Design of Polymeric Dispersants for Waterborne Coatings

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Block and random copolymers of ammonium methacrylate and dimeth-ylaminoethyl methacrylate have been synthesized and tested as dispersants of various organic and inorganic pigments in formulations for waterborne paints. Blockiness of the co-monomer distribution is a prerequisite for good color characteristics in the final paint. It is however noteworthy that a tapered diblock (one-step anionic synthesis), a diblock copolymer with a regular change in composition from one block to the other one, has an interfacial activity quite comparable to the parent "pure" diblock copolymer (two-step anionic synthesis). The most interesting observation is that the poly(dimethylaminoethyl methacrylate) anchoring block can impart stability to dispersions of pigments as different as iron oxide, a blue Cu-phthalocyanine pigment, and a red organic pigment based on pyrrole in representative aqueous paint formulations. This type of diblock copolymer is promising for the design of universal dispersants.

INTRODUCTION

Increasingly strong environmental concerns encourage "green" technology based on water to the exclusion of organic solvents for the production of paints and coatings. Substitution of waterborne paints for the available solvent-based products can be only contemplated if the paint quality, particularly gloss and color characteristics, is maintained if not improved, which above all requires a highly stable pigment dispersion. In solvent-based dispersions, nonionic surfactants are used, and pigments are stabilized by repulsive forces of an osmotic origin.[1] Indeed when two pigment particles approach each other to the point where the lipophilic tails of the adsorbed dispersant start to interpenetrate or to be compressed, the solvent diffuses into this very local region of an increased free energy of mixing and repels these particles from each other[2] (*Figure* 1a).

In aqueous pigment dispersions, although the steric stabilization mechanism may also be operative,[3] stability is usually imparted by electrostatic repulsive forces. The lipophilic tail of ionic surfactants is then adsorbed onto the pigment surface, which is charged accordingly and surrounded by a diffuse electrical layer of the opposite sign (*Figure* 1b). The overlap of the diffuse layer of two particles results in electrostatic repulsion as strong as the interparticle distance is short. The main drawback of this stabilization mechanism is high sensitivity to the ionic strength of the aqueous phase, which can shield out the chemisorbed charges and lead to flocculation.[2]

Quite interestingly, the steric and the electrostatic repulsive effects can be combined into a unique stabilization mechanism, known as an electrosteric mechanism (*Figure* 1c). For instance, a (di)block copolymer consisting of a hydrophobic, and thus anchoring, block associated with a polyelectrolyte block, which plays the role of the stabilizing block, has the advantage of imparting to the coalescence (steric) barrier the additional capability of repelling the particles one from another by electrostatic repulsion.[4] When stabilized by an electrosteric effect, the dispersed particles can accordingly tolerate a higher ionic strength since the steric stabilization can compensate for a diffuse electrical layer of a decreased thickness.

In addition to the ionic strength of the aqueous phase, the pH of this phase and the isoelectric point of the pigment may affect the stabilization efficiency. Indeed, the pigment surface is positively or negatively charged

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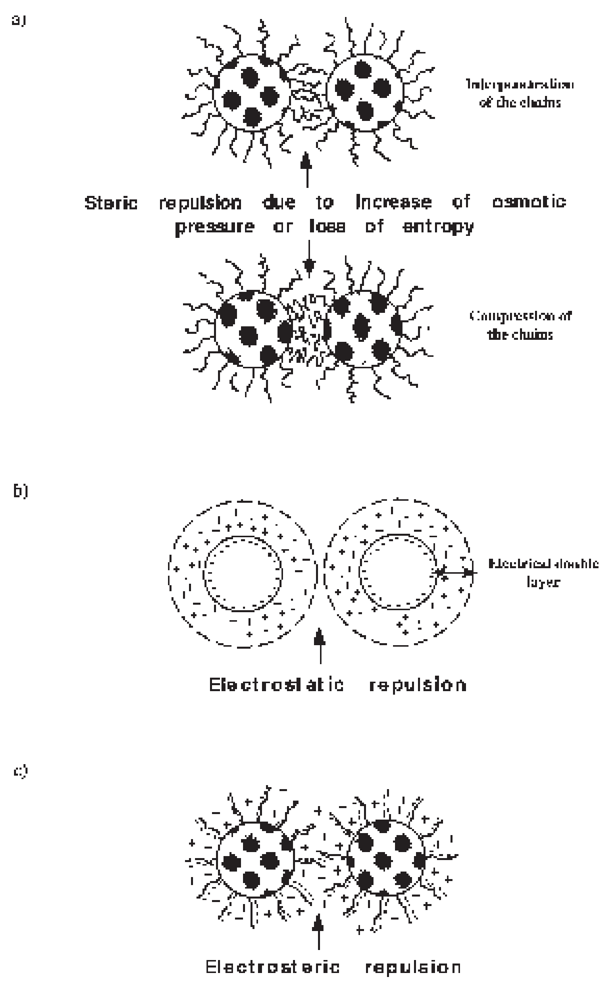


