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Polymers in Cosmetics: Recent Advances

From film-formers to rheology modifiers,
polymers serve various functions.

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Polymers serve multifarious purposes in cosmetic formulations. They are used as film-formers in hair fixatives, mascara, nail enamels and transfer-resistant color cosmetics; as thickeners and rheology modifiers in emulsions, gels, hair colorants and hair relaxers; as emulsifiers in lotions, sunscreens and hair colors and as conditioners, moisturizers, emollients, dispersants and waterproofers. In this brief review, we will survey recent advances in some major areas. The focus in this review is intellectual property as it is revealed in recent patents and patent applications.

Hair Fixatives

Hair fixative polymers generally function by forming films that spot-weld and seam-weld the hair in the desired style. These tiny welds suffer enormous stresses due to the natural movement of the hair. Therefore, resilient, tough polymeric materials are required for this purpose. However, the same polymeric materials should be easily susceptible to breakage by combing or brushing and they must be removed by shampoo. Blocky and graft copolymers can display microphase separation of their component parts during film formation if the structure is designed properly. This can confer toughness on an otherwise glassy polymer. Moreover, if the polymer has an amphipathic nature, shampoo-removability is aided but designers must be careful to avoid incorporating hygroscopic polar moieties that could result in softening of the polymer and loss of hold in humid environments.

In this respect, significant effort has gone into the preparation and application of polymers containing silicone macromonomers.¹ The silicone with its flexible Si-O-Si bond is an ideal candidate for tailoring toughness at the molecular level. For over a decade the U.S. industry has been focused on reducing the level of volatile organic compounds to comply with the Clean Air Act and polymer-containing silicone macromers have been developed to meet these regulatory requirements. Thus, Son, Axel and Volker of BASF have revealed that silicone-containing polyurethanes may exhibit the right properties for low VOC hair treatment compositions.²

The drive toward more water-soluble hair fixative polymers has continued. Ondeo-Nalco invented hair fixative copolymers based on the monomer 2-acrylamido-2-methylpropane sulfate and National Starch has intellectual property on nonionic derivatized starches, poly-N vinylacetamide and amphoteric urethanes.^{3,4,5,6}

Fixative Properties

Current state-of-the-art aqueous hair styling gels comply with volatile organic

compound regulations. However, most of the preferred hair fixative polymers are incompatible with aqueous gels formulated on a base of the most prominent gelling agent, Carbomer. As a consequence, the “workhorse” fixative polymers for most commercial hairstyling gel products have been restricted to water-soluble fixatives such as PVP and water-soluble PVP/VA copolymers. These polymers are marginally effective in imparting and maintaining hairstyle, especially in conditions of high humidity. Moreover, the “feel” of styled hair is an important consumer attribute and, unfortunately, PVP and water-soluble grades of PVP/VA copolymers impart an undesirable tacky or sticky feel to the hair in these same environmental conditions. In this context, it is interesting that Samain et al of L'Oréal have proposed the use of a reactive non-silicone polymer to produce tack on the hair that does not transfer to the hands.⁷

Wella's approach has been to develop essentially water-free hair styling gels, according to a patent application, which lists the inventors as Lede, Birkel, Grasser and Keller.⁸ The impetus for this invention is revealed as the need for faster drying hair gels with improved fixative properties. The systems are based on ethanol as solvent (either pure ethanol or ethanol containing no more than 10% water). The gellant is hydroxypropylcellulose at a level of 3-5% and the fixatives are standard hair spray resins at about a 10% level. It would be interesting in this case to examine the nature of the dried film because the solubility parameter and correlation lengths are likely to be mismatched for hydroxypropylcellulose and the hairspray resins. Mismatch of these parameters would be expected to result in phase-separation as the film dried out on the hair.

Foams and Sprays

In a parallel approach, Kalbfleisch, Birkel and Lede of Wella patented fast-breaking foam products to impart hair volume by means of strengthening the hair shaft. The “fast break” is enabled by alcohol (exemplified by ethanol) in the formulation. This patent is confusing to us because it seems that “hair-shaft strengthening” is defined by a curl-retention test, that could not differentiate between hair-shaft strengthening and inter-hair adhesion. Further, the only curl-retention measurements that are reported are for hair tresses treated merely with alcoholic solutions of conventional hair spray resins that are deficient in the required elements of the independent claims. These claims require that the composition comprise at least 60% water and 0-5% wt. surfactant in addition to the alcohol and hair-fixing polymer.

