

Chapter 8

Polymers in Hair Products

Abstract Polymers have become increasingly important components of cosmetics over the past few decades. The original uses of polymers in hair care were as fixative agents and viscosity controlling additives; however, new polymers today are also used for hair conditioning and for the development of new style control products. Polymer substantivity to hair fibers increases with molecular size, with an increasing number of polar group attachments and especially with an increasing number of cationic groups for attachment to the negatively charged surface of hair fibers. From an anionic shampoo medium the cationic charge on polymers is neutralized and the adsorbing species is essentially a neutral or negatively charged species. The most successful silicone conditioning polymers for hair care have been used in both shampoo and conditioner compositions. Dimethicones in shampoos condition undamaged or lightly damaged hair better than they condition highly damaged, bleached hair or even tip ends because neutral hydrophobic conditioning agents adsorb more readily to an undamaged hydrophobic surface than to a damaged highly polar hair surface. New block co-polymers and a fairly large number of new cationic polymers have been introduced into hair care recently, while fractal polymers (highly irregular shapes) and nanoparticles have been developed and are receiving attention for potential use in hair care.

8.1 Introduction

Several new, useful fixative polymers have been introduced into the cosmetic industry over the past decade to provide improved hair spray formulations in response to the 55% VOC regulation for hair sprays and hair shines that were originally imposed by the California Air Resources Board. In addition, new cationic co-polymers have become available that employ three and sometimes four comonomers. Long chain alkyl groups have been introduced into several of these

and into some other cationic polymers to provide hydrophobicity. Further trends in hair care polymers are summarized in a paper by Lockhead [1].

Over the past two decades, the use of silicone polymers in two in one shampoos has become increasingly important commercially. Several different types of silicone polymers have been introduced into the cosmetic industry in the past decade and our knowledge on the adsorption, conditioning and stabilization of silicones from anionic shampoo systems has increased greatly. As a result, a section summarizing the literature on silicone polymers including their interactions with hair and with other ingredients especially in shampoo systems is included in this chapter.

New block co-polymers and a fairly large number of new cationic polymers have been introduced into hair care this past decade. Fractal polymers or dendrimers (with irregular shapes and surfaces) are receiving attention for potential use in hair care formulations and the area of nanogels and the generation and use of nanoparticles in hair cosmetics is also an area that is beginning to receive attention and is described in this chapter. These areas (fractal polymers and nanoparticles) should prove to be fruitful in the future. However, at this time these innovations are in their infancy for our industry. The above subjects provide the basis for most of the new material in this section on polymers and polymer chemistry in hair products.

Polymers have become increasingly important components of cosmetics over the past few decades. Their more important uses are as primary ingredients or adjuncts in shampoos, conditioning products, styling products (lotions and gels), mousses, and hair sprays. They have been used to condition hair [2, 3] and to improve the substantivity of other ingredients to hair [4, 5], to improve combing [2], manageability [2, 3], body [6], and curl retention [1, 3, 7]; to thicken formulations [8, 9]; and to improve emulsion stability [8].

Because of environmental concerns, a great deal of research has taken place to develop polymers that release water more readily. As suggested earlier, the goal is to provide polymers that are more compatible with water with the aim of developing spray products that can be formulated with lower levels of volatile organic compounds (VOC) and as a consequence more water. The driving force at this time has become the standards proposed by the California Air Resources Board (CARB) that has proposed that the maximum allowable VOC emissions for hairsprays be:

- 80% by January 1, 1993 and
- 55% first proposed for January 1, 1998 and later extended to June 1, 1999.

Since a few other states have adopted the 55% VOC standard for hair sprays and shines, creative formulation and science is necessary to market these products. VOC's in hairsprays in the U.S. have become an issue while hydrocarbon propellants with ethanol solvent are commonly used in some other parts of the world. Thus, the section on hair sprays has been expanded to summarize issues and concerns created by this regulation and to describe how these are being addressed.

Other CARB regulations relevant to hair care are:

Hair mousses, 6% VOC – by December 31, 2002 and Hair styling gels, 6% VOC – by January 1, 1994. These regulations specify a 1-year period after the effective dates above for any company to sell existing products that do not comply with these regulations in the San Francisco Bay Area Air Quality Management District. Hairsprays are an exception. Hairsprays that are not in compliance must be off the shelves by the effective dates.

The following subjects are of special relevance to the application of polymers in hair products and thus are the focus of this chapter:

- The binding interactions of polymers to hair;
- The chemical nature of polymers used in hair products;
- In situ polymerization reaction mechanisms;
- Rheological or flow properties of polymer solutions; and
- Film formation and adhesional properties of polymers.

The major emphasis in this chapter is on the first three of these subjects – the chemical and/or binding interactions of polymers to hair; the chemical nature of hair sprays, setting products, and mousses; and in situ polymerization reactions in hair. Although the rheological properties of polymer solutions are especially important to formula viscosity, and to the sensory perceptions of cosmetics, they will not be emphasized here. It suffices to say that cellulosic ethers [8, 9] are probably the most important thickening agents in hair products, and ethoxylated esters and carboxy vinyl polymers are also important.

For hair sprays, polymer setting products, and polymeric conditioners, film properties as well as the ability of the polymer solution to spread over the fiber surface is important to product performance. The ability of the polymer to spread over the hair surface is governed by its solution viscosity and the wettability of the fiber surface in contact with the polymer solution. For optimum spreading, low solution viscosity is important, and both polar and dispersion interactions have been shown to be important to the ease of spreading over hair fiber surfaces [10]. The surface of cosmetically unaltered hair is generally considered to be hydrophobic, whereas the cortex is more hydrophilic. Kamath et al. [10] have shown that both bleaching and reduction of hair increase the wettability of hair, making its surface more hydrophilic. For a more thorough treatment of wettability and the spreading of liquids on solids, see the following references [10–13].

8.2 The Binding of Preformed Polymers to Hair

Chapter 6 describes the work of Steinhardt and Harris and the affinities of organic acids [14] and quaternary ammonium hydroxide compounds [15] to keratin fibers. It illustrates the importance of increasing molecular size and even non-primary bonds to the substantivity of ingredients to hair. In the case of polymeric ingredients, these same principles are operative, and even more important. Chapter 6 also describes the important interactions leading to deposition of conditioning

ingredients from both anionic and cationic surfactant solutions, including an hypothesis that considers a continuum between a charge driven adsorption process and a hydrophobically driven process. This same hypothesis is not repeated in the current discussion; however, it is highly relevant to the discussion which focuses on factors that are important to the deposition of polymeric ingredients onto human hair.

8.2.1 Chemical Bonding and Substantivity

It is convenient to consider three extreme types of bonds between polymer and hair.

- Primary valence bonds (ionic and covalent bonds).
- Polar interactions (primarily hydrogen bonds).
- Dispersion forces (Van der Waals attractive forces).

It should be noted that bond classifications of this type are not rigorous, and the transition from one type to another is sometimes gradual. Therefore, intermediate bond types do exist [16], although for simplicity in the following discussion a rigorous classification of bond type is presented.

Primary valence bonds include ionic and covalent bonds and are the strongest binding forces. Both of these types of bonds generally provide bond energies of about 50–200 kcal/mol [17]. Ionic bonds are extremely important to the interactions of polymeric cationic ingredients and hair, whereas covalent bonds are probably involved between polymer and hair in certain in-situ polymerization reactions described later in this chapter.

Hydrogen bonds are the most important polar interactions and are the next strongest binding forces, with bond energies generally of the order of 4–10 kcal/mol [17]. These bonds are about an order of magnitude less than covalent or ionic bonds and are important to the binding of polymers containing polyalcohol or polyamide units to hair. Polypeptides and proteins are two examples where hydrogen bonding is important.

Dispersion forces or Van der Waals attractions provide bond energies generally of the order of 1 kcal/mol [18] about two orders of magnitude less than covalent or ionic bonds. Van der Waals attractive forces are relatively weak and are dipolar in nature. Since electrons are in constant motion, at any instant in time, the electron distribution is probably distorted, creating a small dipole. This momentary dipole can affect the electron distribution in an adjacent molecule. If contact is just right, attraction is induced [19]. These attractive forces are short-range and act only between the surfaces of molecules. Therefore, the total strength of Van der Waals bonding increases with molecular surface area, as an approximation with increasing molecular size. Therefore, in polymers van der Waals bonding can approach the strength of primary valence bonds.

For an interaction between molecules, entropy is inversely related to the amount of structural organization of the total system. More randomness or less structural organization of the system is always preferred. In many cases, less structural organization is

required to bind a large hydrophobic molecule to a hair surface than to emulsify it into a lipid-aqueous system. Thus, entropy can provide a driving force to push large hydrophobic polymers out of the solvent system and onto the hair fiber surface.

8.2.2 Molecular Size and Substantivity

Mark [20, 21] described the forces involved in multiple polar and dispersion binding in polymers by means of molar cohesions (see Table 8.1). These data show that in polymers of relatively low molecular weight, 10,000 Da, the cohesive

Table 8.1 Polar and dispersion forces in polymers

Polymer	Structural unit	Approximate molar cohesions for units shown (kcal/mol)
Polyethylene	$(-\text{CH}_2-\text{CH}_2-)$	1.0
Polyisopropylene	$\begin{array}{c} (-\text{CH}_2\text{CH}-\text{CH}_2\text{CH}-) \\ \quad \\ \text{CH}_3 \quad \text{CH}_3 \end{array}$	1.2
Polystyrene	$\begin{array}{c} (-\text{CH}_2\text{CH}-\text{CH}_2\text{CH}-) \\ \quad \\ \text{C}_6\text{H}_5 \quad \text{C}_6\text{H}_5 \end{array}$	4.0
Polyvinyl alcohol	$\begin{array}{c} (-\text{CH}_2\text{CH}-\text{CH}_2\text{CH}-) \\ \quad \\ \text{OH} \quad \text{OH} \end{array}$	4.8
Polyamides	$\begin{array}{c} (-\text{CH}_2\text{CH}-\text{CH}_2\text{CH}-) \\ \quad \\ \text{C}=\text{O} \quad \text{C}=\text{O} \\ \quad \\ \text{NH}_2 \quad \text{NH}_2 \end{array}$	5.8

^aMolar cohesions listed are actually for a chain length of 5 Å. The structural units shown above are approximately 4.6 Å long, assuming a constant carbon-carbon bond length of 1.54 Å [22]

energy approaches that of primary chemical bonds. Therefore, by analogy with the affinity of surfactants and dyes to hair (Chap. 6), one may predict the importance of molecular size to the substantivity of polymers to hair.

Obviously, multiple sites for attachment of even stronger bonds such as polar and especially primary valence bonds are even more important to substantivity. Multiple covalent attachment sites could conceivably occur via *in situ* polymerization reactions and with bi-functional cross-linking agents (see Chap. 4). However for pragmatic reasons, this is not nearly as important as multiple ionic attachments to hair as can occur with cationic polymers.

The appropriate spacing of groups in the polymer so that maximum bonding can occur, especially to ionic and polar groups on the keratin structure, is also important to substantivity. As a first approximation, the maximum frequency of primary bonds and the maximum molecular size will provide maximum substantivity.

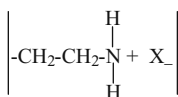
8.2.3 Isoelectric Point of Hair and Polymer Substantivity

Although polymers may penetrate to a limited extent into human hair [23], the key interactions between hair and most polymers occur at or near the fiber surface. Obviously, lower molecular weight polymers are more prone to penetrate than high molecular weight polymers and damaged hair is more penetrable than chemically unaltered hair.

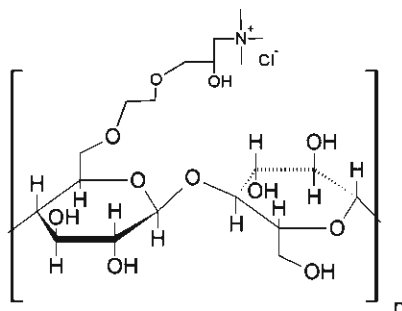
Since ionic bonds are the most important primary valence bonds for binding to hair, under low temperature conditions in an aqueous or aqueous alcohol system, the net charge at the fiber surface is critical to polymer hair interactions. Wilkerson has shown that unaltered human hair has an isoelectric point near pH 3.67 [24]. Therefore the surface of hair bears a net negative charge at all pH values above its isoelectric point. Since most cosmetic hair treatments are formulated above this pH, cationics ingredients are attracted to hair more readily than anionics, and polycationics are more substantive to hair than polyanionics.