Figure 1–a) Steric, b) electrostatic, and c) electrosteric stabilization.

depending on whether the pH is lower or higher than the pigment isoelectric point. The anchoring of an ionic polymeric dispersant onto the pigment surface might then be difficult, in case of charges of the same sign on the dispersant and the pigment surface. In the reverse situation, the polyelectrolyte block might interact with the pigment surface of opposite charge and lose any stabilization efficiency.

In this introduction, we want to limit ourselves to the general concepts of dispersion stabilization and not embark on an overview of the specific information available in the scientific and patent literature, which would deserve a dedicated full paper. The purpose rather is to report on a novel family of diblock copolymers consisting of a poly(dimethylaminoethyl methacrylate) (polyDMAEMA) anchoring block and an ammonium polymethacrylate stabilizing block (*Scheme* 1a) and to discuss their efficiency as polymeric dispersants for waterborne paint formulations in relation to the copolymer structure. These copolymers have previously been studied and optimized as polymeric dispersants for titanium dioxide pigments coated with alumina.[5] Then, they have been used in mill base formulations containing different pigments, i.e., an inorganic pigment (iron oxide: Sicotrans red L2816), a red organic pigment (Irgazin DPP-BO), and a blue organic pigment (Heliogenblue L7101 F), respectively (*Table* 1). The color characteristics of the final paints have been measured and compared to references supplied by Akzo Nobel.

EXPERIMENTAL

The diblock (*Scheme* 1a) and tapered (*Scheme* 1b) copolymers were synthesized by living anionic polymerization of *tert*-butyl methacrylate (tBMA) and DMAEMA in THF at -78°C.[5,6] In case of the diblock, tBMA was first polymerized and used as a macroinitiator for the living polymerization of DMAEMA. The anionic polymerization of the premixed tBMA and DMAEMA co-monomers led to the expected tapered copolymer. The random copolymer (*Scheme* 1c) was synthesized by radical polymerization, under starved conditions, in dioxane at 65°C.[5] tBMA and DMAEMA were premixed and regularly added to the batch reactor all along the polymerization. The main molecular characteristics of the copolymers used in this study are listed in *Table* 2. Finally, the poly(tBMA) block was transformed into a polyacid by acid hydrolysis.

Mill Base

The copolymer in the acid form was solubilized in water according to the recipe reported in *Table* 3. The pH was adjusted between 8 and 9 by addition of 2-dimethylaminoethanol. After addition of the antifoam agent and the pigment, the mill base was ground together with 1.0 mm glass beads with an Eiger Mini

Table 1—Pigments Characteristics

	Pigment	Supplier	Chemical Composition	Specific Surface Area (m^2/g)	Particle Size (nm)	Bulk Density (g/cm^3)
Inorganic red	(Sicotrans™ red L2816)	BASF	Iron oxide (hematite)	93	±10	3.9
Organic red	(Irgazin™ DPP-BO)	Ciba Specialty Chemicals	Diketo-pyrrolo-pyrrol	17	250-400	1.6
Organic blue	(Heliogenblue™ L7101F)	BASF	Cu-phthalocyanine	64	40-50	1.6

Motormill for one hour. The mill base was left standing overnight before characterization.

Masstone

The masstone was prepared according to the recipe reported in *Table* 4 and then homogenized under stirring. It was characterized after overnight aging.

White Reduction

The aged masstone 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.