One perennial objective of manufacturers of hair fixative products is to reduce the loading of fixative polymers within the formulation without compromising styling performance. Dubief, Giroud and Rollat of L'Oréal claimed to achieve this objective by including a non-thickening amphiphilic block copolymer in the formulation with the conventional hair fixative polymer.⁹ “A non-thickening copolymer” is defined as a copolymer which, when dispersed or dissolved in water, leads to dynamic viscosities that are less than 0.1 Pa.s measured at a shear rate of 200s⁻¹. Examples in this patent included the hair fixative polymers and amphiphilic block copolymers shown in Table I. Compositions containing a total of 4% polymer were applied to the hair by means of a pump dispenser and their fixative properties were evaluated by an expert panel. The compositions containing a 50:50 mixture of fixative:block polymer outperformed those containing fixatives alone.

What are the underlying mechanisms that can lead to the claimed invention? One could speculate that this improvement in performance could arise from the influence of the block copolymer on the morphology of the bulk material and/or on the adhesion of the fixatives to the hair surface. Thus, block copolymers tend to exhibit morphology of separated microdomains, each of which is rich in one of the blocks. Separation of discontinuous glassy domains in rubbery matrix confers the properties of an elastomer, whereas separation of rubbery domains in a glassy matrix would confer impact resistance. Separation of ionic microdomains within a nonpolar matrix would confer increases in toughness and tensile modulus. Ionic microdomains might be expected to

confer the added advantage of susceptibility to shampoo that would lead to ease of removability from the hair after use. Alternatively, preferred adsorption of the block copolymer at the hair/fixative interface could lead to improved adhesion and consequently higher fixing of the hair.

Another paradox that is being challenged is that of imparting good style to the hair while maintaining a soft "feel." Dupuis of L'Oréal claims to have met this challenge by including a carboxylated silicone in the formulation. Silicones named in the patent are Huile M 642, SLM 23 000/1 and SLM 23 000/2 from Wacker, 176-12057 from General Electric, FZ 3703 from OSI and BY 16 880 from Toray Silicone.

**Table I: Example Polymers from Dubief, Giroud and Rolla;
U.S. Patent Application 2004/00338246**

Fixative Polymer	Amphiphilic Block Copolymer
Vinylpyrrolidone/vinylcaprolactam copolymer (Luvitec VPC 55K65W, BASF)	poly(styrene-b-2-hydroxyethylmethacrylate block molecular wts: PS=1500, PHEMA= 44,000
Vinylpyrrolidone/dimethylaminoethyl-methacrylate copolymer (Copolymer 845, ISP)	poly(styrene-b-acrylic acid) block molecular wts.: PS=1500, PAA= 44,000
Polyurethane (Luviset PUR BASF)	poly(methylmethacrylate-b-acrylic acid) block molecular wts: PMMA=1200, PAA=38,000
PPG-1/IPDI/DMPA copolymer (Avalure UR 450, Noveon)	
Acrylic copolymer (Avalure AC115, Noveon)	

Restyling

Once the hair has been set in place by conventional hair fixatives, reshaping of the style is usually impossible. Recently this need has been addressed by a trend to develop styling products that allow the hair to be reshaped as desired even hours after the original application of fixative. Samain of L'Oréal has taken inspiration from hot melt adhesives and has designed fixatives that allow remodeling of the hairstyle under the influence of a hair dryer. He formulated compositions containing a film forming and a crystalline hot melt polymer.¹⁰ Mention is made of Structure O from National Starch, which is a copolymer composed of 10% wt. acrylic acid and 90% wt. n-octadecyl methacrylate. Structure O has a crystalline melting point of 46°C. Rollat, Samain and Morel of L'Oréal have been granted patents for a reshapable hairstyling composition based upon heterogeneous polymers of alkyl methacrylates, cycloalkyl methacrylates and hydrophilic monomer units.^{11,12}



Polymers help create a variety of hairstyling products for men and women.

