

Synthesis and Characterization of Comb Polycarboxylic Acid Dispersants for Coatings

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Received 17 April 2011; accepted 10 October 2011

DOI 10.1002/app.36311

Published online in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: Comb polycarboxylic acid dispersants (CPCADs) graft acrylic copolymers which consist of hanging methoxy polyethylene glycol chains and carboxylic acid groups on main acrylic chain. The CPCADs have been synthesized by radical polymerization of methacrylic acid and methoxy polyethylene glycol methacrylate as a nonionic unsaturated hydrophilic macromonomer. The CPCADs are polymeric surfactants that can be used as anionic dispersant. Methoxy polyethylene glycol methacrylate has been synthesized by esterification of methacrylic acid and methoxy polyethylene glycol in the presence of methanesulfonic acid as catalyst. These have been charac-

terized with ¹H-NMR and GPC. Acid values of CPCA dispersants have been determined. The dispersion of CPCA dispersants depends on their molecular weights, length mPEG, and acid values. Dispersion of titanium dioxide in typical solvent-based paint formulation has been investigated. The physicochemical and mechanical properties of surface coatings having CPCADs such as gloss, hardness, and contrast ratio have been investigated. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

Key words: synthesis; graft copolymer; polymeric dispersant; polycarboxylic acid; comb surfactant

INTRODUCTION

Polymeric dispersants have been available for recent years with improved performance over traditional surfactants.^{1–3} Surfactants typically have a two-part structure: a hydrophilic chain for steric stability and a hydrophobic group for pigment wetting or anchoring. Steric stability is achieved by providing a polymeric layer around the pigment particles which overcomes the normal tendency of the particles to associate with each other. The surface activity of these surfactant groups leads to a range of prosperities (foaming/defoaming, wetting/dispersing, emulsification, and solubilization) of which some are desirable and some detrimental to coating performance. The continuing developments in high molecular weight polymeric dispersants are aimed at improving and maintaining the desirable characteristics while minimizing or eliminating the negative aspects, particularly with regard to water sensitivity. In water-based systems, electrostatic stabilization is also often used since a charged double layer will provide interparticle stability, particularly in the wet paint. A dispersant is a term referring to specific additives that improve the dispersion of solid particles in a liquid medium.

Traditional surfactants encompass this behavior and a very broad class of materials falls within this general group.^{4,5}

Polymeric dispersants stabilize colloidal systems via a mechanism commonly known as steric stabilization. In physicochemical terms, polymeric dispersants can reduce interactions between pigment particles much more effectively than conventional dispersants can. The most obvious consequence of this is an ability to reduce viscosity in a pigment-containing formulation. Polymeric dispersants are therefore excellent for reducing the viscosity of millbases, but their influence on the rheology of the final paint or ink depends very much on the type of coating system.^{6–8}

The ability to reduce pigment particle–pigment particle interactions also confers a series of benefits of polymeric dispersants into productivity advantages (higher pigment concentrations), color strength advantages (more efficient use of color), and paint quality advantages.^{9,10} Flooding and floating effects are dependent on the degree of pigment flocculation and the relative densities and sizes of the different pigment particles in the system. A paint system is optimized by balancing these variables, and polymeric dispersants offer a way to modify the flocculation/deflocculation balance. The gloss of a surface coating system is clearly sensitive to the presence of any large particles. By increasing the efficiency of the grinding process, polymeric dispersants can ensure the absence of large pigment particles. The

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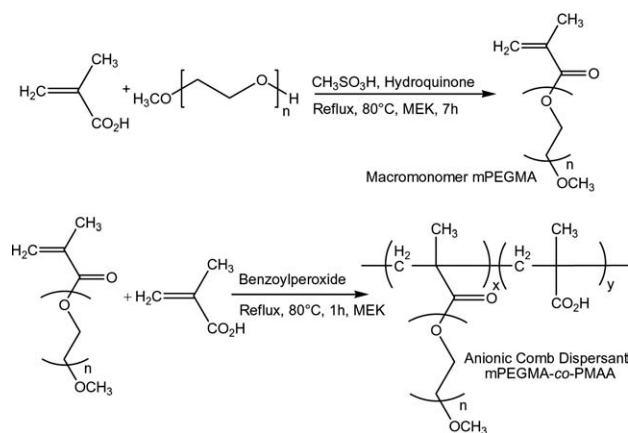


Figure 1 Synthesis of comb polycarboxylic acid (CPCA) dispersants.