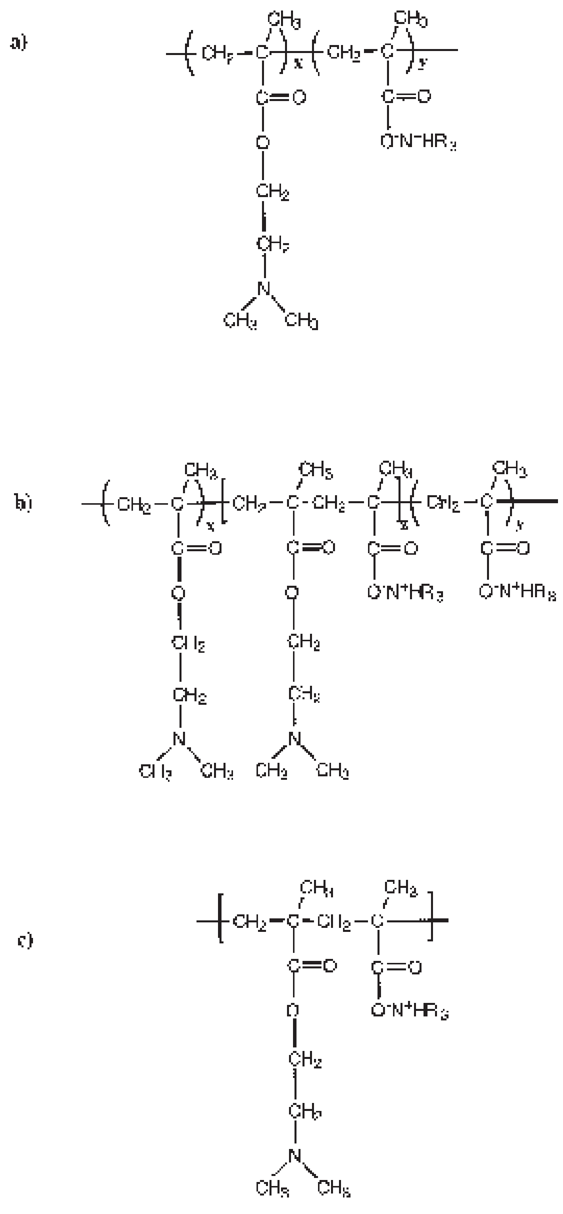
Characterization

Transmissions were measured with a home-built photospectrometer equipped with a daylight source (halogen lamp HLX 64625). All paints (masstone 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 characterization was carried out with the Ultra Scan from HunterLab (ACMP-PC2 software).

RESULTS

The polymeric surfactants used in this study are basically diblock copolymers composed of an anchoring block, thus prone to be adsorbed onto the pigment surface, and of a buoyant polyelectrolyte block, soluble in the aqueous phase and able to provide the pigment dispersion with an electrosteric stabilization. Poly(dimethylaminoethyl methacrylate) has been chosen as the anchoring block, because of possible interactions between the amine groups and the alumina coating through hydrogen bonding and possibly coordinative bonding.[5] An anionic water-soluble block has been preferred to a polycationic block for compatibility with other anionic additives used in the paint formulations, e.g., antifoam agent, binder, etc. Thus although stable dispersions can be obtained with cationic dispersants,[4b] shocking and flocculation might occur by ionic complexation upon the addition of anionic additives. Ammonium polymethacrylate was preferred to a polysulfonate block in order to restrict water uptake by the final paint. Indeed, in contrast to polysulfonate (salt of a strong acid), the ammonium polymethacrylate (salt of a weak acid) will be hydrolyzed in the acid form (and volatile ammonia) by the atmospheric humidity, resulting in a complete loss of water solubility, and therefore, in a substantial decrease of water uptake.

As reported in the experimental part, poly(DMAEMA-b-MANHR$_3$) diblock copolymers have been synthesized by sequential anionic polymerization of DMAEMA and *tert*-butyl methacrylate (tBMA) in THF at –78°C. Since *tert*-butyl is a good leaving group, acid hydrolysis of the polytBMA block easily forms a polymethacrylic acid, which is then neutralized with formation of the expected amphiphilic diblock copolymer. Nevertheless, the one-step anionic copolymerization of some monomer pairs can lead to the formation of copolymer chains with a blocky co-monomer distribution. This type of diblock is known as "tapered" diblock. It is actually the case for the DMAEMA/tBMA pair under consideration in this work. Indeed the reactivity ratios have been measured for the anionic copolymerization in THF at –78°C and found to be $r_{tBMA} = 0.04 \pm 0.07$ and $r_{DMAEMA} = 1.3 \pm 0.4$.[6] These values are consistent with the polymerization of the more reactive monomer, followed by the incorporation of the second monomer as importantly as the residual concentration of the first monomer is decreased



Scheme 1—a) Diblock, b) tapered, and c) random copolymers.

Table 2—Copolymers Characteristics before Hydrolysis of the *tert*-butyl Ester

	Molecular weight[a]	Weight composition[b] (DMAEMA-tBMA)	Mw/Mn[a]
Pure diblock	11000	36 - 64	1.05
Tapered diblock	10500	36 - 64	1.05
Random copolymer	10000	34 - 66	1.9

(a) Determined by size exclusion chromatography in THF/Et$_3$N (see reference 6 for further details).
(b) Determined by ^{1}H NMR.

