

POLYMERIC
ADDITIVES
FOR
HIGH
PERFORMING
DETERGENTS

Paolo Zini

POLYMERIC ADDITIVES FOR HIGH PERFORMING DETERGENTS

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Amicus Plato, sed magis amica veritas

Introduction

THIS book is about the use of polycarboxylated polymers in detergents and cleaners, for both fabric washing, automatic dishwashing and industrial detergents. It is about "performance polymers," i.e., those polymers which improve the final wash end-result of detergents. As such, it does not cover other polycarboxylated polymers, like thickeners, whose function is confined to the physical aspect and characteristics of the marketed product.

The book is intended to be a practical guide on how polycarboxylated polymers are designed, in theoretical terms and from bench testing, and on how they can be employed in modern detergents. Results are reported from many different sources: e.g., polymers producers, detergent producers, and suppliers of the detergents industry. Since several theories on the functional mechanisms of polymers in detergents have been proposed, this book tries to report the different points of view, even though sometimes they seem, and in fact they are, contradictory.

In spite of several years of studies and hundreds of testing protocols, the exact mechanisms by which polycarboxylated polymers help detergency are still the subject of debate. Since the contribution of polymers does indeed show up under different forms and under different types of synergisms, it is conceivable that the measurement of this contribution changes somewhat with the type of testing employed.

Since their earlier introduction in regional detergents in Europe in 1978, the use and selection of polycarboxylates in detergents has been a largely empirical evolution, dictated more by evolving market needs than by a planned development. It was only in the mid 1980s that specific development programs were started in most large detergents companies to anticipate the future needs, characteristics, and performances achievable with polycarboxylated polymers.

Similarly, the polymer producers have engaged in long-range development to provide the industry with safer and more cost-effective polymers, of constant quality and reduced residual monomer content, of tight

molecular weight distribution and of improved environmental compatibility. Publications, conferences, and university studies have continued to give more insights about polymers, the interest in which increases with the increased market demand for more compact detergents which will provide more performance per kilogram.

I would like to thank collectively all the people in the industry and at universities who helped me in this task with data, suggestions, and encouragement. They all made this book possible.

Table of Contents

Introduction ix

1. DESIGNING DETERGENT POLYMERS	1
1.1 A Multivariable Problem	1
1.1.1 <i>Infinite Variations</i>	1
1.1.2 <i>Performance Characteristics of Detergents</i>	14
1.2 Organic Sequestrants	16
1.3 Performance Features of Polymers	30
1.4 Endnotes	64
2. PHOSPHATE REDUCTION AND PHOSPHATE SUBSTITUTION	67
2.1 Polymers and Phosphate	67
2.2 Phosphate in Powder Detergents	68
2.3 Spray-Drying of Tripolyphosphate	70
2.4 Insoluble Precipitates with Phosphates	73
2.5 Formulating Low Phosphate Household Detergents: A Mathematical Model	77
2.5.1 <i>The Analytical Model</i>	79
2.5.2 <i>The Mathematical Model</i>	83
2.5.3 <i>The Determination of the Coefficients</i>	87
2.5.4 <i>Not a Unique Conclusion</i>	90
2.6 A Practical Case of Tripolyphosphate Reduction	91
2.7 Endnotes	95
3. ENVIRONMENTAL CONSIDERATIONS	97
3.1 Detergents and the Environment	97
3.2 Polymers and the Environment	100
3.3 Biodegradation and Elimination Tests	103
3.4 Endnotes	113

