

Future Directions in Water Soluble Polymers for Detergent Applications

Allen M. Carrier
Alco Chemical, division of National Starch and Chemical
P. O. Box 5401
Chattanooga, TN 37406

Introduction

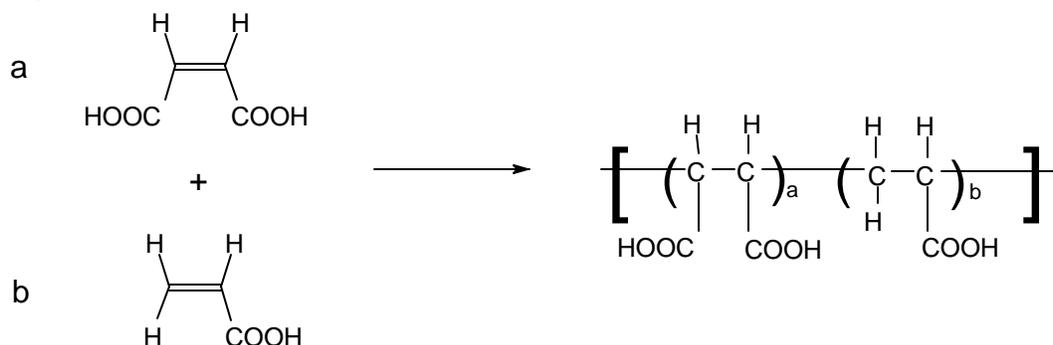
Polymers have found wide utility in detergent and cleaning formulations for the past 25 years (1). While the largest volume has been simple poly(carboxylates), changes in the market place brought on by increased consumer expectations, economic pressures, governmental regulations and environmental concerns are causing formulators to seek new polymers. By looking beyond poly(carboxylates), polymer suppliers are increasing performance options by several methods. One is to create water soluble polymers with increased hydrophobicity, which can improve the soil removing capacity of the polymer by interacting with nonionic surfactants by various mechanisms. Another is to substitute sulfonic acid groups for carboxylic acid groups. By adjusting the amount and type of the sulfonic acid, the polymers show improvements such as increase water hardness ion tolerance, improved surfactant compatibility, improved film substantivity and antistatic behavior. A third means is to select a different polymer backbone, such as a biodegradable polysaccharide or amino acid. By utilizing a wider selection of reactive functionalities, polymers with improved performance and multifunctional behavior can be created. While I will touch on all these areas, it is beyond the scope of this paper to explore each area in great depth.

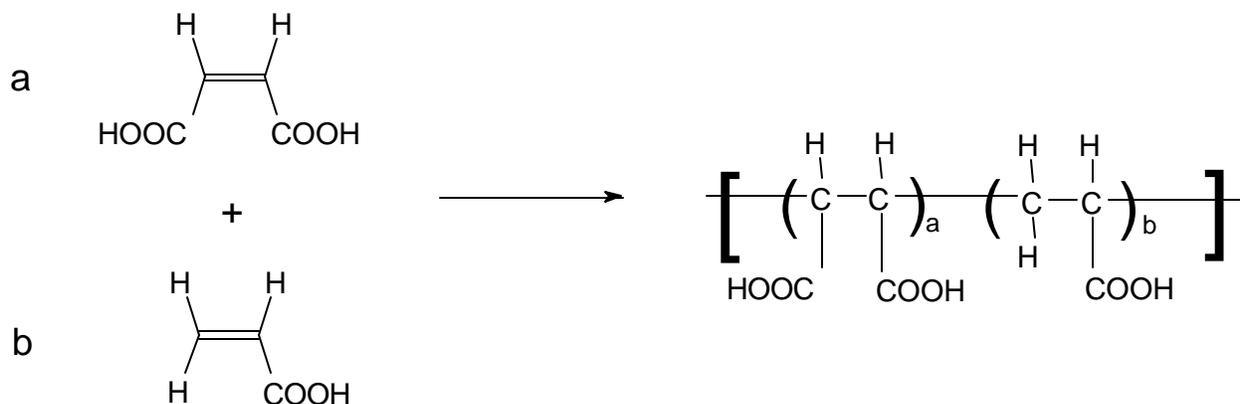
Polymers: The Early Years

In the days when phosphates ruled the world, one-cup formulations were kings and everything was washed in hot water, polymers found little utility in detergent formulations. When they were used, they were primarily process assist agents, helping reduce slurry viscosity prior to spray drying. As their use increased, the added benefits of improved dispersion and anti-redeposition became apparent (2). Polymer usage increased as the cost of raw materials and new technologies for monomer synthesis made these synthetic materials more cost efficient.