Table 3—Mill Base Composition

	Amount in gr.	Amount in gr.	Amount in gr.
Inorganic red	15		
Organic red		25	
Organic blue			25
Polymeric dispersant	7.5	7.5	7.5
2-Dimethylaminoethanol	7	7	7
Antifoam agent	0.5	0.5	0.5
Water	70	60	60

Table 4—Masstone Composition

	Amount in gr.	Amount in gr.	Amount in gr.
Inorganic red (mill base)	13.4		
Organic red (mill base)		24	
Organic blue (mill base)			16
Resins (Neocryl® XK62[a])	96	96	96
Butylglycol	4	4	4

(a) S.C. Johnson Polymer.

in the polymerization medium, and the copolymerization ends up with a block formed by the less reactive monomer. Therefore, a tapered diblock has a molecular structure intermediate between a pure diblock and a random copolymer, since two pure blocks are separated from each other by a transition block of a regularly changing composition (*Scheme* 1b). Since less stringent experimental conditions are required for the synthesis of tapered diblocks compared to pure diblocks, it is worthwhile to check to which extent the blockiness of the copolymer is essential for the stabilization efficiency. In order to complete this analysis, the one-step copolymerization of the DMAEMA/tBMA pair has also been carried out in a radical way, which completely changes the reactivity ratios and leads to a non-blocky co-monomer distribution. The reactive co-monomer mixture has been slowly added into the reactor under starved conditions. This copolymer is expected to be of a much broader molecular weight distribution than the two copolymers prepared by the anionic techniques (*Table* 2).

Three DMAEMA/tBMA copolymers: a pure diblock, a tapered diblock and a random copolymer, have been used as stabilizers for the dispersion of three different pigments, i.e., Sicotrans red L2816 (iron oxide pigment), Irgazin DPP-BO (diketopyrrolo-pyrrol pigment) and Heliogenblue L7101 F (Cu-phthalocyanine pigment) (*Table* 1) in waterborne paint formulations. The mill base composition is shown in *Table* 3. A reference mill base has been made available by Akzo Nobel for each pigment. Although of an undisclosed composition, these references differ from the composition in *Table* 3 by the dispersant which has been optimized for each pigment and by addition of several cosolvents to the aqueous phase. In these optimized reference mill bases, the pigment content was lower by 27% for the Sicotrans red L2816 and by 8% for both the Irgazin DPP-BO and the Heliogenblue L7101 F, compared to data in *Table* 3. Indeed the diblock copolymers used in this study allow the pigment content to be increased because of a smaller dispersion shear viscosity, as result of a better dispersion. This viscosity is indeed ca. one-fiftieth of the reference mill base viscosity. Masstones have been prepared as reported in *Table* 4. The pigment content is then the same for these paints as for the references. The masstone has also been mixed with a reference white paint in a 10/90 wt% ratio (white reduction), and the color characteristics (dL, dC*ab) and gloss have been measured as reported in *Tables* 5-7.

It must be clear that paints prepared from mill bases shown in *Table* 3 are preliminary specimens that will be compared to optimum references. The first question to be addressed is to determine whether the polymeric surfactants considered in this study can be effective dispersants for very different pigments.

DISCUSSION

The iron oxide containing mill base, masstone, and paint after white reduction have been first evaluated as reported in *Table* 5. From the transmission of the mill base, it appears that the two diblocks are much more efficient in stabilizing the Sicotrans L2816 dispersion than the random copolymer. Indeed, the very low mill base trans-

Table 5—Characteristics of Inorganic Red Mill Base, Masstone and White Reduction

	Mill Base	Masstone		White Reduction		
	Transmission (%)	Transmission (Dry paint) (%)	Gloss	dL	dC*ab	Gloss
Reference	72	75	97	0	0	73
Pure diblock	54	48	82	2.0	-4.7	65
Tapered diblock	59	33	80	1.8	-3.5	67
Random copolymer	12	35	84	3.2	-7.9	61

Table 6—Characteristics of Organic Red Mill Base, Masstone and White Reduction

	Masstone	White Reduction		
	Gloss	dL	dC*ab	Gloss
Reference	56	0	0	40
Pure diblock	35	3.63	-6.42	24
Tapered diblock	37	3.31	-6.12	24
Random copolymer	20	4.63	-11	24