8.2.4 Desorption and Breaking Multiple Bonds

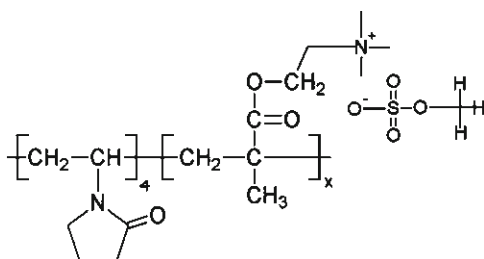
Faucher et al. [25] demonstrated that desorption of a polymeric cationic cellulose (polymer JR) (see Table 8.2) from hair is slower than would be expected from a simple diffusional release predicted by the square root of time law [26]. These scientists suggested that desorption of a polymer occurs only after all sites of attachment are broken. Statistically, the process of breaking all attachments simultaneously is of low probability. Therefore, one would expect high substantivity and a slow rate of release with increasing molecular size and increasing primary valence bonding sites.

Table 8.2 Approximate structures for three cationic polymers used in hair care products

Polyethyleneimine (PEI) with a charge density of 176, assuming 25% protonated at pH =8 [42].



Quaternized hydroxyethyl cellulose with a charge density of 689 (polyquaternium-10).



Quaternized copolymer of PVP and dimethyl aminoethyl methacrylate with a charge density of 616 (Polyquaternium-11).

8.3 Penetration of Polymers into Hair

Low-molecular-weight polypeptides [27] ($M_n = 1,000$) and polyethyleneimine ($M_n = 600$) [28] have been shown to diffuse into hair. Somewhat larger polypeptides ($M_n = 10,000$) [27] and polymer JR, with an average molecular weight of 250,000 [23], have also been reported to penetrate into hair. The polymer JR study involved bleached hair. These data suggest that penetration is limited to about 10% of the hair after 7 days and about an order of magnitude less in unaltered hair [25]. Sorption of a higher-molecular-weight JR polymer (average molecular weight of 600,000) by bleached hair is similar to the smaller polymer by unaltered hair.

It appears that some limited penetration into human hair can occur by the lower-molecular-weight species of low molecular weight polymers (less than 10,000 Da).

Larger polymers, up to 500,000 Da, may even contain species (smaller) that can diffuse into the cuticle and perhaps further. Intercellular diffusion or diffusion through the non-keratin regions is probably the preferred route for these large molecules (see Chap. 6). If the hair is degraded sufficiently or if the degree of polymerization for the polymer provides a broad distribution, intracellular diffusion may also occur. However, it is highly unlikely that large polymers penetrate to a significant extent into human hair. Neutral or anionic polymers have not been studied for penetration effects. However, as a first approximation, one might draw similar conclusions with regard to the size and extent of penetration of these polymers also.

8.4 Cationic Polymers and Their Interactions with Hair

Because of their high degree of substantivity, cationic polymers are one of the more important types of polymers used in hair products. They are even useful in shampoos in addition to their use in hair conditioners. Their major asset, high substantivity, is also a potential problem, because they can be so substantive that they are sometimes difficult to remove from hair by shampooing.

Cationic ingredients in general are highly substantive to hair because of hair's low isoelectric point (IP). The IP of cosmetically unaltered hair is approximately pH 3.67 [24] and even lower in bleached hair. Thus, at any pH above the isoelectric, the surface of hair bears a net negative charge; therefore positively charged (cationic) ingredients are attracted to it.

Even monofunctional cationics are substantive to hair to the extent that they resist removal by water rinsing. For example, stearyl benzyl dimethyl ammonium chloride and distearyl dimonium chloride are major active ingredients in creme rinse products because they are substantive to water rinsing and condition the hair fiber surface.

Dye staining tests [29, 30] shows that substantivity of monofunctional cationics to water rinsing does not occur unless the hydrocarbon portion is approximately 8–10 carbon atoms or longer. This effect occurs because sufficient Van der Waals attractive forces in addition to the electrostatic bond must exist to bind the molecule to the fiber in the presence of the aqueous phase. As the molecular size of the cationic structure is increased, even greater sorption and substantivity result [30]. This enhanced substantivity is partly due to an increase in dispersion bonding and partly due to entropy, that is due to the fact that the structure becomes less hydrophilic and partitions more readily from the aqueous phase to the keratin phase which requires less structural organization.

In many shampoos it has become practice to use cationic surfactants or polymers in an anionic shampoo system. The use of a small amount of a cationic ingredient in the presence of a large excess of anionic surfactant results in charge neutralization by the anionic surfactant forming a cationic–anionic complex which is emulsified by the anionic surfactant. These interactions are described in more detail in the next

section for Polyquaternium-10. In effect the cationic (monofunctional or polymer) is converted into a tightly bound neutral salt species (cationic–anionic complex) which is essentially a neutral hydrophobic ingredient. Therefore, in an anionic shampoo system which always has an excess of anionic surfactant, substantivity to hair depends on hydrophobic interactions and entropy rather than a charge–charge interaction. This interaction is entirely different from a cationic conditioner system. These different interactions are described in more detail in the next section under the title of *Cationic Polymer–Surfactant Complexes*. Approximate structural formulas for three cationic polymers that have been used in hair care applications are described in Table 8.2.

8.4.1 *Interactions of Quaternized Cellulosic Polymers with Hair*

8.4.1.1 Polymer JR (Polyquaternium-10 Formerly Quaternium-19)

Polymer JR has been used in many different commercial hair products as a conditioning ingredient, including several different conditioning shampoos. Polymer JR has a relatively low charge density 670 [31], and a high density of polar groups (hydroxyl), see Table 8.2. Charge density is the residue molecular weight per unit of positive charge. This type of polymer has been studied in three different molecular weight versions – 250,000, 400,000, and 600,000 – in several excellent publications by Faucher, Goddard, and Hannah [23, 25, 31–33].

The chemical structure for polymer JR in Table 8.2 approximates the structure of this polymer and is based on information in the CTFA cosmetic ingredient dictionary [34] and the charge density value of approximately 670 [33]. Note that the positions and numbers of ethoxamer units may vary for this structure, as does the position of the hydroxypropyl quaternary grouping. Polymer JR has been used in several different commercial hair products as a conditioning ingredient, including several different conditioning shampoos.

8.4.1.2 Adsorption and Absorption to Hair

Faucher and Goddard [23] studied the uptake of polymer JR onto bleached and unaltered hair. Their data suggest limited penetration into bleached hair and possibly some penetration into unaltered hair, too, for the lower-molecular-weight portions. At 0.1% polymer concentration, approximately 35 mg polymer per gram hair was sorbed onto bleached hair after 8 days.

After 1 h, 8 mg polymer per gram hair was sorbed (polymer molecular weight: 250,000). A rule of thumb for the uptake of a cationic surfactant (cetyl trimethyl ammonium chloride) onto unaltered hair after 2–5 min reaction time is 1–3 mg

cationic bound per gram of hair. Bleached hair will bind about double that amount, e.g., 4–8 mg per gram (depending on the amount of bleaching). These amounts are essentially surface sorption with limited penetration into the hair.

8.4.1.3 Effect of Molecular Weight

Three different molecular weight versions of Polymer JR (250,000, 400,000, and 600,000) were studied with respect to sorption onto bleached hair [23]. The lowest-molecular-weight species was sorbed fastest and to the greatest extent. The sorption curve for the highest-molecular-weight species shows a rapid uptake followed by leveling, indicating saturation of the hair fiber surface and limited penetration.

8.4.1.4 Effect of Charge

Polymer JR uptake was compared to an analogous uncharged hydroxyethyl cellulose polymer. The uptake of the charged polymer was 50 times that of the uncharged polymer [23].

8.4.1.5 Effect of Concentration

The uptake of polymer JR increased sixfold with concentration, from 0.01% to 1.0% [23]. However, apparent diffusion coefficients from initial slopes indicate a slower diffusion rate with increasing concentration. Faucher and Goddard [23] explain this anomaly by suggesting that a more compact polymer deposits on the hair at the higher concentrations. This may be somewhat analogous to the effects of pH on the activation energy for diffusion of orange II dye into keratin fibers [35]. In this latter situation, the activation energy for diffusion of dye into the fibers increases with decreasing pH where a higher concentration of dye enters the fibers. Apparently, the steeper concentration gradient with decreasing pH increases the energy required for each dye molecule to enter the fibers.

8.4.1.6 Effect of pH

The influence of pH on polymer JR sorption was studied in un-buffered media [23], starting at pH 4, 7, and 10. The largest uptake was at pH 7, with about 15% less polymer sorbed at pH 4 (which can be attributed to a decreasing net negative charge on the fiber surface). However, there is about 30% less polymer pickup at pH 10 than at pH 7, which would not be predicted on the basis of electrostatics or swelling of the hair. Drifting pH caused complications, and the observed differences, although small, await a satisfactory explanation, see *Effects of Salt*.

8.4.1.7 Effects of Salt

Added salt produces a larger effect on the uptake of polymer JR than pH [25]. This salt effect may in fact help to explain the pH effect. The addition of 0.1% sodium chloride decreased pickup by almost two-thirds. This may be attributed to shielding of sorption sites on the hair or competitive inhibition. Although the affinity of sodium ion for hair should be much less than for polymer JR, at this concentration sodium ion has more than 20 times the cationic charge concentration relative to polymer JR.

Other salts, such as lanthanum and calcium, had an even greater effect in decreasing polymer pickup. Trivalent ions (lanthanum, aluminum, and iron) had the largest effect, followed by divalent ions (calcium and ferrous iron). Monovalent ions showed the least effect. Faucher et al. [25] suggested the analogy to hair of a strong acid ion exchange resin and postulated that the decrease in polymer uptake by inorganic cations is due to competitive inhibition.

8.4.1.8 Effect of Hair Damage

Most of the studies with polymer JR employed bleached hair. Bleached hair has a higher concentration of negative sites at and near the fiber surface to attract and bind cations. Bleached hair is also more porous than chemically unaltered hair. As one might predict, uptake of polymer JR onto unaltered hair was an order of magnitude lower than for bleached hair [25].

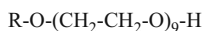
8.4.1.9 Desorption of Polymer JR from Hair

Desorption of polymer JR from hair by distilled water is very slow, and <15% was removed in a time period of 30 min [25, 32]. Sodium dodecyl sulfate (SDS at 0.1 M) solution, analogous to a shampoo, was more effective, removing more than 50% of the polymer in 1 min and nearly 70% in 30 min. However, a small amount of strongly bound polymer was still attached to the hair after SDS treatment [32]. Attempts to remove this strongly bound polymer by multiple treatments with SDS were not examined.

Salts were also found to be effective in removing a portion of the polymer, and trivalent salts were more effective than divalent, which were more effective than monovalent. However, even after 1 week in 0.1 M lanthanum nitrate solution (La^{+++}), approximately 40% of the polymer was still bound to the hair [25]. Most of these results were on bleached hair, but desorption experiments on chemically unaltered hair indicate related behavior.

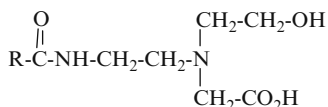
8.4.1.10 Effect of Surfactants on the Sorption of Polymer JR

All surfactants that have been examined, whether neutral, anionic, or cationic, decrease the uptake of polymer JR onto hair [23, 33]. Pareth-15-9, a nonionic surfactant, exhibited the smallest effect in decreasing the uptake of Polymer JR. Faucher and Goddard [23] attribute this to the relatively low affinity of this surfactant for both keratin and the polymer.



Pareth-15-9 (R = C11 to C15)

Cocoamphoglycinate had a slightly greater effect in decreasing the uptake of JR.



Cocoamphoglycinate

Pickup was greater in the presence of potassium laurate than cocoamphoglycinate. Goddard et al. [33] found a relatively thick, nonuniform deposit in the presence of laurate which they attributed to precipitated calcium laurate (soap) with polymer.