The composition of these polymers was typically homo(polyacrylic acid) of various molecular weights. Typically the 60,000 MW material was used. Few acrylic/maleic copolymers were used and those that were produced were expensive and very low in maleic acid content (Figure 1). Values of **a** were usually 0.1 or less.

Figure 1





These polymers were adequate for the light task that they were asked to perform. However, detergents were about to take a drastic turn.

Polymers: Current Chemistry

As the 1980's began, detergent formulators were required to remove phosphates from their products. The pictures of rivers filled with suds and the growing fear of eutrophication from the phosphates prompted several state legislatures to enact laws banning or severely restricting the level of phosphates in consumer laundry detergents. Despite consumer belief, neither the US federal government nor a majority of the states have banned phosphates. The few that have were sufficient to cause wholesale changes to the formulations. Alternate sources of builders were sought with soapers finding solace in zeolites and citric acid. Zeolites however suffered from a unique problem: the surfactant in the detergent was trapped inside the zeolite and took time to diffuse into the wash liquor. During this diffusion period the surfactants were exposed to the water hardness and by the time the zeolites could perform their task, the damage was done. Polymers such as polyacrylic acids were particularly effective at coordinating with the water hardness ions until the zeolites could effectively remove them from solution. Citrate didn't have this problem but making compact formulations was difficult.

As formulations underwent huge changes due to phosphate replacement and the switch to compact rather than one cup formulations, a curious development occurred in the marketplace. As usual, it started in Europe with a tremendous increase in market share by private label detergents. These value priced products have resulted in substantial price reductions in detergent formulations in the past 10 years. To meet the consumer demand, less expensive raw materials need to be used. One of the least expensive builders is sodium carbonate, commonly known as soda ash.

Increasing the level of soda ash in powder detergent formulations caused another problem. The typical polyacrylates or acrylate/maleate copolymers used at that time could not prevent precipitation of calcium carbonate from the wash liquor. As such, newer polymers had to be created that would still function as effectively as previous materials in the area of process assists, dispersion and antiredep, but also need to be effective precipitation threshold inhibitors and crystal modifiers. Crystal modification is important in preventing calcium carbonate encrustation (3). If the amount of soda ash is increased beyond the polymer's ability to handle, then precipitation will occur. By altering the crystal morphology,

you can make the precipitate so it will not adhere to the fabric surface (Figure 2). The calcium carbonate is removed in the waste wash solution. Polymers have been prepared that are particularly effective in preventing encrustation in high soda ash based formulations (4). Table 1 gives performance data for one such polymer. The detergent was prepared for the study and contained 80% soda ash, 5% Sodium Silicate, 8% anionic surfactant and 3% nonionic surfactant. The water hardness was varied and is reported as ppm calcium as calcium carbonate. The wash temperature is 25 degrees C.

Table 1. Terpolymer in soda ash formulation

Polymer	Water Hardness	% Calcium Carbonate OWF
1% Terpolymer	150	0.89
2% Terpolymer	150	0.47
4% Terpolymer	150	0.19
None	150	1.17
4% Terpolymer	200	0.41
4% Acrylate/Maleate	200	1.27
None	200	1.78
4% Terpolymer	250	0.96
6% Terpolymer	250	0.71
None	250	1.61

As can be seen, adding Terpolymer as compared to a standard copolymer can vastly improve the performance of even high soda ash containing formulations. One can alter a zeolite based formulation to contain significant amounts of soda ash while reducing zeolite concentration while maintaining equivalent builder performance by adding of one of the newer polymers.