4. MODERN DETERGENTS	115
4.1 Efficient Raw Materials	115
4.2 Polymers for Compact Detergents	125
4.3 Waterless Polymers	135
4.3.1 <i>Granulometry</i>	136
4.3.2 <i>Hygroscopicity</i>	139
4.3.3 <i>New Properties from Waterless Granules</i>	139
4.4 Endnotes	143
5. POLYMERS FOR FABRIC WASHING: THE HARDWARE	145
5.1 Laundry Washing Machines	145
5.2 Laundry Washing Habits	151
5.2.1 <i>Temperature</i>	152
5.2.2 <i>Load Composition</i>	156
5.2.3 <i>Mechanical Energy</i>	162
5.3 Influence of Washing Conditions on Polymer Performance	165
5.4 Endnotes	176
6. POLYMERS FOR FABRIC WASHING: THE BUILDER SYSTEMS	179
6.1 Binary Builder Systems	179
6.2 Multicomponent Builder Systems	197
6.3 Endnotes	212
7. POLYMERS FOR AUTOMATIC DISHWASHING	213
7.1 Low and Zero Phosphate Autodishwashing Products	213
7.1.1 <i>Low Phosphate Formulations</i>	217
7.1.2 <i>Zero Phosphate Formulations</i>	223
7.2 A Factorial Analysis of the Key Variables	228
7.3 Endnotes	248
8. POLYMERS FOR INDUSTRIAL DETERGENTS	251
8.1 Market Trends	251
8.2 Key Features of Polymers	254
8.3 Warewash and Laundry Applications	263
8.4 Endnotes	271

<i>Bibliography</i>	273
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Designing Detergent Polymers

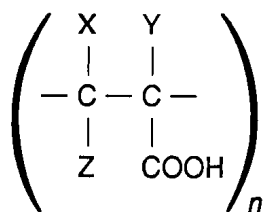
1.1 A MULTIVARIABLE PROBLEM

1.1.1 INFINITE VARIATIONS

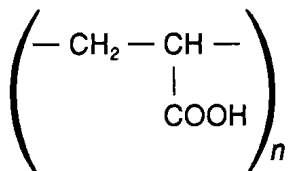
PROGRESS in the synthesis of relevant organic molecules has been so dramatic in the last twenty years that most of the “theoretical” structures one can design on a piece of paper, to try and reach a certain performance attribute, can in fact be obtained through a polymerization process of industrially scalable sequence.

While this may be seen at an early stage as very exciting and the source of a broad spectrum of possibilities, it is also a dangerous trap for the polymer scientist and for the detergent formulator working on these problems. There are in fact too many variables which can be tested, and too many variables which look promising for further testing: the experimental design in most cases becomes very complex and heavy to run, to follow, and finally to analyze statistically. The actual exploitation of the large data bank becomes a real obstacle to product development, or at least to conveniently fast product developments like those a specialty chemical industry should run to keep afloat in modern, competitive markets.

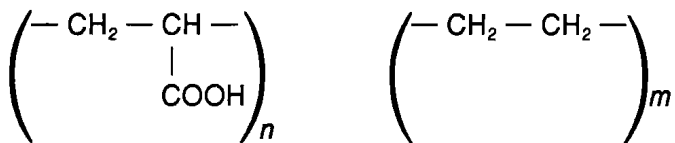
As an initial example, we can consider the case of a “straight” polycarboxylated polymer, one in which only carboxylic groups are considered as active groups for the task under study. This polymer would be described by the following structure:



The “minimum configuration,” i.e., the structure with the lowest carboxylate density in the schema above, will be when all X, Y, and Z are hydrogens and the shown monomer is the acrylic acid:

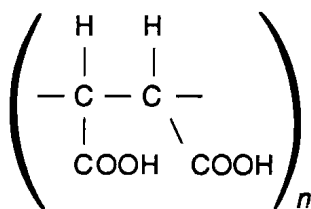


However this formulation contains already a misleading information about the density of the charges along the chain: although the acrylic acid could be described as the lowest charge density monomer responding to the schema, a homopolyacrylate polymer would definitely not be the lowest density charge chain, as one could quickly conclude. In fact it is possible to copolymerize uncharged monomers within the sequence of the acrylic acid monomers and actually obtain a polymeric chain of a total charge density inferior to the homopolyacrylate chain. For instance by copolymerizing ethylene monomers in the acrylate chain one can get to a polymeric structure having the following structure:



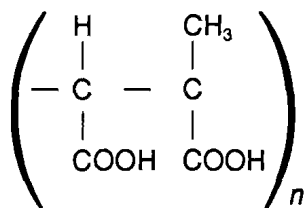
The net result is that we have increased the distance between adjacent carboxylates by several times, which will for sure modify their interactions with both soluble ions and surfaces.