Anionic and cationic surfactants show the largest effect in decreasing polymer JR uptake onto hair. The cationic myristyl benzyl dimethyl ammonium chloride probably functions via competitive inhibition. Anionic surfactants probably function by forming association complexes that neutralize the cationic charge on the polymer most likely forming a negatively charged species in a large excess of anionic surfactant such as in most shampoos. Nevertheless, small amounts of polymer JR were still detected on the hair even in the presence of excessive amounts of anionic surfactant [33].

8.4.2 Cationic Polymer–Surfactant Complexes

Polymers have been shown to form association complexes with surfactants in solution [36–40]. Goddard and Hannah [31] studied the interaction of polymer JR with anionic surfactants such as sodium dodecyl sulfate (SDS) and concluded that this interaction occurs in two stages when anionic detergent is in excess. The first stage involves adsorption of surfactant to the polymer, forming a primary layer that neutralizes the cationic charge on the polymer. A decrease in solubility occurs at this stage, and the new polymer complex is highly surface-active. As the ratio of anionic surfactant to cationic polymer increases, adsorption of a secondary layer results, accompanied by reversal of the net charge of the total polymer complex species. Increased solubility also occurs.

Manuszak-Guerrini et al. [41] expanded on this understanding of the interaction of cationic polymers with anionic surfactants. These scientists confirmed that cationic polymers interacting with anionic surfactants do precipitate at the theoretical charge neutralization ratio. With the polymers studied including Polyquaternium-10 precipitation occurs at concentrations above 0.010% polymer and anionic surfactant. At concentrations <0.010% polymer, a fixed concentration of sodium dodecyl sulfate is required to produce precipitation. The fixed concentration decreases as the charge density of the polymer increases. Further, these scientists demonstrated that the charge density of the polymer is more important than the spacer length for a mono-quaternary derivative. Also these authors demonstrated that the relaxation rate of polymer–surfactant mixed micelle complex is very dependent on the polymer structure.

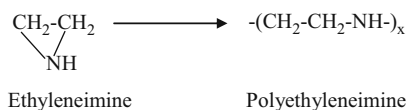
Hannah et al. [32] determined that this type of anionic–cationic complex, formed from 0.1% polymer JR and 1% SDS, does indeed sorb to the hair. Water can remove only some 30% of this JR-SDS complex. SDS and salts are no more effective, leaving some 60% (approximately 0.1 mg complex per gram hair) strongly bound to the hair. Analogous complexes with other cationic polymers have been used for binding or for increasing the substantivity of ingredients to the hair [3, 4].

8.4.3 Polyethyleneimine

Polyethyleneimine (PEI) was used commercially in the 60s and shortly thereafter removed from hair products. However, because of new and improved synthetic techniques, it started making a comeback. Furthermore, several interesting scientific studies have been conducted with this polymer. These studies illustrate some useful principles relevant to the adsorption of cationic polymers to keratin fibers. There are two significant structural differences between PEI and polymer JR:

- PEI has a higher charge density than polymer JR.
- PEI is not quaternized, but is a polyamine.

Polyethyleneimine is formed from the aziridine ethyleneimine, and its chemistry has been reviewed by Woodard [42]. Although PEI is not quaternized, it is highly cationic, since a large number of its amine groups are protonated even near neutral pH. Woodard [42] indicated that at pH 10.5, 4% of the amine nitrogens are protonated; at pH 8, 25%; and at pH 4, 50%. Therefore, PEI would have a charge density of approximately 176 at pH 8, or nearly four times the frequency of cationic sites as polymer JR.



Three different polyethyleneimines have been described with regard to their interactions with human hair; PEI-6 (molecular weight 600); PEI-600 (molecular weight 60,000); and PEI-600E, which is PEI-600 reacted with an almost equivalent amount of ethylene oxide. This reaction with ethylene oxide forms quaternary nitrogen groups and increases the molecular weight to approximately 100,000 [28, 42].

Chow [28] provided evidence for penetration of the lower-molecular-weight PEI-6 into hair. Woodard [42] demonstrated that sorption increases with concentration and with bleaching of hair, similar to polymer JR. Sorption of PEI-6 was also slightly greater at neutral pH compared with acidic or alkaline pH. However, since the charge density of PEI decreases with increasing pH, this result is not unexpected. This PEI study was conducted in an un-buffered medium.

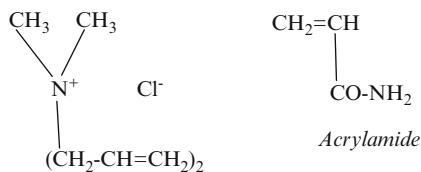
Although a direct comparison has not been made, PEI appears to be even more substantive to hair than polymer JR, probably because of its higher charge density. PEI-600 was sorbed onto hair and tested for desorption toward a 10% shampoo system. After 30 min, less than 20% of the PEI was removed and only approximately 30% after 6 h [42].

The rate of PEI desorption has also been examined with radiolabeled PEI on the hair, desorbing with unlabeled PEI. Most of the polymer, >60%, could not be removed in 24 h by this procedure [28, 42]. This result is consistent with a slow degree of release of PEI due to multiple ionic binding sites to the hair, because it is difficult to uncouple all of the binding sites simultaneously.

PEI polymers, like polymer JR, also interact with anionic ingredients. PEI polymers have been used for increasing the substantivity of other molecules to hair [3, 4]. PEI was formerly used in one commercial shampoo, but has since been removed, presumably because ethyleneimine monomer has been labeled as a carcinogen.

8.4.4 Polyquaternium-6 and -7 Formerly Quaternium-40 and -41 (Merquats)

Polyquaternium-6 and 7 were originally called Merquat polymers and are another type of cationic polymer used in hair care products [43]. One of these (Polyquaternium-6) is a homopolymer of dimethyldiallylammonium chloride (DMDAAC). Polyquaternium-7 is a copolymer of DMDAAC and acrylamide. Polyquaternium-6 has an average molecular weight of approximately 100,000. Polyquaternium-7 has an average molecular weight of approximately 500,000, although different molecular weights may be obtained from the suppliers. Polyquaternium-7 has been used commercially in several different conditioning shampoos.

*Dimethyldiallylammonium chloride*

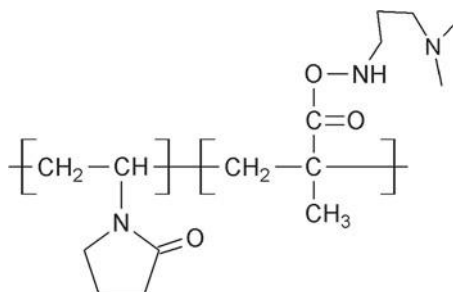
The homopolymer has a charge density of approximately 126, and the copolymer 197. Thus, both of these polymers have a relatively high charge density compared with polymer JR or many other cationic polymers available for use in hair care.

Sykes and Hammes [43] described the adsorption of both of these cationic polymers onto hair from solutions of different amphoteric and anionic surfactants. Analogous to the adsorption of polymer JR, uptake values were greater onto bleached hair than unbleached hair, and greater from amphoteric systems like cocobetaine or cocoamphiglycinate than from anionic surfactants like sodium lauryl sulfate or triethanolammonium lauryl sulfate. The following rationale accounts for these findings. Sodium lauryl sulfate interacts with polymer primarily through an electrostatic interaction. The net result is to neutralize the charge of the polymer and thereby reduce its affinity for keratin. Amphoterics do not neutralize the charge of the cationic polymer as effectively as do anionics. Therefore, cationic polymers demonstrate a greater affinity for keratins in an amphoteric surfactant system than in an anionic surfactant system.

8.4.5 Other Cationic Polymers

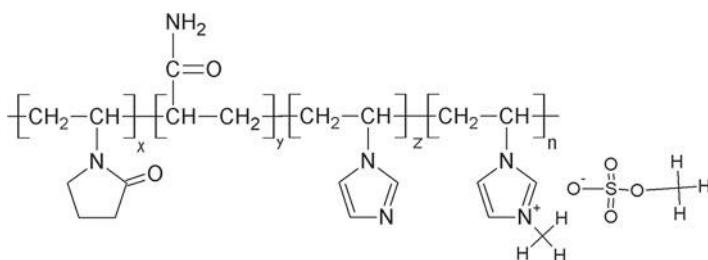
Chemical suppliers to the hair products industry have made a large number of cationic polymers available and many additional cationic polymers have been developed over the past decade. Some of these polymers are carbohydrate derived such as polyquaternium-4 (a grafted copolymer with a cellulosic backbone and quaternary ammonium groups attached through the diallyl dimethyl ammonium chloride moiety; see the section on mousses and Polyquaternium 6 [44]); cationic guar gums such as Guar hydroxypropyl trimonium chloride for example, Jaguar C-13-S or Guar C-261; Ucare polymer LR, a lower-charge-density cationic cellulose derivative of polymer JR; copolymer 845 (PVP/dimethyl aminoethyl methacrylate copolymer derivative of polyquaternium-11, but of lower charge density); copolymers of vinyl imidazole and vinyl pyrrolidone of varying charge density called Luviquats; and even quaternized and amino silicone polymers and copolymers of varying charge density. For additional details on some of these "older" cationic polymers, see the article by Idson and Lee [45]. PVP/DMAA (vinyl pyrrolidone, dimethylaminopropylacrylamide copolymer) has also been

synthesized and through one study provided indications of thermal protective effects against hair damage [46].



PVP/DMAPA acrylates copolymer

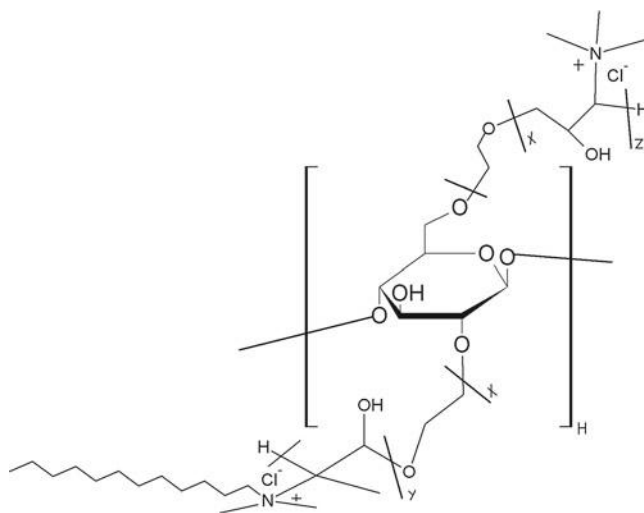
Some additional more recently developed cationic polymers contain three and sometimes four monomeric groups such as Polyquaternium-55 (consisting of copolymers of vinyl pyrrolidone, dimethylaminopropyl methacrylamide and methacryloylaminopropyl lauryldimmonium chloride provided by ISP), or Polyquaternium-53 by Nalco (copolymers of acrylic acid, acrylamide and methacrylamidopropyltrimonium chloride) or Polyquaternium-48 by Goo Co. (a betaine, quat polymer consisting of methacryloyl ethyl betaine, 2-hydroxyethyl methacrylate and methacryloyl ethyl trimethyl ammonium chloride) and Polyquaternium-45 (methacrylamide, methacrylamido propyl trimonium and methacryloylethyl trimethyl ammonium chloride) sold by Rohm and Rohm and Haas and an interesting Silicone Quaternium 18 (linear cationic amino silicone block co polymer) and Polyquaternium-68 with the trade name of Luviquat Supreme by BASF. This latter cationic styling polymer contains four different monomeric units consisting of N-vinyl pyrrolidone, methacrylamide, vinyl imidazole and vinyl imidazole quaternized with methyl sulfate. The four different monomeric units of this polymer are shown below.



Polyquaternium-68

Some other cationic polymers that should prove to be useful are: Polyquaternium 65 that is based on copolymerizing 2-methacryloyloxy ethyl phosphorylcholine with other monomers, Polyquaternium 69 (trade name Aqua Style 300) by ISP is a copolymer of vinyl caprolactam, vinyl pyrrolidone, N-3-(dimethyl amino propyl)-methacrylamide and 3-(methacryloyl-amino) propyl-lauryl-dimethylammonium

chloride and has been used in hair styling gels. Polyquaternium 86 has also found use in hair styling gels and is composed of four monomers: vinyl pyrrolidone, vinyl imidazole, vinyl imidazole quaternized with methyl chloride and methacrylic acid. Polyquaternium 67 is an interesting structure composed of hydroxyethyl cellulose that is quaternized and polymerized with two different quaternary groups. One is n-propyl-2-hydroxy-3-trimethyl ammonium units and the second quaternary group is n-propyl-2-hydroxy-3-dimethyl dodecyl ammonium units.