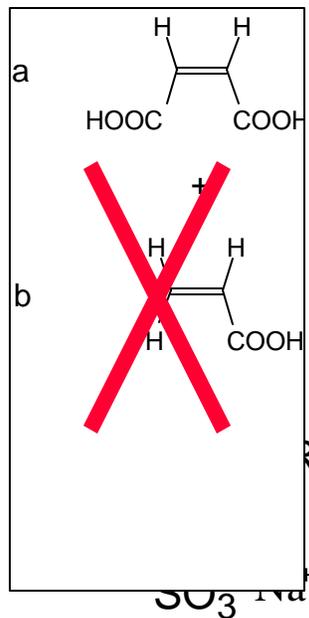
Other specialty polymers have been used in more recent years, aimed at problems not readily handled by poly(carboxylates). The chief among these is poly(vinyl pyrrolidinone) or PVP. This polymer interacts with dye molecules in solution and prevents them from transferring to other fabrics in the wash. More recently, other types of polymers (poly(amine oxides) and poly(vinyl imidazoles)) have been reported in the patent literature. These polymers are usually dye specific and they do not interact with a broad spectrum of dyes. They also tend to lose performance in formulations high in anionic surfactant.

Liquid detergents have been increasing in popularity in the U. S. over the last several years. They have not gained in popularity in Europe for several reasons. One of the reasons is the lack of inexpensive means to add builders to liquid detergents. In order to add a soluble builder a material known as a hydrotrope is added. The hydrotrope is a coupling agent and typically adds no more functionality. This made liquid detergents more expensive to use than their powder counterparts. Recently, several polymers and new methods of manufacturing them have appeared in the marketplace (5-7). These

polymers have one common feature; they have a level of hydrophobicity added to them. The added hydrophobicity in these polymers is aimed at permitting them to interact with structured surfactant droplets, giving a stable, concentrated, low viscosity built liquid detergent. These types of liquid systems require electrolyte to function. While this is often the builder, it is not necessary. One can create a stable liquid with zeolite or other particulate suspended evenly and without heterogeneity over long periods of time.

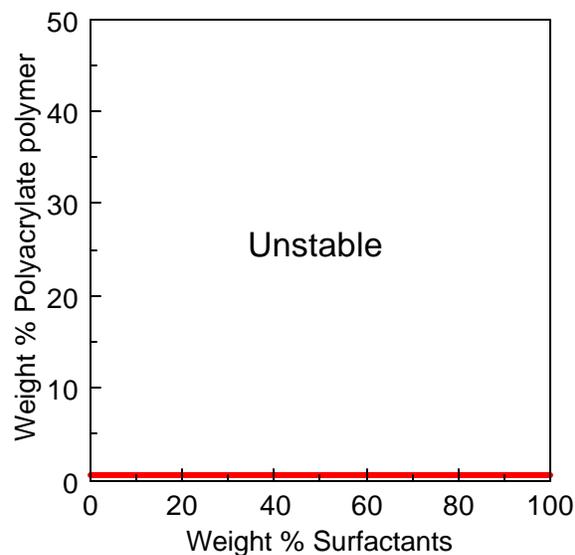
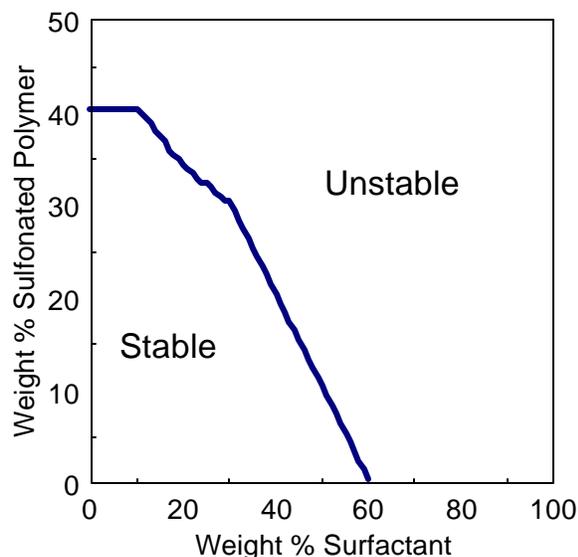
Another type of hydrophobic modification uses a monomer that has a sulfonated aromatic ring (Figure 2). Polymers made from this monomer have the unique ability to interact with nonionic surfactants to form stable solutions at high concentrations of polymer and surfactant (8, 9).

Figure 2



The effect, shown in Figure 3, is different from a hydrotrope. The binary phase diagrams indicate the interaction of the polymer with a C9-C11 6 mole ethoxylate nonionic surfactant.

Figure 3: Phase behavior with nonionic surfactant



The phase diagrams show the region of stability at 50 degrees C over one week. As seen, the polymer/surfactant mixture is stable over large concentrations of polymer and surfactant. No area of compatibility is seen using a 4500 MW poly(acrylic acid). The polymer does not alter the phase behavior of the nonionic surfactant. This composition is also effective in preventing several different types of scales, not just calcium carbonate. By adjusting the level of the sulfonated monomer, it may be possible to extend the window of formulatability. Polymers of this type will undoubtedly be of increased importance in future detergent formulations.