mission observed in the presence of the random copolymer confirms a partial flocculation of the dispersion. In contrast, the addition of the binder erases the difference in transmission and leads to comparable gloss for the masstone whatever the polymeric stabilizer. Clearly, a large amount of binder (Neocryl XK62) decreases the opportunity for the pigment particles to flocculate, and, in case of the random copolymer, compensates for a poor stabilizing efficiency. This might be due to the surfactant present in the binder. Nevertheless, after white reduction, the superiority of the diblocks over the random copolymer is confirmed by the color characteristics (dL, dC*ab), but not by the gloss. This might indicate that gloss is less sensitive to some flocculation than the color tone (value L and chroma C) in the case of the very small iron oxide pigment. With respect to the reference, the final paint is lighter (ΔL>0) and less vivid (ΔC*<0) when a DMAEMA containing copolymer is used. The comparison of the three copolymers analyzed in this study is in favor of the block copolymers, which cannot be discriminated. Compared to the best reference, the novel, but not yet optimized, mill base and paint have lower performances. However, it must be emphasized that these mill bases are purely aqueous dispersions, in contrast to the reference which cannot be prepared without the addition of some organic solvent. The higher pigment content that the mill bases stabilized by the diblock copolymers can tolerate is another important advantage over the reference.

In order to know whether the DMAEMA containing copolymers are suitable for the dispersion of organic pigments, a red organic pigment, Irgazin DPP-BO, has been substituted for the iron oxide, and the reference has been prepared with a dedicated dispersant. Transmission of the mill bases has not been measured because of the opacity of the Irgazin DPP-BO pigment. The two diblock copolymers provide the paint, before (gloss) and after white reduction (dL, dC*ab), with better dispersion and stability than the random copolymer (*Table* 6). Differences with respect to the reference are more important in the case of this organic pigment compared to the previous inorganic one. The blockiness of the added copolymers is again a prerequisite for efficient dispersion and stabilization and thus for paints with good color characteristics. The poorer results in *Table* 6 compared to *Table* 5 might be attributed to the absence of coordinative interactions between Irgazin DDP-BO and the DMAEMA units of the stabilizer. Only hydrophobic interactions can occur, although coordination of the amine groups onto the iron atoms of Sicotrans are more likely responsible for a stronger anchoring of the diblocks in case of this inorganic pigment. A more hydrophobic polyaminated block is expected to improve the data reported in *Table* 6, independently of any possible improvement of the formulations reported in *Tables* 3 and 4 for the mill base and the masstone, respectively.

In order to support that specific interactions between the anchoring block and the pigment surface have a decisive effect on the pigment dispersion, a Cu-phthalocyanine pigment has been considered. Indeed, the polyamine anchoring block can strongly interact with the pigment surface by complexation of the copper cations along the edges of the crystalline structure.[7] The random copolymer cannot provide the dispersion with stability during the milling process, so that no color characteristic has been measured. In contrast, the pure diblock copolymer is at the origin of color characteristics as good as the reference formulation (*Table* 7). The tapered diblock also gives excellent properties, although slightly inferior to those shown in presence of the pure diblock.

Thus, polymeric dispersants consisting of a major polyelectrolyte stabilizing block and a minor polyaminated block are as efficient as more specific interactions can occur between the pigment surface and the anchoring block while all the other conditions remain the same. These water-soluble polymeric dispersants also have the advantage to be used without any additional organic cosolvent, and to tolerate a higher pigment content for the mill base, compared to the optimum reference. In fact, the pigment loading should be increased further in order to increase the shear viscosity of the dispersion and accordingly the transfer of the mechanical energy to the aggregated pigment particles. Indeed, the shear viscosity of the mill bases reported in *Table* 3 is much lower (by ca. 50) than to the parent references. The transmission difference between references and the samples could be caused by the very low viscosity—and consequently very bad milling efficiency—of the mill base. This is often the case and was later proved in additional experiments. The experimen-

Table 7—Characteristics of Organic Blue Mill Base, Masstone and White Reduction

	Mill Base	Masstone	White Reduction		
	Transmission (%)	Gloss	dL	dC*ab	Gloss
Reference	29	80	0	0	71
Pure diblock	32	76	0.7	-0.4	68
Tapered diblock	31	82	2.1	-1.0	68
Random copolymer	No stable dispersion				

tal data reported in *Tables* 5-7 may be improved in a way that would make high-solid paints available. The reported combination of a low mill base viscosity and the possible increase of the pigment loading may allow a progressive shift from traditional waterborne paints to more desirable high-solid paints.

CONCLUSION

The preliminary results reported in this paper have shown that organic solvent-free paints can be produced with very favorable color characteristics. Copolymers of ammonium methacrylate and dimethylaminoethyl methacrylate have a great potential as polymeric dispersants for waterborne paints provided that the co-monomer distribution is blocky enough. The copolymer composition must be such that it is water-soluble and allows a strong enough anchoring onto the pigment surface. In this respect, the polyaminated component can be regarded as "universal," since it is able to stabilize the fine dispersion of pigments as different from each other as inorganic pigments (iron oxide) and organic pigments.

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