Polyquaternium-67

8.5 Other Polymers

8.5.1 Polypeptides and Proteins

Polymeric collagen peptides should be somewhat substantive to hair, since they contain multiple ionic and polar sites for bonding, in addition to offering large molecular surfaces with many sites for Van der Waals attachment. Methionine, tyrosine [47], and tryptophan [48] are amino acids or monomeric species of proteins that have been shown to sorb onto hair from aqueous solution. Collagen-derived polypeptides, or polymers of amino acids, have also been shown to have an affinity for hair [49–51]. One would predict that these should be more substantive to hair than their amino acid monomers.

Uptake of this type of species by hair has been shown to increase with either increasing hair damage or increasing polypeptide concentration. An average molecular weight (M_n) of about 1,000 provides optimum pickup, which decreases with higher molecular weight [52] suggesting that diffusion into hair is involved.

Bleaching produces an increase in uptake at neutral pH, whereas thioglycolate-treated hair sorbs more polypeptide at alkaline pH, as does unaltered hair [48]. Bleaching should lower the isoionic point of hair more than thioglycolate, producing more swelling at neutral pH and additional anionic sites to bind polypeptides. Penetration of polypeptide mixtures into hair has been shown by Cooperman and Johnson [51] and is described earlier in this chapter.

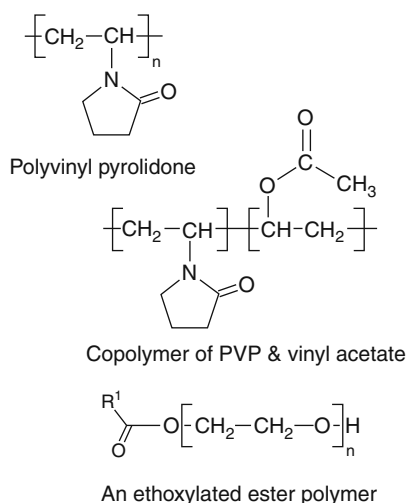
The desorptive action of surfactants and salts on polypeptides already sorbed to hair has not been examined as fully as for polymer JR. On the basis of theory, one would not expect collagen-derived polypeptides to be as substantive to hair as high-charge-density cationic polymers such as Merquats [43] or Luviquat FC 905 [53].

8.5.2 Neutral and Anionic Polymers

The low isoelectric point of hair, near pH 3.6 [24], suggests that the net charge on the hair fiber surface is negative in the presence of most hair care products (at any pH above the isoelectric point). Table 8.3 describes structural formulas for some of the neutral and anionic polymers that have been used in hair products.

These structures and the isoelectric point of hair suggest that the primary binding of these molecules to hair is by polar and Van der Waals interactions. Since shampooing is in an aqueous system, and water is a good hydrogen bond breaking

Table 8.3 Some neutral and anionic polymers used in hair products



agent, the principal binding to resist shampooing for this kind of structure comes from Van der Waals attractive forces. Therefore, anionic and neutral polymers are not highly substantive to hair. Therefore, they have been used in applications where their ease of removal by shampoos is almost as important as their adhesional and film properties.

8.5.3 Some Newer Polymer Types for Hair Care

A few block copolymers have been described in the scientific literature for hair care products [54] as well as in patents. These would seem to provide an excellent new type of polymer to provide unique properties for hair products. Fractal polymers or dendrimers, which are large molecules with regular branching, would also appear to be another new area to offer promising new molecules for hair care formulation [55]. Dendrimers are produced by stepwise synthesis in which branches are linked in stages. One example of such a structure is FPEC (fractal poly-epsilon caprolactam) which has been touted to provide enhanced cleaning efficacy at very low concentrations in surfactant solution [55]. Silicone Quaternium 18 (linear cationic amino silicone) is another interesting relatively block co-polymer used in hair care products.

8.5.4 Nanochemistry, Nanoparticles and Hair Care Cosmetics

The area of nanogels and the generation and use of nanoparticles in hair cosmetics is an area that is beginning to receive attention. Nanogels of polyacrylamide and polyacrylic acid have been created and shown to be capable of encapsulating molecules [56]. These have been suggested to offer the slow release of fragrances and the potential for improved release of active ingredients such as antidandruff agents, etc. In addition, a symposium was conducted in 2006 in which one of the major topics was nanochemistry for cosmetics. Therefore, this subject is one of increasing interest yet is in its technological and applied infancy in our field.

8.6 Hair Fixatives

8.6.1 Hair Sprays

The Liquinet Corporation in Chicago introduced aerosol hair sprays into the marketplace in 1949 [57]. Hair sprays have enjoyed considerable commercial success for several decades. However, hair spray sales peaked during 1969 and

began to decline owing to public acceptance of more natural hairstyles not requiring hair fixatives.

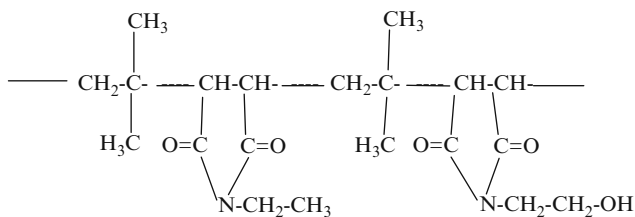
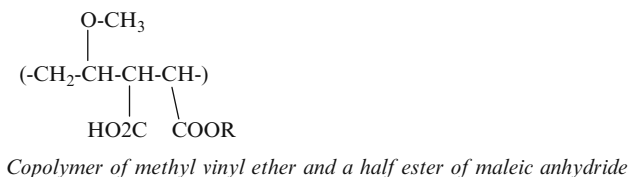
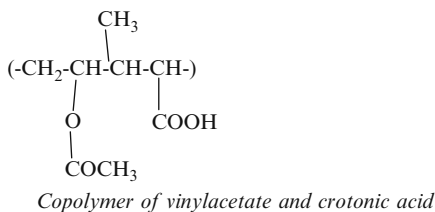
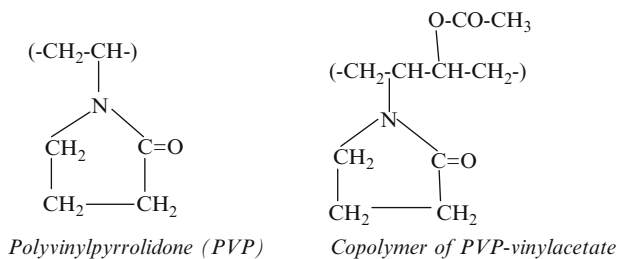
In the early to mid 1970s, hair spray sales declined even further because of environmental pressures to restrict the use of fluorocarbons in aerosol products. The large drop in hair spray sales occurred in 1975, after Roland and Molina theorized how fluorocarbons deplete the ozone layer in the stratosphere. As indicated in the introductory section to this chapter, there has been a great deal of research concerned with lowering VOC's in hair care products, and in particular for hair sprays. Furthermore, the California (CARB) regulations outlined in the introduction are the driving force behind these efforts.

Three types of hair sprays are being produced today: pump hair sprays, hydrocarbon or dimethyl ether aerosols, and carbon dioxide aerosols. The first two of these products account for the major sales for this type of product. Hydrocarbon aerosol hair sprays contain an alcohol-hydrocarbon solvent-propellant system, a synthetic polymeric resin, a base to neutralize the resin if it is a carboxylic acid-containing resin, plasticizer(s), fragrance and, in some cases, surfactant(s) to improve the spreading characteristics of the polymer. Most of the new low VOC aerosol hair sprays contain alcohol-water as the solvent system and dimethyl ether as the propellant. Together the alcohol-dimethyl ether content must be below 55%. For cost considerations, dimethyl ether is a useful propellant, although Hydrofluorocarbon 152-A is exempt as a VOC and provides acceptable, but expensive formulations with most resins including previously used resins [58]. In several counties, there are no VOC limits so hydrocarbon-alcohol systems with virtually no water in these systems can be formulated and sold.

The new low VOC systems with high water content for many of today's "older" resins provide too high a viscosity for spraying. As a result, newer, low molecular weight versions of some of these resins or totally new resins are being touted for the low VOC solvent-propellant systems [59]. For example, Polyurethane-1 (Luviset PUR, a polyesterdiol-dimethylol propionic acid capped with diisocyanate-amine ends and 100% neutralized with AMP) is useful. A lower molecular version of National Starch's Amphomer LV-71 consisting of (octylacrylamide/acrylates/butylaminoethyl methacrylate copolymer) can be used in low VOC systems, but other newer resins are even more effective for low VOC products [60].

Other useful polymers are DynamX from National Starch (polyurethane-14 AMP acrylates copolymer), Aquaflex FX-64 (isobutylene/ethylmaleimide/hydroxyethylmaleimide copolymer, see Table 8.4) and Allianz LT-120 (acrylates/C1-2 succinates/hydroxyacrylates copolymer) from ISP, Luviset PUR and Polyquaternium 68 both from BASF. The structure of Polyquaternium-68 is described above under cationic polymers.

Improved dispensing systems to handle the new formulations are also useful [58] and are generally recommended with some of the formulations offered by the leading resin suppliers cited in the previous paragraph. Sometimes single polymers show deficiencies (performance or cost) in low VOC systems and mixtures of polymers are sometimes employed to overcome these deficiencies [61]. Normally, higher concentrations (about 30% more) of the lower molecular weight polymers

Table 8.4 Some resins used in hair sprays (see text and [1, 58–68] for newer polymers)*Copolymer of isobutylene, ethyl maleimide and hydroxy ethyl maleimide (Aquaflax FX-64)*

must be used to provide equivalent holding power to the higher molecular weight resins. Because of the high water content in the new low VOC systems low levels of corrosion inhibitors such as sodium benzoate or cyclohexylamine are often used, but usually at low concentrations (about 0.1–0.2%).

Pump sprays are very similar to aerosol sprays and consist of solvent(s), a synthetic polymeric resin, a base to neutralize the resin (for carboxylic acid-containing resins), plasticizer(s), and in some cases a surfactant and a fragrance. For the low VOC pump systems, ethanol-water is the preferred solvent.

The resins of all hairsprays are usually synthetic polymers and are the primary ingredient that determines the holding properties of the hair fixative product. Nevertheless, considerable control over the properties of the ionic resins may be achieved by altering the spray characteristics of the product. The degree of neutralization and the type of neutralizer, plasticizer, or type of surfactant employed are also important to the properties of the hair fixative.

Set holding under conditions of changing humidity (especially changes to a higher humidity) is critical to hair spray performance. At the same time, the hair spray fixative system must also be capable of being washed out of the hair by an aqueous detergent system. Thus careful balance of these properties is required to ensure good set stability at high humidity with good washout characteristics.

Synthetic polymeric resins selected for hair spray use are generally anionic or neutral resins rather than cationic to help ensure good washout characteristics. Prior to development of synthetic polymers with a wide range of properties, “hair lacquers” were generally alcoholic solutions of benzoin, rosin, or shellac [62]. These products provided excellent style retention; however, they were difficult to wash out of hair. In the early 1950s, polyvinyl pyrrolidone (PVP) was introduced as a hair-setting agent. This polymer permitted moderate set properties with good washout characteristics. A few years after the introduction of PVP, even better hair setting resins were developed.

Hair sprays, setting lotions, and mousses are related in the sense that each of these products applies a resinous material to the hair and helps to maintain style retention by enhancing interfiber interactions. If the hair is not combed after the resin has set (after the solvent evaporates), rigid contact sites of resin are formed between fibers, analogous to strip welding (Figs. 8.1 and 8.2). This type of interfiber bonding provides the mechanism for set retention of a hair spray.