Polymers: The Future

Looking forward, we have to determine the factors driving change in detergent formulations and what roles the polymers may have in them. While standard poly(carboxylates) and new terpolymers will be used for many years, new polymers must be created that will fill needs imposed by:

- Governmental/Environmental Regulations
- Equipment Changes
- Consumer Demands
- Physical changes in formulations
- Changes in textiles and/or dye chemistry

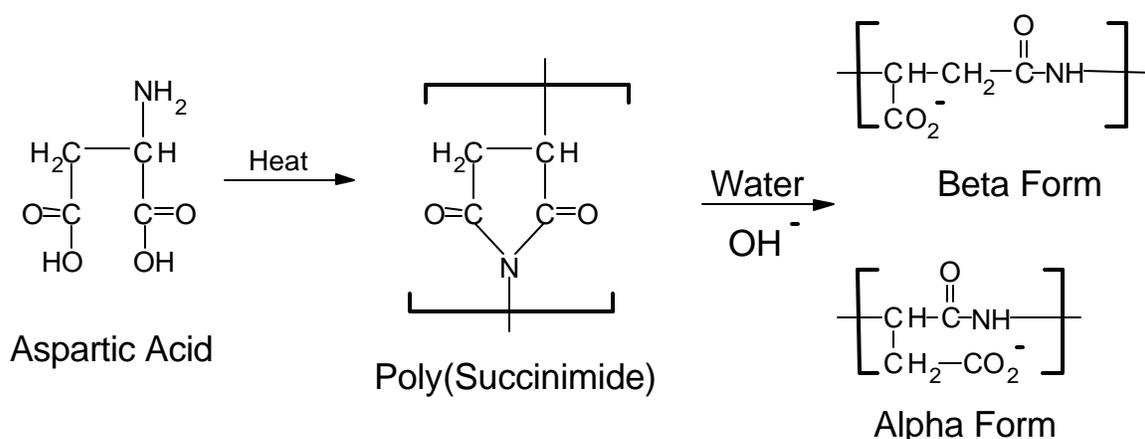
Let's examine how each of these may alter the requirements of polymers in formulations.

In the U. S., changes in governmental regulations may force equipment changes. Washing machines in the near future may be horizontal axis in design to meet the energy requirements imposed by the regulations. Alternately, if not horizontal axis, then other radical changes will be necessary. To save energy, wash temperatures and water volumes will likely be drastically reduced. Polymers can play a major role in making new formulations clean effectively by improving soil removal, preventing dye

transfer or acting as color protection agents. These will be discussed later.

Environmental regulations have already caused widespread reformulating in the recent past. This includes events such as phosphate replacements and change to LAS surfactants to ensure biodegradability. The quest for a biodegradable polymer that could be used as part of a builder system occupied many research labs for years. The most reasonable materials produced to date are poly(aspartic acid) polymers. These polymers are most easily prepared by the thermal condensation of aspartic acid followed by the hydrolysis of the resulting poly(succinimide), making the thermal polyaspartic acid (TPA) (Figure 4).

Figure 4. Synthesis of TPA



These polymers are more effective if the mole % of beta form is maximized. This may be due to the structural similarity to poly(acrylic acid). When compared to 4500 MW poly(acrylic acid) (PAA), reasonable results for antiredep, dispersion and encrustation (Table 2) are obtained.

Table 2. Encrustation values of various TPA polymers

Polymer	Encrustation
TPA-1, 4500 MW	1.63
TPA-2, 4500 MW	1.72
TPA-3, 3000 MW	1.60
PAA, 4500 MW	1.38
None	2.05
LSD	0.11

In addition, modified starches are being marketed that improve wash performance. However, in the author's opinion, biodegradation cannot and will not, in the near future, be sufficient reason for PAA and other non-biodegradable polymers to be abandoned. The major detergent formulators have no legislative reason to change to biodegradable polymers without substantial economic or performance

advantages. At present, TPA is 5 to 10 times as expensive as PAA. The benefits from modified starches are still under investigation.