Caballada, Kuhlman and Schneider of Procter & Gamble tackled this problem by

including a polyalkylene glycol in which the hair-fixative resins is soluble.¹³ They note that this provides “reformable welds” that are liquid or semisolid at ambient temperature. Exemplary polyalkylene glycols are PEG-8, PEG-12 and PEG-18. Examples of film-forming polymers in this invention are polyvinylpyrrolidone/vinylacetate (Luviskol VA 73W from BASF), polyurethane-1 (Luviset PUR from BASF or PUR 28-001A from National Starch), polyvinylcaprolactam (Luvitec VCAP from BASF), polyvinylpyrrolidone/polyvinylcaprolactam (Luvitec VPC from BASF), polyvinylpyrrolidone/dimethylaminopropylmethacrylamide (Styleze CC-10 from ISP), polyvinylpyrrolidone/polyvinylcaprolactam/dimethylaminopropylmethacrylamide (Aquaflex SF-40 from ISP), isobutylene ethylmaleimide/hydroxyethylmaleimide (Aquaflex FX-64 from ISP), polyvinyl-pyrrolidone/dimethylaminoethylmeth-acrylate (Copolymer 845 from ISP), quaternized polyvinyl-pyrrolidone/di-methylaminoethylmethacrylate (Gafquat 734, Gafquat 755, or Gafquat 755N from ISP), polyvinylpyrrolidone/polyvinylcaprolactam/dimethyl-aminoethylmethacrylate (Gaffix VC-713 from ISP), and poly(vinylacetate/ crotonates/vinylneodecanoate) (Resyn 28-2930 from National Starch) and octylacrylamide /acrylate/butylamino-ethylmethacrylate (Amphomer from National Starch).

In contrast, Tamareselvy and Ramey, of the Noveon division of Lubrizol Corporation, have revealed a new family of polymers that are capable of providing simultaneous thickening and hair fixing from aqueous and/or hydro-alcoholic systems.¹⁴ Noveon has introduced a new product, (Fixate Plus), that exhibits these properties. The polymers named rheology modifying hair setting (RMHS) polymers are the product of a monomer mixture comprising an acidic vinyl monomer (for example, methacrylic acid), a nonionic monomer (for example, ethyl acrylate), an associative monomer (for example a long chain alkyl ethoxylated methacrylate) and optionally a semi-hydrophobic monomer (for example, an alkyl polyethoxylated methacrylate) and a cross linker (for example, trimethylolpropanetriacrylate). There are significant technical hurdles that must be overcome in the discovery and development of these hybrid materials:

- produce a rheology modifier that provides acceptable thickening, and desired rheology while meeting fixative expectations for styling;
- produce crystal clear gels despite the difference in refractive index of the component comonomers. The contrasting properties could result in incompatible systems that would show cloudiness and/or phase separation;
- achieve a sufficiently high glass transition temperature of the final film, especially in humid environments in which plasticization could occur;
- ensure a good, glossy film with minimal specular reflectance (ASTM 523-89) and
- confer the property of restylability with good high humidity curl-retention after wetting the hair and reshaping.

The Noveon patent teaches that all of these challenges have been met.

National Starch has approached the challenge of simultaneous gelling and fixing of hair by introducing a natural polymer—dehydroxanthan gum—to provide both thickening and hair fixative properties. This polymer is claimed to provide high holding even in humid conditions. Moreover, fixative compositions based upon this material can be restyled by merely spritzing with water and combing or brushing.¹⁵

Conditioning Shampoo

Since their inception in the 1970s, conditioning shampoos have been based upon the formation of dilution-deposition coacervates of polyquaternium-10 or guar hydroxypropyltrimonium chloride with anionic surfactant bases. Pader and Bolich introduced silicones into these formulations for better combing benefits and a multitude of variants has been introduced over the last quarter century.¹⁶

However, although these cationic conditioning polymers and silicones make the hair easier to disentangle and impart softness, they can also weigh the hair down and cause a lack of sleekness from the root to the tip of the hair. Under the conditions of shampooing, the hair would be expected to exhibit a negative surface charge. Cationic polymers of sufficient charge density are known to bind to anionic surfaces in a flat conformation. Such adsorption is often irreversible and the deposited agents can build up with successive applications of conditioning shampoo. Dry hair attributes that are expected from the conditioning shampoo are good cleansing efficacy, long lasting smooth moisturized feel, manageability control and no greasy feel.