When the product is applied to wet hair and the hair is set and combed, after the solvent evaporates (as for styling lotions and mousses), the deposited polymer still influences the hair assembly character, by increasing the interfiber forces, but not as

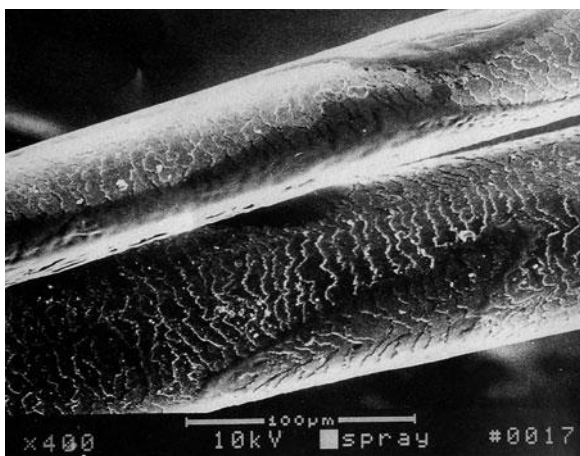


Fig. 8.1 Two hair fibers bonded together with hair spray

Fig. 8.2 Two hair fibers bonded with a hair spray where the resin is beginning to flake

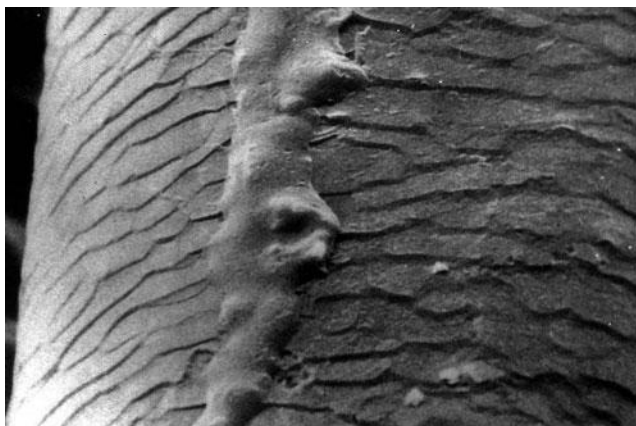
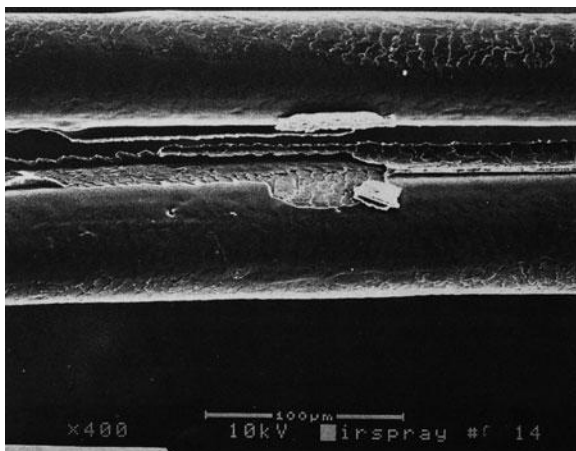


Fig. 8.3 Setting lotion deposit on hair surface

much through rigid interfiber contacts (Fig. 8.3). Many different types of synthetic polymers have been introduced into the marketplace for hair spray use. Chemical structures for three functional and popular types of resins in use today are described in Table 8.4. The polyvinyl pyrrolidone-type resins are usually copolymers of polyvinyl pyrrolidone and vinyl acetate (PVP-VA). These copolymers are more functional than PVP itself, although PVP is widely used in setting lotions and in cheaper hair sprays. A second system widely used for several years is a copolymer of vinyl acetate and crotonic acid. This resin is generally superior to the PVP type resins for hair spray use. Another very functional and popular hair spray resins in retail sale today is the ethyl ester of the copolymer of polyvinyl methyl ether and maleic anhydride (Table 8.4). This product is difficult to use in a low VOC high water

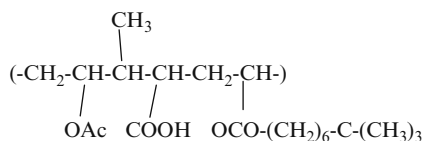
system, even with lower molecular weight modifications. The butyl ester of this copolymer has also been used and is generally superior to the ethyl ester for style retention; however, because of some limitations in fragrance selection for the butyl ester, the ethyl ester has been the most frequently used derivative of this copolymer.

Other, more structurally complex resins, that are highly functional, and in use today are this copolymer of three monomers (vinyl acetate, crotonic acid, and vinyl neodecanoate), and a polymer formed from octylacrylamide, t-butylaminoethyl methacrylate, and two or more monomers consisting of acrylic acid, methacrylic acid, or their simple esters (Table 8.5). This type of polymer provides a low molecular weight version acceptable in low VOC systems; however it is very expensive when used at 30% higher concentration for optimal holding power.

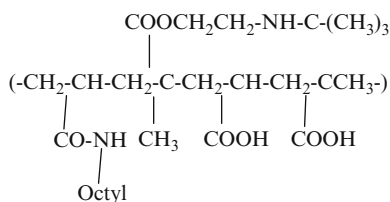
The solvents in pump sprays are limited to alcohol-water mixtures and are therefore not as complex as the solvent-propellant mixtures of aerosols. Generally, ethyl alcohol is the primary solvent, and water the secondary solvent. In some cases, small quantities of propanols or even glycols are used. The solvent and of course the pump spray system largely determine the spray characteristics of a given product which are very important to the functional character of the product [58]. The solvent-propellant systems of today's hydrocarbon aerosol hair sprays used outside the US generally consist of alcohol combined with hydrocarbons such as isobutene, butane or propane and virtually no water. For low VOC systems, dimethyl ether is a useful propellant and acetone may be used as high as 10% and is useful because it is not considered a VOC.

For additional details on aerosol propellants for hair sprays see the previous discussion on VOC propellants and the article by Root [57]. The solvent-propellant in both aerosol and pump sprays contain the VOC and present the apparent

Table 8.5 Two structurally complex, but effective hair spray polymers

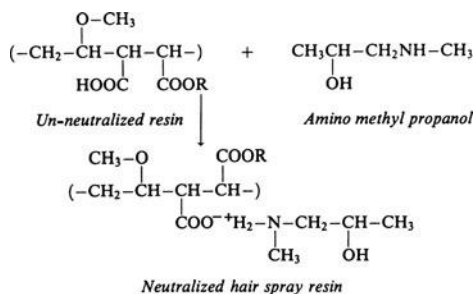


Simplified structure for copolymer of vinyl acetate, crotonic acid, and vinyl neodecanoate



Simplified structure for copolymer of octylacrylamide, t-butylaminoethyl methacrylate, acrylic acid (or ester), and methacrylic acid (or esters)

Fig. 8.4 Neutralization of a hair spray resin

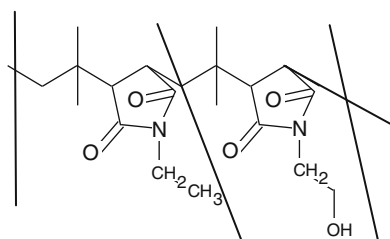


environmental problem. As stated, the CARB regulations for 1999 of 55% VOC present the target that has stimulated research and development in this area.

The ability of the resin to spread over the hair surface is largely a function of the resin and is determined by its surface tension and the viscosity of the system. Nevertheless, spreading characteristics of resins can often be improved by adding surfactants [69]. Nonionic or cationic surfactants are generally preferable to anionics for this purpose.

For resins containing carboxylic acid groups, the type of base used to neutralize the resin [69], and the degree of neutralization (see Fig. 8.4) are adjusted to provide optimum film properties and solubility. Organic bases such as aminomethyl propanol, triisopropanol amine or aminomethyl propanediol are generally preferable to inorganic bases as hair spray resin neutralizers.

The structures in Table 8.5 are simplified descriptions of these copolymers and are provided primarily to illustrate the monomers forming the basic structure of some of these polymers. Some of the newer resins used in low VOC hairsprays and other fixative products have already been described in the section on cationic polymers. Others include Aquaflex FX-64 from ISP which is Isobutylene/ethylmaleimide/hydroxyethylmaleimide and is highly compatible with water and has been adapted for hair sprays. This structure is shown below. A very novel one from ISP based on Vinyl acetate/butylMaleate/Isobornyl Acrylate copolymer has also found some use in hair sprays as a fixative polymer.



Isobutylene/ethylmaleimide/hydroxyethylmaleimide

Plasticizers such as dimethicone, cetyl alcohol, dioctyl sebacate, or related ingredients are often added to provide more flexible, less brittle films to minimize flaking and thus to maximize luster and set holding.

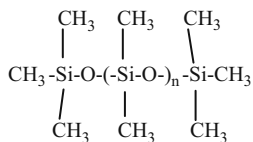
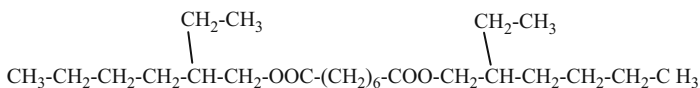
*Dimethicone**Cetyl alcohol**Diocetyl sebacate*

Figure 8.2 illustrates two hair fibers with hair spray resin as the resin begins to flake from the fibers. Plasticizers as above can minimize flaking of resinous products used in hair styling products.

8.6.2 Some Hair Fixative Formulations

These are hair spray concentrates and represent 85% of the total product. The concentrates will be diluted with 15% A-46 Propellant (isobutane and propane) to obtain an acceptable pressure. The spray character will be adjusted with the appropriate valve system. These hair sprays contain 80% VOC and meet the requirements outside of California (Table 8.6).

Table 8.6 Aerosol hair spray concentrates for 80% VOC hair sprays

Ingredient	Holding power		
	Regular (%)	Extra (%)	Super (%)
<i>Octylacrylamide acrylates</i>			
Butylaminoethyl methacrylate	1.5	2.0	3.0
Aminomethylpropanol (AMP)	0.23	0.3	0.4
Glycerine	0.4	0.4	0.4
Dimethicone Copolyol (SF-193)	0.15	0.2	0.3
<i>Octadecyltrimethylammonium</i>			
Chloride 0.06	0.06	0.06	
Fragrance	0.15–0.5	0.15–0.5	0.15–0.5
Alcohol	q.s.	q.s.	q.s.
Water (deionized)	22.5	22	21
Total formula%	85%	85%	85%

8.6.2.1 Hair Spray Making Procedure

Add the alcohol or alcohol and water into the main mixing tank and begin stirring. Add the resin and stir until a clear solution is obtained. Adjust the pH with AMP to 8.5. Add the glycerine, the silicone, the quat and perfume with stirring. Add the water with stirring and when a clear uniform solution is obtained transfer the concentrate to the aerosol filling line for filling and pressurizing (Tables 8.7 and 8.8).

Table 8.7 Examples of aerosol hair sprays that meet the 55% VOC standard

Ingredient	% concentration (extra hold)	[63]	[64]
Polyurethane-1 (Luviset P.U.R.)	4.5		
DynamX		17.85	
Allianz LT-120			12.77
AMP-95			1.0
Ammonium hydroxide			0.25
Alcohol	29.5	17.54	27.0
Water	39.9	31.41	23.7
Dimethyl ether	25	33	28
Dimethicone copolyol	0.2	0.5	
Fragrance	0.2		
Sodium benzoate	0.1		
Cyclohexylamine	0.1		
Triethyl citrate		0.15	
MEA Borate/MIPA borate			0.25
Propellant 152 A			7.0

Table 8.8 Pump hair spray formulations

Ingredient	80% VOC compliant	55% VOC compliant	
		[65]	[66]
Alcohol	79.2	54.18	51.36
DynamX		3.28	14.58
Balance 47		5.10	
Triethyl citrate		0.1	0.15
AMP-isostearoly hydrolyzed wheat protein			0.1
AMP-95		1.2	
Cropeptide W			0.05
Octylacrylamide/acrylates			
Butylaminoethyl methacrylate copolymer	4.5		
Cyclopentasiloxane		0.2	
Diisobutyl adipate	0.05	0.05	
Silsoft A-843	0.05	0.05	
Fragrance	0.3	0.1	
Panthenol		0.1	
Uvinul MS-40		0.05	
Water	15.5	33.59	33.76

The above products are made by the same procedure as for the aerosol hair spray, except no propellant is used and the above represents 100% of the formula. A spritz product can be made from the above formulas by proportioning all ingredients except solvent by about 150%. The 55% VOC product is satisfactory, but not as acceptable as the 80% VOC product primarily because of the slower drying time. Combinations of resins and tailored spray systems may be used to improve this system further.