Liquid detergents are gaining in popularity, especially in the U. S. The major reason liquids are not as popular in other parts of the world is the lack of performance, either real or perceived, when compared to powders. Structured liquids, mentioned previously, overcame these technical problems. Consumer acceptance worldwide has not been overwhelming. If new polymers are able to improve the performance of liquid detergents to be equivalent to powders, the global marketplace may undergo a revolution.

One area that is rarely examined is the impact the textile, dye and fashion market can have on detergents. If a new type of fiber, or dye chemistry or fashion style become popular, detergents may have to be altered to safely clean them. This could happen concurrently or independently with equipment changes. Polymers would be important constituents of formulations aimed at these changes.

From the above discussion, it seems clear there are several areas polymers can play major roles in the next 10 to 20 years. They will continue to be important components within builder systems, their role as dye transfer inhibitors or color protectors will increase greatly, and they must be tailored to improve the cleaning performance of detergents, especially on cotton. The improvement in cleaning must be over and above that available from surfactants. The polymers must also offer multiple benefits, as ingredients that offer only one function in a formulation are being critically examined.

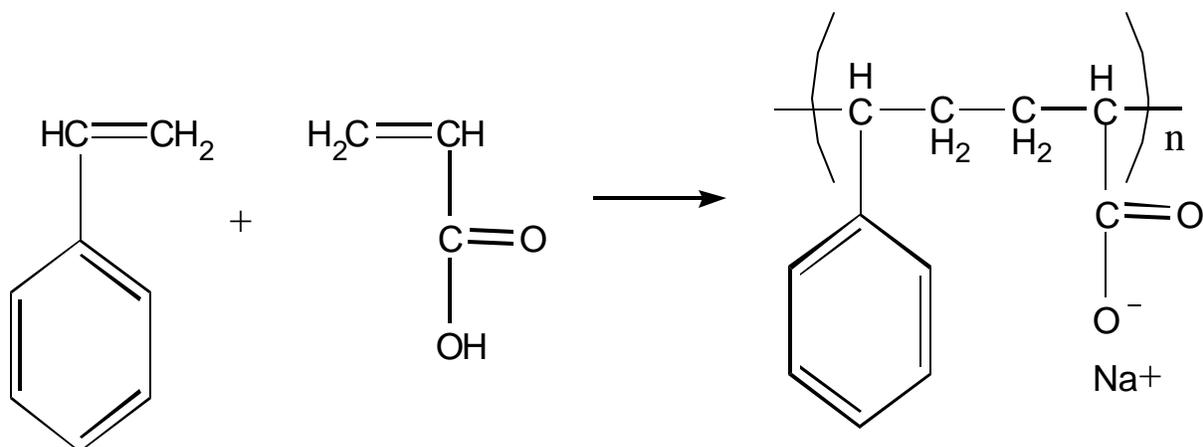
-The Future may be closer than we think

As we look forward toward new polymer developments, it is important to look at some of the recent trends in polymer compositions and synthetic techniques. More and more water soluble polymers are being created with a certain degree of hydrophobicity. The amount and type of the hydrophobe is an area that needs extensive exploration. As these polymers increase in hydrophobicity, one may be tempted to revert to organic solvents for polymer synthesis. This is clearly not desirable nor would it be acceptable in the marketplace. Significant advances have been made in creating high performance polymers in water and the detergent formulators are not willing to worry about residual solvents that may have detrimental environmental impact.

Several methods have been devised to make these hydrophobically modified polymers. The most acceptable means to date is the use of environmentally benign cosolvents that can be easily removed from water. The most economical and widely used is 2-propanol (7, 10), commonly known as isopropyl or rubbing alcohol (IPA). This cosolvent is then removed by azeotropic distillation to a level acceptable to detergent formulators, typically below 0.3%. Using this technique, some unique water soluble polymers have been produced that behave as hydrotropes and improve the wash performance of high nonionic containing formulations (10).