At the other extreme of the chain modification, as far as the charge density along the polymer chain is concerned, we can homopolymerize maleic anhydride, a monomer which still is described by the initial schema, once the Z group is also a carboxylate and both X and Y are hydrogens:

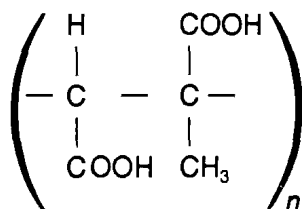


Here we have reached the charge density of one carboxylate group per carbon atom in the backbone chain, which is a quite high charge density obtainable with a relatively inexpensive monomer, readily available around the world.

Two other structures which reach the same charge density are the two isomers:

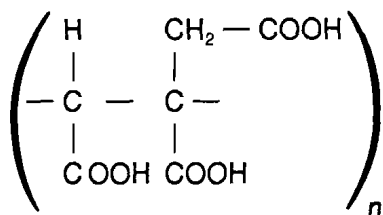


of the citraconic acid, and:

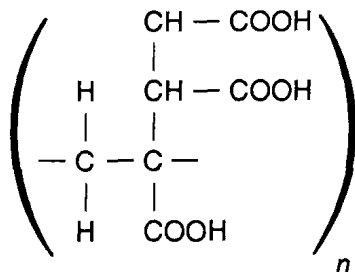


of the mesaconic acid. Both introduce a steric impediment of a CH_3 group with respect to the straight maleic anhydride and are not used in practice for detergent polymers.

Other high charge density monomers are more theoretical than practical, i.e., they are for the moment only a laboratory curiosity without clear viability in the marketplace. One is aconitic acid:



and the other is 3-butene-1,2,3-tricarboxylic acid:



In both of them the structure is rather complex and the actual charge density does not exceed that of the polymaleic polymers.

The two copolymerization examples of maleic anhydride and of ethylene show that we can already count here a multitude of polymer variants: in both cases, i.e., copolymerizing the nil charge monomer of ethylene or the high charge density monomer of maleic anhydride with the “medium” charge density acrylic acid, we get two polymer series of step by step change in charge density. Since we can copolymerize with the acrylic acid “any” proportion of comonomer, from say 0.5 % molar to say 99 % molar, we have access to an infinite variability in the average charge density along the chain.

The charge density along the chain is a key parameter determining the performance features of a polymer. The charge density determines very important effects like the interaction with surfaces, for the adsorption and desorption mechanisms, and the interaction with positive soluble ions, for the sequestration and the solubility of the polymer-ion complex.

The second key parameter which can vary across very large ranges is the molecular weight. The first measure usable for describing a polymeric chain is the number-average molecular weight, M_n , defined by the mathematical equation:

$$M_n = \frac{\text{total weight of the system}}{\text{molecules in the system}}$$

or in this case:

$$M_n = \frac{N_i * M_i}{N_i^*}$$

where:

N_i = number of molecules having a molecular weight M_i

Clearly this average molecular weight is an extremely basic measure, which only superficially describes the actual polymer under consideration. As an example we can consider two homopolyacrylate polymers produced by different plants and characterized in detail by the two molecular weight distributions shown in Table 1.1. The two distributions show the percentages of molecules in each polymer batch having the molecular weight between the limits indicated in the first column.

Both homopolyacrylate polymers will be described by the mathematical equation as having very close number-average molecular weights: 4150 for polymer A and 4100 for polymer B, considering the molecular weight of each group equal to the average of the group range (i.e., 1500 for the first group, 3000 for the second, and so on).

TABLE 1.1.

Molecular Weight	Polymer A	Polymer B
1000-2000	10%	20%
2000-4000	40%	30%
4000-6000	40%	30%
6000-8000	10%	20%

But clearly the two polymers are indeed different. In particular, polymer B has more short (below 2000) and more long (above 6000) molecules than polymer A. This latter has a tighter distribution curve of the molecular weights, with 80% of the molecules between 2000 and 6000 molecular weights. Independent of the differences in performance, which could be measured subsequently, the minimum we can say is that the plant producing polymer A has a better process control, i.e., it can manage the homopolymerization of the acrylic acid in a more consistent way. This is really not reflected by the simple M_n values.

A second method of measuring the polymer molecular weight has been therefore devised to cope with the above problem and to give an indication of the possible differences in the molecular weight distribution of the polymer. This method consists in calculating the weight-average molecular weight, M_w , from the equation:

$$M_w = \frac{N_i * M_i^2}{N_i * M_i}$$

where N_i and M_i have the same meaning as before.