8.6.3 *Mousses*

Mousses are related to both hairsprays and setting lotions. Their formulations are generally more complex sometimes consisting of two or more polymeric resins and additives in a water-hydrocarbon (solvent-propellant) system similar to shaving creams. As indicated in the introduction, the CARB standard for January 1, 1994 for mousse hair products was 16% but has been lowered to a maximum of 6% VOC by the end of 2002. Therefore 6% VOC is the standard today.

The resins of mousses are generally cationic such as polyquaternium-4 or polyquaternium-11, or cationic and neutral, or cationic and anionic combined or even amphoteric. Polyquaternium-4 contains both hydroxyethyl cellulose and diallyldimethylammonium chloride. This polymer is related to the quaternized hydroxyethyl cellulose polymer depicted in Table 8.2, except the cationic groups are formed from the diallyldimethylammonium chloride moiety attached to the cellulosic backbone. Polyquaternium-11 (quaternium-23 – Gafquat) is a copolymer of vinyl pyrrolidone and dimethylaminoethyl methacrylate quaternized with dimethyl sulfate. This polymer is related to the quaternized copolymer of PVP depicted in Table 8.2. One mousse product in retail sale contains both of these cationic polymers. Others contain one cationic polymer and either a neutral or an anionic resin such as polyvinyl pyrrolidone, vinyl acetate copolymer or a resin such as the butyl ester of polyvinyl methyl ether, maleic anhydride copolymer. Polyquaternium-68 is a newer resin that has been recommended for use in styling and conditioning mousses. Its structure is described in the section on polycationic polymers.

Surfactants and oils are also present in most mousse formulations. Surfactants function to lower the surface tension to help spread the polymer film over the hair surface and to support the foam character of the product. Mousses are added to wet hair. They are combed through the hair without rinsing, to distribute the product throughout the hair. The hair is then styled and dried. Mousses improve wet manageability by lowering combing forces and they enhance body and style retention (Table 8.9).

With these products, the hair is combed dry, after the solvent has evaporated. Therefore, they cannot provide a large number of rigid contacts as hair sprays do; however, they do enhance interfiber attractive forces to provide increased body and improved style retention.

Table 8.9 A styling mousse formulation [67]

Ingredient	Percentage
<i>Part A</i>	
Celquat L-200	1.0
Gafquat 755N	3.5
Balance CR	1.5
AMP Regular	0.09
DC 200 fluid	0.25
Trideceth-12	0.25
Cetyl trimethyl ammonium chloride (CTAC)	0.25
DMDM hydantoin and iodopropynyl butylcarbamate	0.15
Fragrance	q.s.
Water	72.01
<i>Part B</i>	
Propellant A-31	6.0
Propellant 152A	15.0

Making procedure: For Part A, charge the water into the mixing vessel and with stirring add the Celquat until it is completely dispersed. Then add the GAFQUAT and mix until homogeneous. Add the AMP followed by the Balance polymer. When the solution is homogeneous, transfer this concentrate to the aerosol filling line for filling with propellants and pressurizing.

8.6.4 Setting/Styling Lotions and Gels

These products are related to both hair sprays and mousses. They are more similar to mousses, because they are aqueous-based or alcohol-water solvent systems. These products are applied to wet hair or sometimes to dry hair prior to setting as opposed to spraying onto dry hair (Fig. 8.3). Remember, the CARB standard for hair styling gels for January 1, 1994 is 6% VOC and is still in effect.

The resins of styling or setting lotions are usually cationic, for example, polyquaternium-11 (copolymer of vinyl pyrrolidone and dimethylaminoethyl methacrylate quaternized with dimethyl sulfate, similar to the quaternized copolymer of PVP depicted in Table 8.2) – anionic – for example, butyl ester of polyvinylmethyl ether and maleic anhydride – neutral – for example, copolymer of polyvinyl pyrrolidone, vinyl acetate – or even polyvinyl pyrrolidone itself with polyacrylate thickeners. Two more recently developed cationic polymers recommended for styling gels are: Polyquaternium 86 from BASF and Polyquaternium 69 from ISP.

Since the mode of application of these products is similar to the mousse type of product and involves combing the product through wet hair prior to setting and drying and then re-combing the hair after it has dried, these products do not function by forming rigid bonds in the same manner as hair sprays. Nevertheless, these

products do enhance interfiber forces to provide increased hair body and improved style retention (Table 8.10).

Making procedure for the setting lotion formulation:

Charge the alcohol into the mixing vessel. Add the Gafquat resin with stirring and mix until completely dispersed. Add the Solulan, Ammonyx and Emulpor with stirring until the system is homogeneous. Add the water with stirring, and then add the colors and the fragrance.

Making procedure for setting Gel 1 of Table 8.11:

Gel 1: Dissolve the PVP/VA resin in the alcohol and then add about 10% of the formula amount of water. Make a homogeneous solution of the Carbomer in about 80% of the formula amount of water. Deaerate this solution and then add the EDTA and the TEA. In a separate container add, with heating (to about 50°) and stirring, the PEG-40 hydrogenated castor oil to about 10% of the formula amount of water and stir until it is homogeneous. Add dimethicone copolyol with stirring until it is

Table 8.10 A setting lotion formulation

Ingredient	Percentage
Gafquat 755	5.0
Solulan 98	0.5
Ammonyx 4002	0.1
Emulphor AM-650	0.1
Colors	q.s.
Fragrance	0.2–0.5
Alcohol	35.0
Water (deionizer)	59.06

Table 8.11 Setting/styling gel

Ingredient	Percentage	
	Gel 1	DC Gel [68]
Alcohol	5.0	
PVP/VA 64	2.2	
Triethanolamine	0.6	to pH 7–8
Carbomer 940	0.6	
Carbomer (Carbapol ETD 2020/ Noveon Inc.)		0.43
DMDM Hydantoin		0.1
Water	q.s.	84.77
Dimethicone copolyol	0.3	
Fragrance	0.15–0.4	
PEG-40 hydrogenated castor oil	0.3	
Tetrasodium EDTA	0.1	
Colors	–	
Glycerine		8.0
DC 5-7070 Si Amino Elastomer Emulsion		6.7

Table 8.12 Spray-on gel formulation

Ingredient	Percentage
PVP/VA copolymer	4.0
Isostearth-20	1.0
DMDM hydantoin	0.7
Octyl salicylate	0.3
Disodium EDTA	0.2
Fragrance	0.2
Water (deionized)	93.6

homogeneous. Cool and add the benzophenone and fragrance to this solution and then slowly mix it into the PVP/VA solution and stir until the system is homogeneous. Add this solution to the Carbomer solution and mix until a clear gel is obtained. Be careful to not aerate the system too much.

Making Procedure for Dow Corning Setting Gel (DC of Table 8.11):

Add the Carbomer to the water and DMDM Hydantoin with stirring. Adjust the pH to between 7 and 8 with triethanolamine. Then add the glycerine and the silicone emulsion with stirring.

The actual products above are in the form of a gel. However, products have appeared in the marketplace that provide hair styling properties like a gel but are not in gel form, but nevertheless, they are called gels. For example, the “spray gel” or “spray-on gel” is such a product (Table 8.12).

Making procedure: Charge the water into the mixing vessel and add the isostearth-20 with stirring while heating to 50°. Cool to room temperature and add the PVP/VA polymer with stirring. When the system is homogeneous add the remaining ingredients. Polyquaternium-69 and Polyquaternium 86 both described earlier under cationic polymers are newer resins that have found use as styling gel polymers.

8.7 Evaluation of Hair Fixative Products

To develop and evaluate hair sprays, setting products, and mousses, a variety of methods have been developed. Many of the methods described in this section were developed primarily for hair spray formulation and evaluation. Style retention is without question the most important property of hair sprays, therefore several approaches to evaluating hair spray holding power have been described in the literature [70–72]. One novel approach by Ganslaw and Koehler [73] involves measurement of the rate of untwisting of hair swatches treated with hair fixative solution. This method has been called twist retention analysis. It correlates with curl retention and is claimed to allow for more rapid evaluation of data.

Frosch and Vogel [74] developed an approach involving measurement of the force required to break polymer treated hair strands. Another approach, is the

method by Wickett and Sramek [75, 76]. This method involves determining the adhesive strength of hair/hairspray junctions by determining the force required to pull apart two hair fibers joined by a fixed quantity of hair spray. Another approach called dynamic hairspray analysis involves determining the stiffness, rate of drying, duration of tack and maximum tack forces of hair tresses in the form of omega loops [77].

Most of these methods are also used to develop and to evaluate hair setting products and mousses. Very recently, Lang and Sendelback [78] reviewed a large number of test methods for the evaluation of hair spray polymers and products. One of their primary conclusions was, although several interesting and useful methods have been introduced into the scientific literature for fixative polymer evaluation, the well-known curl retention test is still the fastest and most accurate method for obtaining useful information about the holding properties of hair spray polymers.

But, in addition to style or curl retention, several other laboratory tests are helpful to characterize the following properties of hair sprays:

- Product spray characteristics.
- Film properties.

Among the more important spray characteristics are spray rate, spray pattern, and droplet size. Of course, safety considerations related to flammability are also important.

For mousses, measurement of foam properties including foam volume, foam quality, and foam stability is critical to the performance of this type of product. Although such tests have not been described for mousse evaluation, per se, minor modification to shave cream foam tests should provide satisfactory procedures.

Film properties of these products are crucial to performance, and several methods to evaluate film properties of hair spray products have been developed [70, 79, 80]. Erlemann [70] described a variety of methods both subjective and objective to evaluate hair spray films formed on different substrates including metal plates or glass, on flexible foils or tissues, and on hair. Ayer and Thompson [79] describe evaluation of hair spray properties by scanning electron microscopy.

8.8 Silicone Polymers in Hair Care Products

Dimethicones described above in the fixatives section are probably the most widely used silicones in hair care. They are the primary active ingredients of two in one shampoos and of many hair conditioners. As a general rule, the higher the molecular weight the more deposition and conditioning provided by this type of silicone. However, the higher the molecular weight the more difficult the silicone is to formulate into an aqueous composition especially an anionic shampoo system. As a result, optimum effects are generally achieved at a viscosity of 10,000–40,000 cps. Many functionalized silicones have been introduced into the patent literature and some of these into the market place [79–87]. Some examples of these are

aminosilicones, anionic silicones, alkyl-modified siloxysilicates [81] and even silicones containing quaternary groups [88]. As a general rule the dimethicone type silicones without other functionality have proven to be the most widely used to date for many compositions.

Dimethicone copolyols or silicone glycol copolymers have been used as plasticizers for resins and as co-solubilizers in shampoo systems. Because of the high water solubility (affinity for water versus hair) and low total Van der Waal's bond strength, the lower molecular weight copolyols and glycol copolymers are not good conditioning agents for a rinse off hair product. However, Yahagi [87] concluded that high molecular weight dimethicone copolyols with small amounts of copolyol and therefore a low HLB (hydrophile lipophile balance) can deposit onto hair and function as conditioning agents, but they are not as effective as dimethicones. Nanavati and Hami [86] described the adsorption of dimethicones and dimethiconols of higher molecular weight (10,000–64,000 for dimethicones and 220,000–280,000 for dimethiconol gums) onto hair.

Dimethicones formulated into a shampoo can protect the hair against some damaging abrasive actions of combing and brushing [89]. Some silicone polymers containing phenyl groups have high refractive indices (near 1.5) and are reported to enhance the shine of hair fibers. Siloxysilicate polymers containing alkyl groups longer than C12 have been described by Berthiaume and Baum [81] to increase hair body. These same authors describe ester siloxysilicate polymers for conditioning hair, but they are less substantive to hair than alkyl siloxysilicates where the alkyl groups are C 12 or longer.

Gamez-Garcia [90] demonstrated that an aqueous solution of a protein polysiloxane copolymer at 2% could prevent cuticle cracking from thermal cycling, see Chap. 9 for details of this effect. A cystine polysiloxane polymer has been shown by Gamez-Garcia [91] to be capable of re-cementing cuticle scales that have been previously lifted.