The polymer is a low molecular weight acrylic acid/styrene copolymer, prepared without any organic solvent (Figure 5). The polymer can interact with nonionic surfactants altering their

Figure 5. Preparation of acrylic acid/styrene copolymer



phase behavior. When compared to standard hydrotropes such as Sodium Xylene Sulfonate (SXS), the polymer has weaknesses and benefits (Figure 6). However, this polymer exhibits some multifunctional behavior by improving the cleaning performance of a nonionic surfactant based detergent and permitting greater removal of soil. In this test, (Figure 7) the detergent is zeolite built with no other polymer. The soil was clay and iron oxide. The wash temperature was 40 degrees C in a European washing machine at 100 and 300 ppm hardness. While the mechanism of this detergency improvement has not been determined, it is reasonable to assume the polymer is interacting with the nonionic surfactant under wash conditions altering its phase behavior. This may improve the soil removing or soil dispersing ability of the surfactant. Even though the polymer contains carboxylic acid functionalities, it is not interacting with the water hardness to any appreciable extent, as evidenced by no significant change in cleaning performance at different water hardnesses. It appears the carboxylic acid groups serve more to provide water solubility to the polymer.

Figure 6. Hydrotropic effects of acrylic acid/styrene copolymer compared to SXS

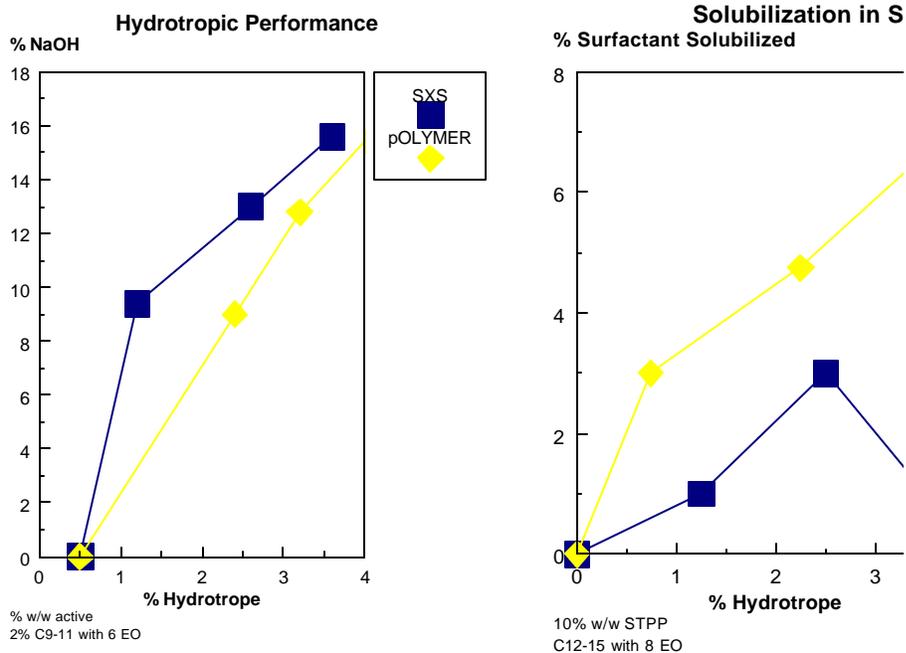
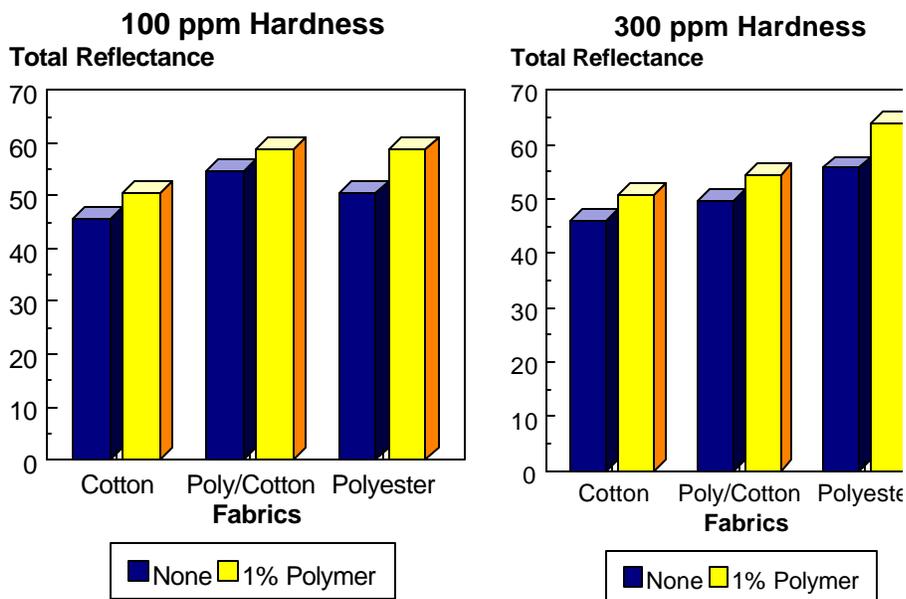


Figure 7. Detergency under European Conditions at different water hardnesses



Using the success of the acrylic acid/styrene copolymer, we have begun investigations in our laboratories to make polymers that will improve the performance of detergents, especially on cotton.