particle size distribution in a dispersed pigment system is known to influence the brightness of a surface coating. Polymeric dispersants can improve the brightness through their effect on the efficiency of the grinding process. Through their ability to reduce interactions between pigment particles, polymeric dispersants can improve the flow (i.e., reduce the viscosity) of surface coating systems, especially high pigment concentration systems such as high-solid paints and high-built paints. Completely synthetic polymers as dispersing agents have come in use only in recent decade and they have contributed significantly to the formulation of higher quality coatings. The following classification is useful for polymeric dispersant: (a) micromesh waxes, (b) polyelectrolyte, (c) acrylic graft copolymer, and (d) acrylic random copolymer.^{11–14}

Molecular structure of surfactants encompasses two groups of very different solubility or opposite polarity. For dispersants, the key properties are the wetting, dispersing, and stabilization of solid particles (such as pigments) into the liquid. After the initial wetting of the pigment surface, the particle agglomerates formed by pigment production processes are further broken down by mechanical milling. The dispersant absorbs onto the freshly created surface forming a stabilizing polymer layer.^{15–17} This steric stabilization helps to create an energy barrier around each particle and prevents the natural tendency of the particles to reagglomerate due to the attractive London-van der Waals forces. An alternative to steric barrier, especially in water-based systems, is charge or electrostatic stabilization. The steric and electrostatic stabilization (DVLO theory) mechanisms have been extensively reviewed and a more detailed examination of these mechanisms can be found in literatures. In a complex formulation, there may be a number of different surface active species involved which lead to the problems. Most problems can be categorized by surface tension defects (cratering, fish

eyes, crawling, orange peel, Benard cells) or pigment dispersion problems (flooding, floating, poor gloss, or color development). The development of high molecular weight polymeric dispersants has been driven by the need to improve the desirable characteristics of this additive group while minimizing or eliminating the negative aspects.^{18,19}

In this research, our aim was to design, synthesize, and characterize novel water-soluble polycarboxylate ether copolymers (mPEGMA-co-PMAA) that can be used as an anionic dispersants in formulation of solvent paints.

EXPERIMENTAL

Materials

Materials in this research were methacrylic acid, benzoyl peroxide, acetone, methyl ethyl ketone, toluene, *n*-hexane, hydroquinone, and butyl acetate from Merck. The methoxy poly(ethylene glycol) mPEGs ($M_w = 350, 550, 750$) were used as received from Fluka without further purification. Acrylic resin (STR 30) and TiO_2 obtained from Simab Resin Co. and Chemira.

Instruments for characterization of acrylic dispersants were $^1\text{H-NMR}$ 500 MHz Bruker and GPC 150C Waters. Instruments for dispersing of TiO_2 by comb acrylic dispersants were mixer IKA, Gloss Meter Gardner BYK, Konig (Sheen) Hardness Tester and a Grindometer (Brave Co.).

Methods

Synthesis of comb polycarboxylic acid (CPCA) dispersants

The comb polycarboxylic acid dispersants have been prepared from macromonomer methoxy poly

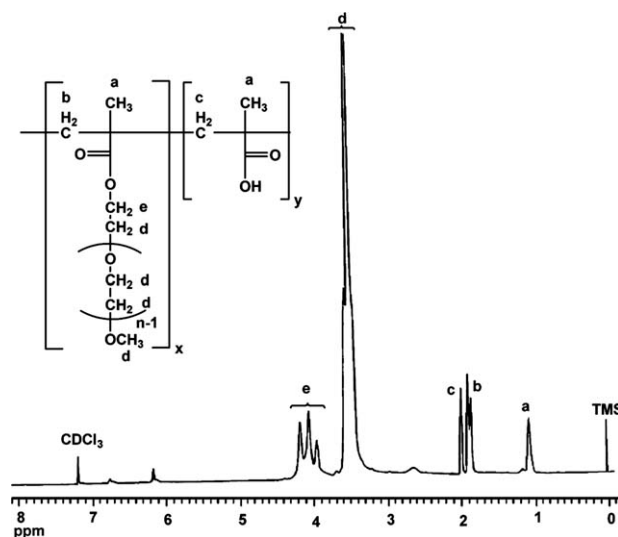


Figure 2 $^1\text{H-NMR}$ spectrum of anionic comb dispersants (mPEGMA-co-PMAA).