This is an average of second order for the molecular weight with respect to the number of molecules: the long polymer chains are not only counted by their number, but their weight is counted as the square of their value. Therefore there is a certain compensation vs. the possibility of being "overruled" in the calculation of the number-average molecular weight by the number of short molecules in the polymer mix.

By its calculation equation, and more in general by its calculation philosophy of giving more importance to the short molecules, the number-average molecular weight cannot be higher in value than the weight-average molecular weight, which by contrast favors the long molecules in the calculation. It is therefore possible to calculate another parameter, called the ratio S :

$$S = M_w/M_n$$

which gives an indication of the spread of the molecular weights around the

average. For example we can re-calculate the average number molecular weight (both the number-average and the weight-average) and the spread coefficient S for the two polymers shown in Table 1.1. These results are shown in Table 1.2.

We see now that we have two additional pieces of numerical information to better judge if the two polymers are indeed equal to each other, as we were led to believe from the initial number-average molecular weight M_n figures. In fact this new information allows us to conclude that they are not, and that polymer A, with its lower spread coefficient, has a tighter distribution of molecular weights around the average. The calculations based on the weight-average molecular weight would tend to say polymer B is on average longer than the polymer A, whilst the calculations based on the number-average molecular weight would have come to the opposite conclusion.

But the measured molecular weight, whether the weight molecular weight or the number molecular weight, can still be a source of miscommunication among polymer scientists and detergent formulators if we consider more complex copolymers than those discussed based on acrylic acid. For instance, there is the case of copolymers where one of the monomers has a molecular weight greatly different from the other.

As an example, we can consider the two copolymers in Table 1.3. Except for the fact that the comonomer is different, the two polymers could seem to be rather similar to each other (low molecular weight, equal amount of comonomer in the chain, similar spreading of the molecular weights around the average). However, this is not the case since MAA has (as monomer) a molecular weight of 86, whilst DMAEMA has a molecular weight of 157.

Since the acrylic acid has a molecular weight of 72, the copolymers are rather different as far as the "chain modification" is concerned. We see this in Table 1.4.

Copolymer X has about 6.2 molecules of methacrylic acid over the 42 monomers in an average polymer molecule, whilst copolymer Y has only 3.4 molecules of DMAEMA in an average polymer chain. When we try to depict the two copolymers in terms of possible configuration in water, they

TABLE 1.2.

Molecular Weight	Polymer A	Polymer B
1000-2000	10%	20%
2000-4000	40%	30%
4000-6000	40%	30%
6000-8000	10%	20%
Avg. number M_n	4150	4100
Avg. weight M_w	4463	4888
Spread coeff. S	1.08	1.19

TABLE 1.3.

	Copolymer X	Copolymer Y
Molecular weight (M_w)	4500	4500
Molecular weight (M_n)	3000	3000
Spread coefficient S	1.5	1.5
Acrylic acid (w/w)	85%	85%
Comonomer (w/w)	15%	15%
Comonomer type	methacrylic acid (MAA)	dimethylaminoethyl methacrylate (DMAEMA)

look very different as far as the number of modified sites per chain. The same would apply to the steric effect those modifications bring to the molecule. Said in other words, the two copolymers are much more different one to the other than what we could have thought at the start based on the relative percentages of the comonomer (15%) over the main monomer in the chain (acrylic acid at 85%).

The variations obtainable using only carboxylate active groups do not stop here. In the paragraphs above we have implicitly considered that when a comonomer is put into the chain of the polymerizing acrylic acid, it distributes itself uniformly along the chain: we have assumed a structure of the type

A B A B A B

which would spread the charge modifications brought by the comonomer, whether as charge density increase like with the maleic anhydride, or as charge density decrease like with the ethylene, in a uniform manner all along the chain.

This case is indeed not very frequent if we leave the monomers free to polymerize according to their natural tendency. A perfectly alternating monomer distribution such as the one above could be obtained via natural polymerization only if the three monomer-to-monomer reactivities $R_{(i,j)}$ are:

$$R_{(i,i)} = R_{(i,j)} = R_{(j,j)}$$

TABLE 1.4.

	Copolymer X	Copolymer Y
Average number of comonomer units per chain	6.2	3.4