Soil Release Polymers

Soil Release Polymers (SRP) have been in existence for several years. The current technology is aimed at removing soils from polyester fibers only. These polymers are typically low molecular weight polyesters themselves. They work by interacting at the surface of the fiber and permit the surfactants to function more efficiently by lowering the surface energy of the fiber. The water and surfactant mixture can then spread out on the fiber and remove the soil. They are not particularly effective on cotton, however. Recent literature (11) point to compounds based on polyethyleneimine as having soil removing properties on cotton.

To aid in understanding the following discussion, it is necessary to provide some operational definitions. The mechanism of a polymer interacting with a fiber surface, usually through several prewashings prior to staining to permit removal of soil, is called **soil guard** or soil shield. The improvement in detergency in a single wash is called **soil removal**.

We have prepared a number of experimental polymers where the amount and type of hydrophobicity has been carefully controlled. Also, we are controlling, though to a lesser extent, the tertiary structure of the polymer. We have found that these types of polymers can be effective soil guard materials on cotton. The data, shown in Table 3, are on an olive oil/bandy black clay soil. The fabric was washed 3 times in the detergent with and without polymer prior to staining. The values given are ΔL . The results are for washing the stained fabric in detergent with and without added polymer during the washing cycle. As can be seen, the soil is removed more completely if the fabric has been washed prior to staining. There is a noticeable difference if polymer is withheld from the wash cycle after staining. This could be due to some soil removal properties of the polymer.

Table 3. Soil Guard on cotton.

Detergent contains polymer in Prewash	Detergent With Polymer in Wash after staining	Detergent without polymer in wash after staining
Yes	37.9	35.5
No	30.2	30.2

It is also possible to make polymers that exhibit substantial soil removal properties. By increasing the amount of hydrophobicity, a non-polyester based polymer can be made with soil removal properties similar to commercial SRP's on polyester. The data in Table 4 show the cleaning of a spaghetti sauce stain on cotton and polyester fabric. A zeolite built detergent was used and the fabric was washed under U. S. conditions in a tergotometer. The soil removal was calculated using the following equation:

$$\% \text{ soil removal} = \frac{\text{soil removed}}{\text{total soil}} \times 100 = \frac{\Delta E_{a-s}}{\Delta E_{b-s}} \times 100$$

Where ΔE is calculated using the following equation:

$$\Delta E = [(L_1-L_2)^2 + (a_1-a_2)^2 + (b_1-b_2)^2]^{0.5}$$

and ΔE_{a-s} is the difference in E after the stain is put on and after the swatch with the stain is washed and ΔE_{b-s} is the difference between after the stain is put on and no stain. The hydrophobic ratio is arbitrary using polymer B as reference.

Table 4. Soil removal of spaghetti sauce on cotton and polyester

Polymer	Hydrophobic Ratio	% soil removal on polyester	% soil removal on cotton
None	0	53.8	51.8
Polyester based SRP	ND	72.0	ND
Polymer A	18	74.0	52.1
Polymer B	1	74.3	65.5