Amino functional silicones, on the other hand, have been used in hair conditioners and shampoos for several years to improve hair conditioning. Because of the potential cationic charge on amino functional silicones, it is sometimes mistakenly accepted that all amino silicones are more substantive to hair than dimethicones in all systems. Several years ago we conducted a study among amodimethicones of varying molecular weight (about 1,000–60,000 Da) and charge density. We found that adsorption to hair from an anionic shampoo in an aqueous medium is more a function of molecular weight than charge of the silicone. Consistent with this effect is the fact that the amount of dimethicone adsorbed to hair generally increased with increasing molecular weight. Apparently, for silicone polymers that are emulsified or dispersed in an aqueous medium, because of their low water solubility, entropy is important to the adsorption process.

There is oftentimes more entropy or random structural organization for a silicone molecule to adsorb to a hair fiber surface than to emulsify or disperse it into an aqueous system. To form such a stable emulsion or dispersion requires a great deal of structural organization. Therefore, when the silicone can adsorb with an increase in entropy the process becomes entropy driven. For lower molecular weight

silicones in a neutral medium, charge could be more important and could override entropy-involved factors.

Dimethicone conditioning agents in anionic shampoos are dispersed as large particles generally about 20 μm in diameter. The particle size of the dispersed dimethicone and the dispersing agents are important to the overall conditioning delivered. For example, if one takes a good conditioning dimethicone shampoo and homogenizes it so that the particle size decreases appreciably conditioning is decreased and can be totally eliminated. The stabilizing agents or suspending agents used in the formulation are also important to conditioning. In one of the first patents on dimethicone containing conditioning shampoos the stabilizing agent was claimed to be fatty amide. However, intensive study revealed that the polymeric gum also played a significant role in product stability. Furthermore it has been shown that one can decrease conditioning by simply increasing the amount of polymeric gum stabilizer in the system. Long chain fatty alcohols have also been used as stabilizing agents. These alcohols have also been shown to adsorb onto the hair with the dimethicone.

It is well known that dimethicone polymers formulated into a shampoo system adsorb more readily onto undamaged hair than onto damaged hair and even more readily onto root ends of hair than tip ends. This is because dimethicones are so hydrophobic that the more the hair is damaged, the more hydrophilic the hair surface becomes and the less the hydrophobic silicone adsorbs to it. One way to compensate for this poor affinity that results from increasing hair damage is to use cationic polymeric bridging agents. Some cationic polymers can function as bridging agents, especially on damaged hair by increasing the affinity between the hair and the hydrophobic silicone. This concept is related to the work of Nanavanti and Hami [86], and others, who demonstrated that adsorption and conditioning of dimethicones onto bleached hair can be enhanced by formulation with quaternary ammonium compounds.

The concept of bridging agents in these systems is useful because the quaternary ammonium polymer has both hydrophilic and hydrophobic sites. Therefore it has a higher affinity for the hydrophilic damaged hair fiber surface than the silicone. Thus, the bridging agent creates more binding of silicone to the hair surface in one of two possible ways. It either binds to the hair surface making that surface more receptive to the hydrophobic silicone or it binds to the silicone making the silicone particles more attractive to the hair surface. In either event, more silicone is adsorbed onto the hair surface and conditioning of damaged hair is made more effective. Berthiaume and Jachowicz [92] demonstrated that polydimethyl siloxanes from 50 to 12,500 cSt in aqueous emulsions deposit more readily onto hair that has been pretreated with a cationic polymer (poly-dimethacrylamidopropyltrimethyl ammonium chloride) than onto untreated hair. This one experiment suggests that the cationic polymer likely first deposits onto the hair surface increasing the affinity of the hair for the hydrophobic silicone. One must also keep in mind that a quaternary ammonium polymer (at a low concentration) in an anionic shampoo system (with a high concentration of anionic surfactant) is neutralized and suspended partly by the anionic surfactant. Therefore, it becomes a negatively

charged species, but it still can have a higher affinity for the damaged hair surface than the very hydrophobic silicone.

Similar to cationic polymers, low concentrations of amino silicones in an anionic shampoo are essentially anionic species because of complex formation with the excess anionic surfactant. These complexes help to explain why the adsorption of amino silicones from an anionic shampoo is largely dependent on molecular weight (sorption increases with molecular weight) rather than on charge density of the amino groups. Sorption is also dependent on the structure of the anionic surfactant employed.

8.9 In-Situ Polymerizations in Hair

With the exception of oxidation hair dyes, in situ polymerizations in hair have been only laboratory and concept curiosities. However, remarkable changes to the chemical [93] and physical properties [94] of the fibers have already been achieved using this technology. In the future, through the combination of science and imagination, some in-situ polymerization hair treatment may end up in the marketplace. The remaining sections of this chapter describe oxidation dyes as in-situ polymerization hair treatments and in-situ vinyl polymerization reactions in human hair.

8.9.1 *Oxidation Dye Reactions as In Situ Polymerization Reactions*

Although not generally described as such, certain reactions of oxidation hair dyes are examples of in-situ polymerizations in hair. These consist of the oxidation of electron-rich aromatic amine and phenol monomers that condense with each other and perhaps even attach to amino acid residues of hair. The net result, at least with products containing p-phenylenediamine (PPD) and resorcinol, is the formation of polyindophenol-type polymeric pigments [95–97] that render color to the hair. (See the discussion on oxidation hair dyes in Chap. 5 and its references for additional details.)

8.9.2 *In-Situ Polymerization of Vinyl Monomers in Hair*

Several techniques have been employed for the polymerization of vinyl monomers on and in wool fiber.

- Reduction of the fibers, followed by reaction with vinyl monomer and oxidizing agent in an inert atmosphere [98, 99].

- Radiation grafting [100, 101].
- The Wurlan Process [102] – which is the condensation of diamines and diacid chloride in the presence of wool fiber.

The procedure that has been most thoroughly studied for polymerization into human hair is related to the first procedure above, that is the reduction of the fibers (in an air atmosphere) [103, 104] followed by reaction with vinyl monomer and an oxidizing agent.

8.9.3 Mechanism of Action

Polymerization of a vinyl monomer into human hair is a complicated, multi-step process that may be summarized by the following reaction scheme:

1. Diffusion of reducing agent into the fibers.
2. Nucleophilic cleavage of the sulfur-sulfur bond by reducing agent.
3. Water rinse.
4. Diffusion of oxidizing agent into the fibers.
5. Reaction of reduced hair and oxidizing agent.
6. Diffusion of vinyl monomer into the fibers.
7. Chain-initiating reactions.
8. Chain-propagating reactions.
9. Termination of free radical chains.

Steps 1 through 3

Among the reducing agents that have been employed in this type of process are thioglycolic acid (TGA) [90], bisulfite [79], and tetrakis (hydroxymethyl) phosphonium chloride (THPC) [104]. The critical point in this step is the extent of reduction, since each of these reducing agents provides increasing polymer add-on with increasing time of reduction (Fig. 8.5). Comparison of the TGA system with the bisulfite system shows a faster rate of polymerization with TGA than with bisulfite. This rate difference is consistent with a faster rate of reduction of hair by TGA. Since the reaction of TGA with human hair is diffusion-controlled [105], step 2 is extremely important to the overall kinetic scheme. But, since cleavage of the sulfur-sulfur bond by TGA is faster than diffusion, Step 2 seems of lesser importance to the overall kinetic scheme than Step 1. However, the extent of disulfide fission is a controlling factor in the remaining steps: the diffusion of initiator (oxidizing agent) and monomer into the fibers.

The effect of pH during reduction is very important to both the TGA [103] and the THPC [104] systems. In the case of the TGA system, reduction rate increases with pH, and polymer add-on increases similarly. For the THPC system, pH is also critical, but not for entirely the same reason. According to Jenkins and Wolfram

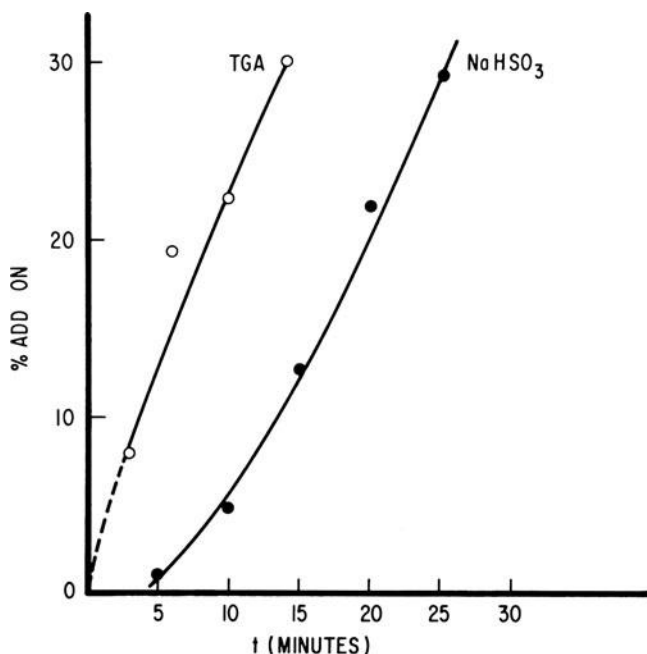
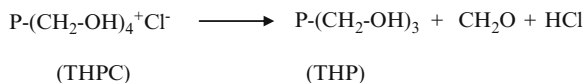


Fig. 8.5 Influence of the reduction step on polymer add-on [103] (Reprinted with permission of the Journal of the Society of Cosmetic Chemists)

[106], THPC dissociates in aqueous solution to Tris (hydroxymethyl) phosphine (THP), and THP is the actual ingredient that reduces the hair.



Wolfram [104] has shown that polymer add-on increases with pH of the reducing solution, up to pH 7, where it appears to level. Thus, THPC dissociation and sulfur-sulfur bond cleavage also increase with pH up to 7. The fact that polymer add-on is not higher at pH 9.2 than at 7.0 suggests interference of alkalinity in a subsequent reaction step. The most probable complications are in the chain initiation or propagation steps, since Wolfram indicates that the cysteine-persulfate redox system is optimal in the pH region of 1.5–3.5.

Steps 4 Through 9

Both TGA-hydroperoxide and THPC-persulfate systems show a linear relationship between polymer add-on and the square root of time, (Fig. 8.6) [107]. In both of these systems, the amount of polymer add-on can be influenced by concentration changes in both oxidizing agent and vinyl monomer. Therefore, the diffusion of vinyl monomer and oxidizing agent into the fibers can also be rate

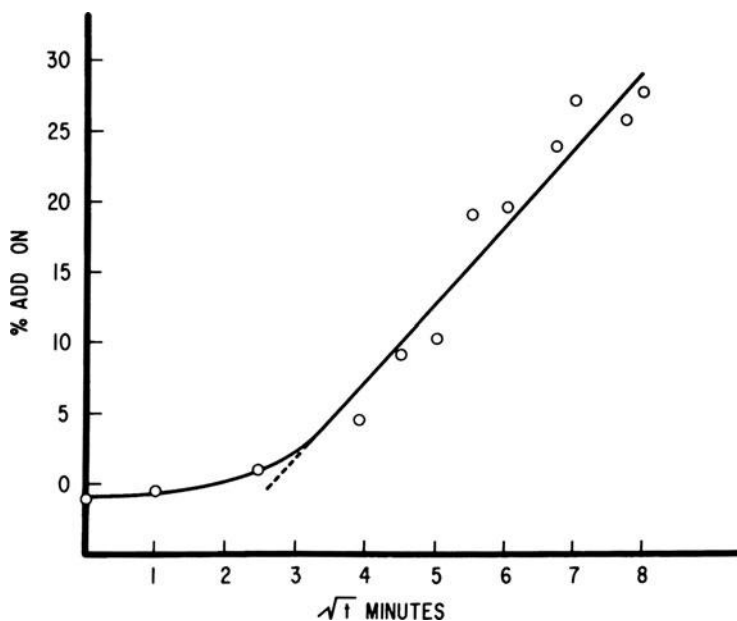


Fig. 8.6 Influence of reaction time (steps 4–9) on polymer add-on [103] (Reprinted with permission of the Journal of the Society of Cosmetic Chemists)

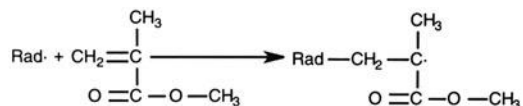
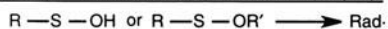
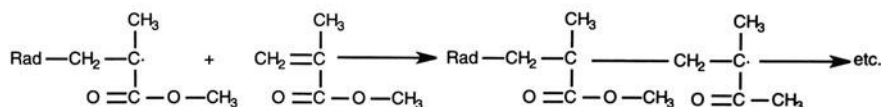
limiting. As a result, any variable that can accelerate diffusion of oxidizing agent and/or vinyl monomer into the fibers is capable of increasing the rate of polymer add-on.