TABLE I
Properties of Comb Polycarboxylic Acid Dispersants

mPEGMA- <i>co</i> -PMAA	mPEG (M_w)	Molar ratio (mPEGMA/MAA)	M_w	Acid value (mg KOH/g)
CPCA-1	350	1 : 0.25	3720	113
CPCA-2	550	1 : 0.25	4486	108
CPCA-3	750	1 : 0.25	9720	80

(ethylene glycol) methacrylate (mPEGMA) and methacrylic acid (MAA) by radical polymerization in special conditions.

The mPEGMA has been prepared by condensation of methacrylic acid (MAA) and mPEG ($M_w = 350, 550, \text{ or } 750$) in presence of methanesulfonic acid (MSA) as the catalyst and hydroquinone as the radical polymerization inhibitor, in methyl ethyl ketone (MEK) at 80°C for 7 h. The product was collected by precipitation in *n*-hexane twice and dried in an oven.

The anionic comb dispersants (mPEGMA-*co*-PMAA) have been prepared from mPEGMA and methacrylic acid through free radical polymerization. Figure 1 shows the synthesis of anionic comb dispersants schematically. Benzoyl peroxide was used as the initiator. In this typical synthesis, the molar ratio of mPEGMA:MAA was 1 : 0.25. The mixture in MEK was refluxed at 80°C for 1 h by purging N_2 gas. After the reaction was completed the mixture was precipitated and washed with *n*-hexane, then the remaining precipitate which is mPEGMA-*co*-PMAA was dried in an oven till a constant weight is reached. In this study, copolymers with different molar ratio of mPEGMA and MAA monomers have been synthesized.

RESULTS AND DISCUSSION

Figure 2 shows the $^1\text{H-NMR}$ spectrum of anionic comb dispersants (mPEGMA-*co*-MAA) in CDCl_3 . The CH_2 protons of mPEG segments in graft copolymeric surfactants were in 3.5–3.6 ppm on $^1\text{H-NMR}$ spectrum. The protons of CH_2 on the backbone were in 1.8–2.0 ppm. The CH_3 protons of substitution on the backbone were in 1.2–1.3 ppm. The CH_3 protons of methoxy mPEG were in 3.6 ppm. Molecular weight and acid value of CPCA dispersants have been shown in Table I.

Action of comb polycarboxylic acid (CPCA) dispersants in surface coatings

The concept behind polymeric dispersants is very simple. A layer of polymeric material must be adsorbed onto the surfaces of particles in a colloidal system, and then, for the thermodynamic reasons, the particles can be kept apart. The polymeric dispersant must therefore have a structure that meets two very different requirements: (1) The molecule must contain polymeric chains that give steric stabilization in the required solvent or resin solution system, and (2) it must be capable of being strongly adsorbed onto the particle surface.

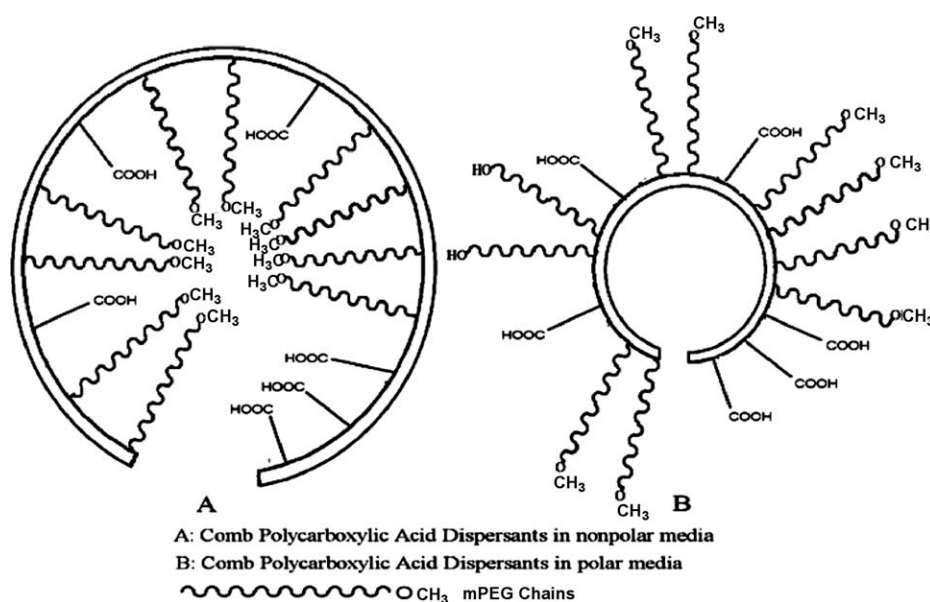


Figure 3 Self-assembly of comb polycarboxylic acid dispersants in (A) organic solvent (B) water media.