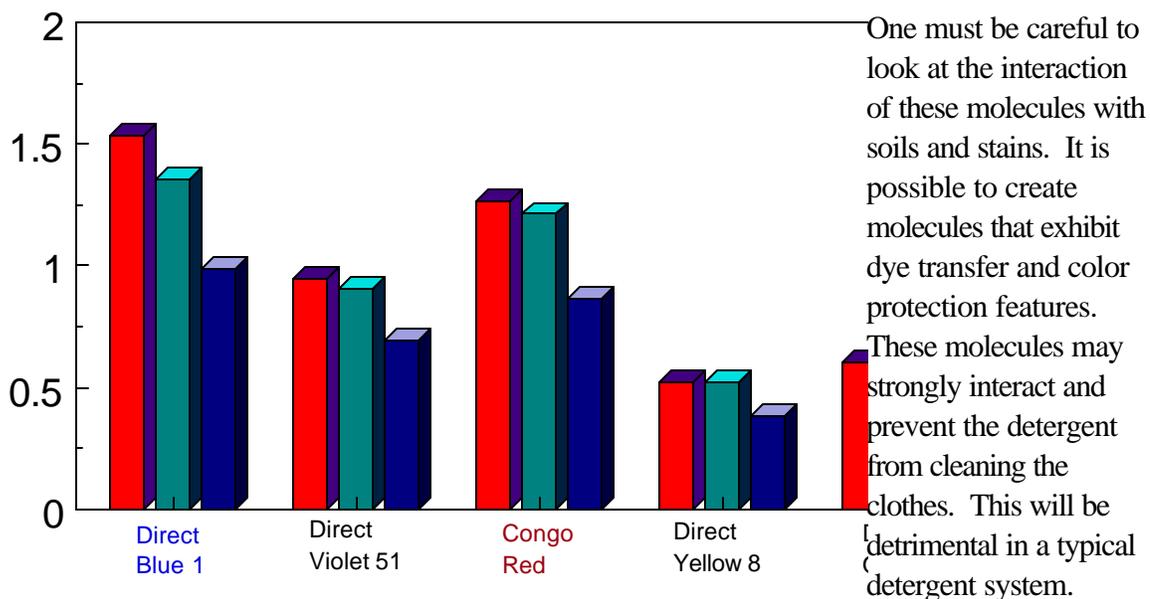
While these results are encouraging, we still see significant formulation specificity in the selection of polymer backbone and hydrophobic sidechains. The critical parameters used to select the best polymer for the application have not yet been developed. It is clear from the limited data that polymers can be an important part of detergent formulations in the future where improved soil removal on cotton is desired.

Dye Transfer and Color Protection

As described previously, polymers are already the state of the art in dye transfer inhibition. By dye transfer, I mean preventing the deposition of unwanted dyes from the wash liquor or due to physical contact onto fabric. This differs from color protection where the dyes are held onto the original fabric and are not transferred through the wash water or by contact. In dye transfer inhibition, your whites stay white but your colors fade. In color protection your colors don't fade. PVP is the most widely used polymer for dye transfer inhibition. It is reasonably effective at preventing transfer of some dyes but it will not treat a broad spectrum of dyes. We have developed several new polymeric systems that are more effective than PVP at preventing many dyes from transferring. As can be seen in Figure 8, this polymer works where PVP may not. The dyes and polymer are mixed together and the decrease in absorbance at λ_{max} is determined. The greater the decrease, the stronger the interaction of the polymer with the dye molecule. We have found this translates to less dye transfer in the wash.

Figure 8. Interaction of polymer with dye in solution

Absorbance



By carefully choosing the monomeric units that make up the polymer, it should be possible to create a material with a balance of color protection and dye transfer properties that do not interfere with the cleaning ability of the detergent. We have seen some evidence of this with polymers that exhibit about the same effectiveness as PVP in preventing dye transfer but at one half the amount of active polymer (Table 5). Increase the dosage also prevents the removal of dye from the color fabric. In this experiment, we use a modified version of ASTM D5548-95 where the acid dyes are removed. The blue swatch has the dye that is transferred onto the white fabric. Here, lower numbers are better for the blue swatch, indicating less dye has been removed while higher numbers are better for the white, showing less dye has been transferred.

Table 5. Dye transfer inhibition and color protection

Polymer	Blue Swatch reflectance	White Swatch Reflectance
None	40.4	73.3
1 % PVP	40.9	77.7
2 % PVP	40.7	79.4
1 % Polymer C	40.1	79.7
2 % Polymer C	39.3	82.1

Summary

Poly(carboxylates) will continue to offer many performance advantages to detergents in the future. However, polymeric materials can also be effective at improving soil removal, especially on cotton. We have found that hydrophobically modified polymers of low molecular weight seem to be a reasonable route to improving detergent performance. These products are made via an environmentally acceptable

cosolvent that is readily removed from and replaced by water. By adjusting the apparent HLB of the polymer, it should be possible to tailor the soil guard or soil removal properties of the polymer for the application and formulation in a manner similar to the current method of choosing the correct surfactants.

Polymers must also be created that offer improved dye transfer inhibition properties. The current technology is too dye specific and suffers when high levels of anionic surfactant are present. New polymers must overcome this deficiency preferably by offering color protection without impairing the detergent's ability to clean.

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