Step 5, the reaction between reduced hair and oxidizing agent, generates the free-radical species that initiates polymerization. For the system of Wolfram [104], this step involves reaction of THP or mercaptan of reduced hair with persulfate. But, for the TGA system, it involves reaction of mercaptan with cumene hydroperoxide.

The remaining reactions, steps 8 and 9, are classical free-radical propagation and termination reactions, summarized by Fig. 8.7. If the chain-initiating radicals are from cysteine residues or other residues of the hair, then the resultant polymer is grafted (i.e., covalently bonded to the hair protein). However, if the chain-initiating radicals are from oxidizing agent or reducing agent, then the polymer, if inside the hair, may become entrapped as it grows.

8.9.4 Solvent System and Its Effect on Polymerization

For the TGA-cumene hydroperoxide system, an ethanol water solvent was employed for monomer and initiator. The data clearly demonstrate maximum

CHAIN – INITIATING REACTIONS (step 7):CHAIN – PROPAGATION REACTIONS (step 8):CHAIN – TERMINATION REACTIONS (step 9):

RADICAL COMBINATION
 ABSTRACTION OF ATOM (GENERALLY HYDROGEN ATOM)
 DISPROPORTIONATION

Fig. 8.7 Chain initiation, propagation, and termination steps

Table 8.13 Polymerization into bleached hair with methyl methacrylate [93]

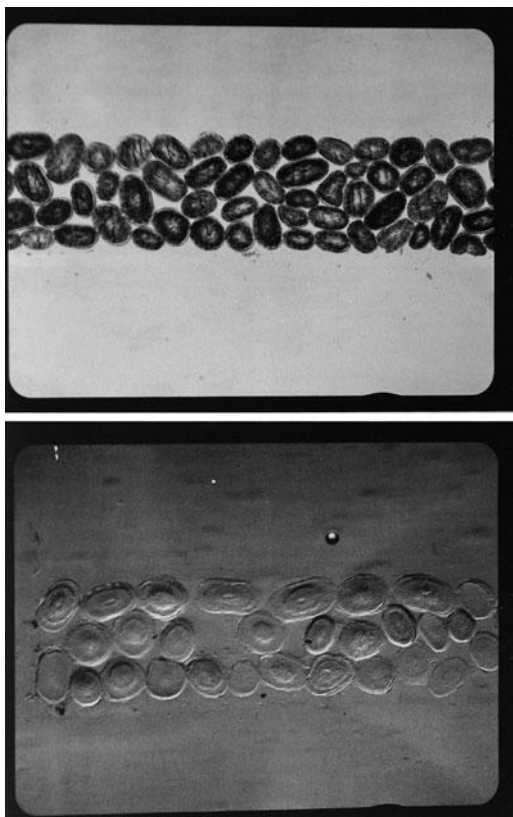
% cystine in hair	% add-on
18.1	12
15.9	18
15.4	21
14.5	25
10.9	38

add-on with larger proportions of water in the system, providing greater hair swelling, consistent with diffusion rate control [101].

8.9.5 Polymerization into Chemically Altered Hair

Bleaching increases the permeability of hair. However, bleaching also decreases the disulfide content, and the disulfide bonds are potential sites to form mercaptan groups, a part of the redox system. Therefore, it was of interest to determine which of these two parameters, permeability or mercaptan content, might contribute more to the rate of polymer add-on. Hair was bleached to varying extents with alkaline hydrogen peroxide and then treated with a bisulfite-cumene-hydroperoxide system, using methyl methacrylate monomer. The data clearly show increasing polymer add-on with decreasing disulfide cross-links (Table 8.13), once again emphasizing the importance of diffusion rate control to this process [103]. Figure 8.8 shows

Fig. 8.8 Cross-sections of hair fibers containing two different amounts of polymethyl methacrylate. *Top*: Fibers containing 16% add-on. *Bottom*: Fibers containing more than 100% add-on



cross-sections of polymethyl methacrylate grafted hair fibers with a low add-on (top – 16% add-on) and a high add-on (bottom >100% add-on). Grafting was also carried out on reduced-oxidized hair, that is, hair that was permanent waved to varying extents prior to treatment with the polymerization system [103]. This hair also provided very large add-ons.

8.9.6 Evidence for Polymer in the Hair

Hair after treatment with TGA-cumene hydroperoxide using methyl methacrylate monomer was hydrolyzed, using 5 N hydrochloric acid. Acid hydrolysis dissolved away the keratin from the polymer. Part of the resultant fiber-like residue was dissolved in organic solvents. The solute (in the organic solvents) was shown to be poly methyl methacrylate by refractive index and infrared spectroscopy [101].

Viscosity average molecular weights of this polymer were determined from bleached, permanent waved and chemically unaltered hair and found to be relatively constant near 90,000 Da. This result suggests an average degree of polymerization of approximately 900.

Scanning electron micrographs of the surface of hair fibers treated with the TGA-cumene hydroperoxide system using methyl methacrylate monomer show a thick coating of polymer on the hair fiber surface. However, the fibers still retain repeating irregularities perpendicular to the fiber axis, which correspond to scale edges covered with a thick coating of polymer (Fig. 8.9) [103].

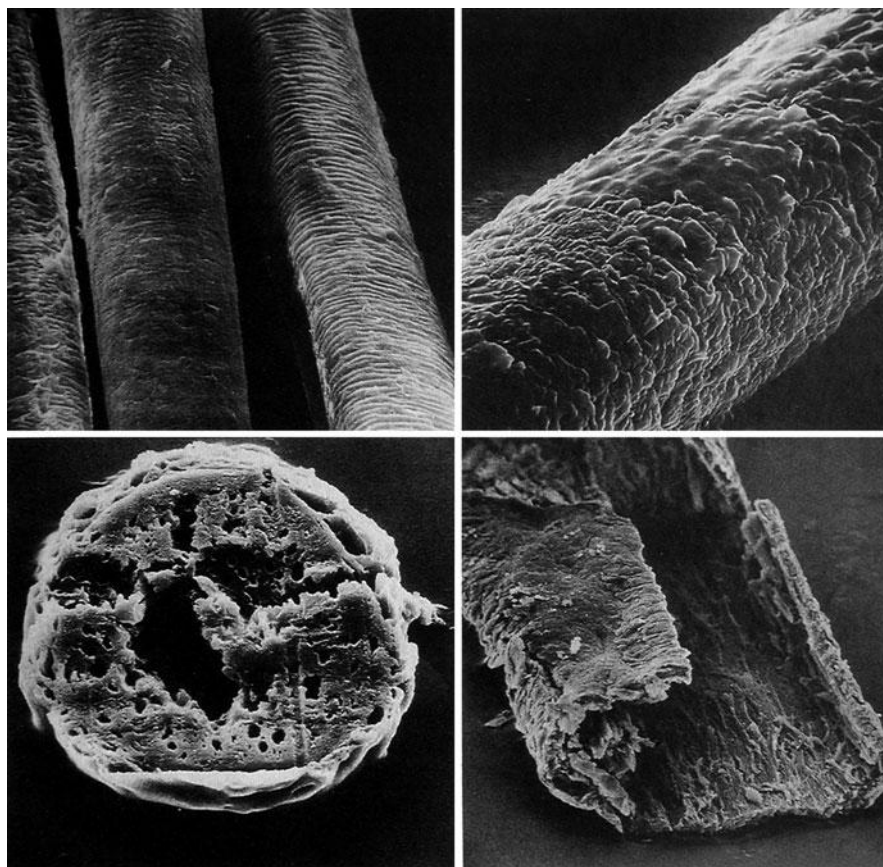


Fig. 8.9 Scanning electron micrographs of PMM-containing hair fibers [103]. *Upper left:* Surface of hair fibers containing 16% PMM add-on. *Upper right:* Surface of hair fibers containing 119% PMM add-on. *Lower left:* Cross section after hydrolysis of hair fibers containing 119% add-on. *Lower right:* End view after hydrolysis of hair containing 16% add-on (Reprinted with permission of the Journal of the Society of Cosmetic Chemists)

Fig. 8.10 Hair fiber containing 119% polymethyl methacrylate reacted with sodium sulfide to remove a large portion of the hair from the polymer [103] (Reprinted with permission of the Journal of the Society of Cosmetic Chemists)

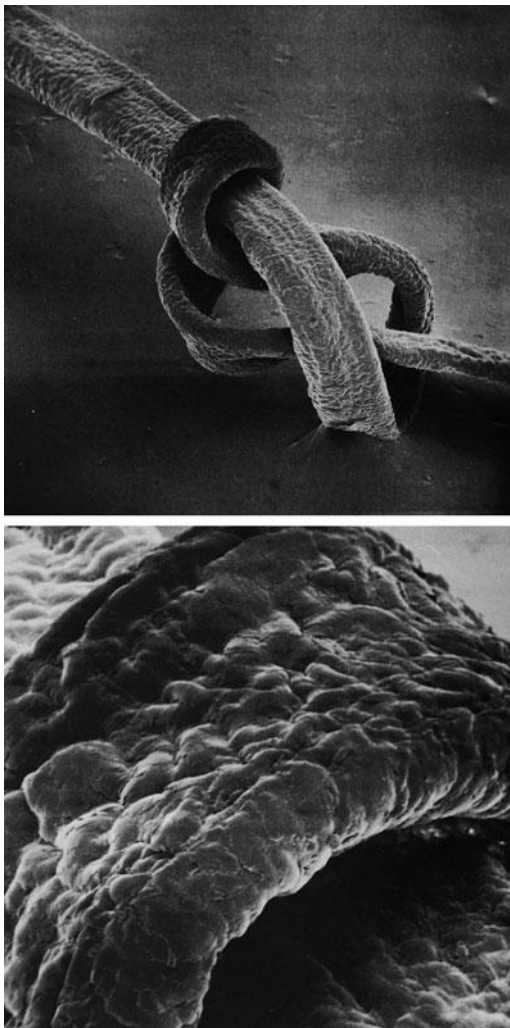


As indicated, fiberlike fragments were isolated from polymethyl methacrylate after hydrolyzing away much of the keratin with 5 N hydrochloric acid. These “synthetic fibers” after hydrolysis were examined in cross section and at the ends. From hair with large amounts of polymer add-on (near 100% weight gain), these “fibers” were almost complete cylinders of porous polymethyl methacrylate threads, whereas hair with lower polymer add-ons (10–20% weight gain) yielded thin-walled hollow cylinders (Fig. 8.9). The fibrous structure illustrated in Fig. 8.10 was obtained after treatment of polymethyl methacrylate containing hair with nearly 100% add-on with sodium sulfide to partially dissolve away much of the hair proteins. Note the hollow cylinder of polymer remaining reminiscent of ring dyed hair. Figure 8.11 depicts additional micrographs illustrating the polymer-hair structures after polymerizing methyl methacrylate onto and into hair (no hydrolysis) with very large add-ons of about 100%. These observations are consistent with diffusion rate control for this *in situ* vinyl polymerization process.

8.10 Safety Considerations for Polymers

Safety considerations for products containing polymers are often related to the components other than the polymer (monomers, catalysts, etc.) rather than the polymers. The polymers themselves are usually relatively safe ingredients. Protein polymers should be tested for sensitization; however, such problems are not frequent for the types of protein hydrolysates used in hair care. “Pure” synthetic polymers (with no monomer contaminant) are generally mild ingredients of

Fig. 8.11 *Top:* A knotted fiber containing more than 100% polymethyl methacrylate. *Bottom:* A close up of the same fiber



relatively low toxicity, one example being polyvinyl pyrrolidone originally used as a blood plasma extender in medicine.

Safety concerns for synthetic polymers are sometimes due to contamination with monomeric impurity. Monomers are sometimes highly toxic such as acrylamide [108], or even carcinogenic such as ethyleneimine [109] or vinyl chloride [110], or highly irritating to skin, such as acrylamide [108] or acrylic acid [108]. Therefore, control of unreacted monomer level can sometimes be critical to the safety performance of synthetic polymers.

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