TABLE II
Formulation of Acrylic Coatings

Ingredients	Weight (%)
Acrylic resin (STR 30)-Simab resin	74.4
TiO ₂ (Chemira)	16.3
Comb polycarboxylic acid dispersants (CPCADs) in MEK (30%)	0.2
Thinner: toluene (75%), MEK (15%), acetone (5%), and butyl acetate (5%)	9.1

Clearly, homopolymers are not going to meet these two different requirements. Obviously, some form of functionalized polymer or copolymer offers the best opportunity. Self-assembling of comb polycarboxylic acid dispersants may be of two forms as shown in Figure 3. Possible arrangements of CPCA dispersants depend on kind of media and charge of pigment. Configuration A in Figure 3 is suitable for organic solvent media. Also the steric stabilization pigment particles are built by graft mPEG chains on backbone of CPCA dispersants. Table II shows formulation of acrylic paints having comb polycarboxylic acid dispersants.

Some properties such as dispersion rate, glossiness, and hardness of surface coatings are affected by kind dispersants. Therefore, for assessment of dispersants efficiency, mentioned properties have been considered.

Reducing the particle sizes of TiO₂ in paint is an important factor in dispersion process; also reduced particle size is an effectiveness parameter for selecting dispersant. Increasing the rate of dispersion leads to decreasing the cost. The dispersants were formulated according to Table II, then at the period of 60 min, decreasing of TiO₂ particles in acrylic resin (STR 30) was considered (Figure 4). At first, particle size in each formulation was up to 100 μm . According to results, overall the dispersion rate of TiO₂ in presence of CPCA dispersants increased with rising acid values and also lengths of mPEG in CPCA. Of course, the effect of increasing acid value was more important than arising of graft mPEG in CPCA. Maximum rate of dispersion is obtained when surfaces of particles and chains of resin are bonding each other.

The results show that decreasing rate of TiO₂ particle sizes by CPCA-3 dispersant in acrylic resin is

TABLE III
The Hardness, Gloss, and Contrast Ratio of Acrylic Coatings Having TiO₂ Affected from Dispersants in Particle Sizes of 10 μm

mPEGMA-co-PMAA	Konig hardness ASTM-D4366	Gloss in 20° ASTM-D 5767	Contrast ratio
CPCA-1	31	31	91.2
CPCA-2	26	27	93.6
CPCA-3	30	36	90.2

higher than other dispersants. On the other hand, CPCA-1 dispersant has the dispersion rate lower than of CPCA-3 dispersant, but in the end of dispersion process, TiO₂ particle sizes were lower than other dispersants. The dispersion mechanisms of synthesized CPCA dispersants are through steric stabilization. The dispersion mechanism of CPCA-3 dispersant is mainly through steric because of long mPEG chains on the backbone of dispersant and higher absorption of dispersant onto the surface of pigments. CPCA-3 dispersant has higher M_w and lower acid value, so the solubility in the paint media is lower than other samples. The lower the solubility, the higher the absorption and the lower desorption probability.

In the ideal dispersion, particle size will be fine and amount of adsorbed resin on the particles increases, so surface of final film will be smooth and reflectance of film surface increases. Glossiness of acrylic coatings depends on some parameters such as shape, size, and kind of dispersants. As results show, the presence of the dispersant may increase the efficiency of the grinding process and ensure the absence of the large pigment particles which results in smoother surfaces and higher gloss of the final paint film.

For assessment of hardness, acrylic coatings with thickness 90 μm are applied on glass surface by applicator. Then hardness of samples is measured

