed to be efficient dispersants for high solid dispersions. As result of their amphiphilic structure, they are anchored onto the pigment surface as strongly as the adsorption enthalpy of the hydrophobic block is high. They can accordingly stabilize a polyelectrolyte brush, which is actually an electrosteric barrier against flocculation.

As far as the copolymer architecture, i.e. diblock vs. triblock copolymers, is concerned, a triblock copolymer containing an inner PDMAEMA block cannot stabilize dispersions, in contrast to the 4VP equivalent. This observation suggests the stronger anchoring of the 4VP units. As a rule, diblock copolymers are at least as efficient as-if not superior to-the triblock equivalents, in which the outer blocks are the stabilizing blocks. Although triblock copolymers with anchoring outer blocks can stabilize dispersions, they should be disregarded, since the bridging of pigment particles can occur to some extent, which will depend on the anchoring strength. Moreover, the simultaneous adsorption of the two outer blocks on the same particle has to result in the bending of the inner stabilizing block, so that the thickness of the stabilizing layer is decreased and the dispersion stability, as well.

This study has confirmed that the blockiness of the comonomer distribution in binary copolymers has a decisive effect on the dispersant efficiency. Since most of the commercially available copolymers have no pronounced blockiness, the "controlled" radical polymerization is now raising optimistic prospects for the synthesis of new (blocky) polymeric dispersants of an attractive cost-performance balance.

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