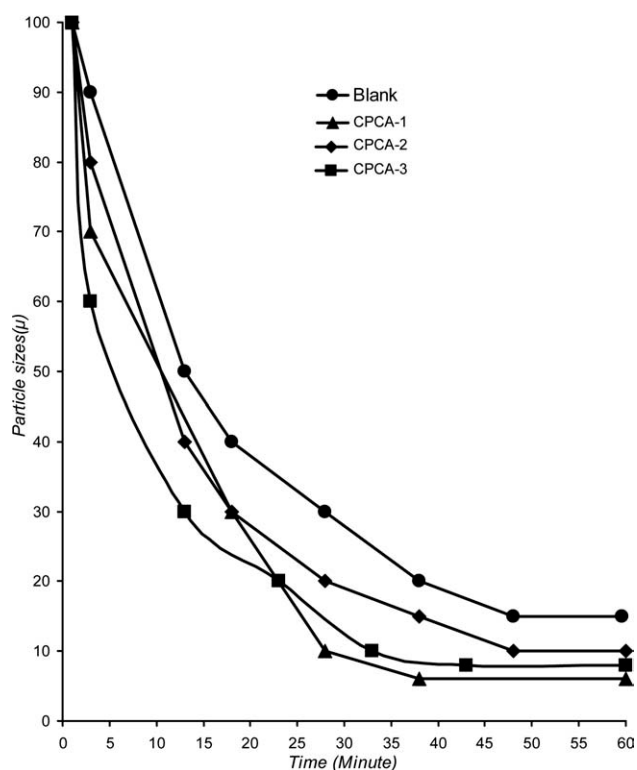


Figure 4 Decreasing particle size of TiO₂ in an acrylic paint during 60 min.

by König hardness meter (Sheen) and pencil hardness (Table III). Hardness of final films depends on kind of pigment, filler, kind of resin, kind and amount of dispersant, and crosslink density of final film. In this, parameters such as kind of resin and kind of pigment and filler are identical, so difference in hardness depends on action of dispersants. It seems that the presence of dispersant has no negative effect on the hardness of final paint film.

Contrast ratio at a specified film thickness is a useful hiding power parameter; it shows the ability of a coating to prevent the transmission of light. As Table III shows, the contrast ratio is high enough in all samples and there is no significant difference between different samples.

CONCLUSIONS

Comb polycarboxylic acid dispersants (CPCADs) are graft acrylic copolymers that have been synthesized by radical polymerization. Chemical structure of CPCA dispersants has been formed from PMAA blocks having COOH acidic groups and graft methoxy polyethylene glycol (mPEG) chains as hydrophilic segments. The dispersion mechanisms of CPCA-3 dispersant are mainly through steric because of long mPEG chains on the backbone of dispersant, but for CPCA-1 dispersant, dispersion mechanism is mainly electrostatic due to high acid value (a lot of carboxylic acid groups) on the backbone of dispersant. According to results, overall the

dispersion rate of CPCA increased with rising acid values and also length of mPEGs in CPCADs.

References

1. Liu, Q.; Li, Y.; Yao, L.; Yao, Sh. *J Sep Sci* 2009, 32, 4148.
2. Yoon, Ch.; Choi, J. H. *Color Technol* 2008, 124, 355.
3. Kim, S.; Lee, J. *Int J Pharmaceut* 2010, 397, 218.
4. El-Dougoud, W. I. A.; El-Mossalamy, E. H. *Appl Surf Sci* 2006, 253, 2487.
5. Büyükyavaş, A.; Tuzcu, G.; Aras, L. *Cement Concrete Res* 2009, 39, 629.
6. Nasu, A.; Otsubo, Y. *Colloid Surf A: Physicochem Eng Aspects* 2008, 326, 92.
7. Deshmukh, S.; Bharambe, D. P. *Fuel Process Technol* 2008, 89, 227.
8. Yoon, Ch.; Choi, J. H. *Color Technol* 2008, 124, 355.
9. Farrokhpay, S. *Adv Colloid Interface Sci* 2009, 151, 24.
10. Farrokhpay, S.; Morris, G. E.; Fornasiero, D.; Self, P. *Powder Technol* 2010, 202, 143.
11. Calbo, L. J. *Handbook of Coatings Additives*, Marcel Dekker: New York, 1992; Vol. 2.
12. McKay, R. B.; Smith, F. M. In *Dispersion of Powders in Liquids*, 3rd ed.; Parfitt, G. D., Ed.; Applied Science: London, 1981, p 471.
13. Napper, D. H. *Polymeric Stabilisation of Colloidal Dispersions*; Academic: London, 1983, p 114.
14. Doroszkowski, A.; Lambourne, R. J. *Colloid Interface Sci* 1973, 43, 97.
15. Menger, F. M.; Littau, C. A. *J Am Chem Soc* 1991, 113, 1451.
16. Menger, F. M.; Keiper, J. S. *Angew Chem Int Ed* 2000, 39, 1906.
17. Zana, R.; Xia, J. *Gemini Surfactants: Synthesis, Interfacial and Solution-Phase Behavior, and Applications*; Marcel Dekker: New York, 2004.
18. Cairns, R. J. R.; Ottewill, R. M.; Osmond, D. W. J.; Wagstaff, I. *J Colloid Interface Sci* 1976, 54, 45.
19. Patton, T. C. *Paint Flow and Pigment Dispersion*, 2nd ed.; Wiley: New York, 1978, p 597.