Cationic Polymers

Royce and Wells of Procter & Gamble note that high charge density cationic polymers in anionic shampoo systems bind or flocculate polyalkylene oxide alkyl ether particles to form large flocs (20-500) microns that provide good deposition on hair and deliver good wet-conditioning.¹⁷ Polyalkylene oxide alkyl ethers include PPG-15 stearyl ether (Arlamol E from Uniqema), polyoxypropylene (9) decyl ether, polyoxypropylene (4) polyoxyethylene (6) cetyl ether, and polyoxyethylene (12) behenyl ether.

The inclusion of ester oils are thought to provide conditioning benefits such as moisturized feel, smooth feel and manageability control to the hair when the hair is dried, without leaving a greasy feel.¹⁸ An example formulation is given in Table II.

Addition of polybutene increases the deposition of silicone conditioners, and provides improved conditioning benefits such as wet and dry feel and combing.¹⁹ Wells and Johnson have also revealed the use of cationic guar for enhanced deposition of pigment particles for color, friction-conferring particles for style (titanium dioxide, clay, pearlescent mica, silica) and platelet or spherical particles for slip and conditioning (hollow silica, hollow polymer).²⁰ The deposition of silicone and the realization of conditioning properties here is taught to be achieved by inclusion of silicon acrylate graft copolymer (Carbopol Aqua SF-1 from the Noveon division of Lubrizol).²¹

Temperature can enhance deposition if the polymer is soluble under ambient conditions but phase separates during shampooing due to transition through a Lower Critical Solution Temperature. Findlay, Jones and Kuku of Unilever depend upon this mechanism to provide enhanced deposition from conditioning shampoos that contain polysaccharide-g-silicones.²²

Dubief and Restle of L'Oréal have reported that the disadvantages of buildup and greasy feel can be mitigated by the addition of an amphoteric polymer with fatty chains.²³ One can speculate on the theoretical reasons for the advantageous properties of these hydrophobically-modified amphoteric polymers. It is known that, for amphoteric polymers, in aqueous solution the positive and negative ions along the polymer molecular chain would be expected to show an attractive interaction that would cause the molecular chain to be restricted in its volume. This can cause these polymers to phase separate in aqueous solution.

Table II: Example Conditioning Shampoo Formulation

Ingredient	Function	%Wt.
Ammonium laureth-3-sulfate	anionic deterative surfactant	10.0
Ammonium lauryl sulfate	anionic deterative surfactant	2.0
Cocamidopropyl betaine	amphoteric surfactant	2.0
Cetyl alcohol	cosurfactant	0.6

Cocamide MEA	cosurfactant/foam booster	0.8
Polyquaternim-10	conditioner	0.5
Ethylene glycol distearate	suspending agent	1.5
Dimethicone	conditioner	2.0
Pentaerythritol adipic acid	conditioning polyester	2.0
Polymeric ester perfume solution	fragrance	0.7
Sodium citrate	fragrance	0.4
Citric acid	pH adjustment	0.4
Water		q.s. 100

The Laws of Attraction

In salt solutions, however, the salt ions can shield the attractive interaction between the polymer ions if the chemical potential of the salt is sufficiently high. Under conditions of high ionic strength, polyampholytes expand and interact more strongly with solvent. Hydrophobically-modified hydrophilic polymers will also tend to phase-separate from aqueous solution if the hydrophobic interaction between the polymers is sufficient. Because hydro-phobic interaction is enhanced by salt, phase separation would also be expected to increase with ionic strength.

A polyampholyte might be expected to expand in the ionic strength of a typical shampoo formulation and the hydrophobically modified polymer might be expected to be solubilized by the surfactant micelles in such a formulation. Therefore, it is not unreasonable to expect that a polymer molecule having each of these moieties might be expected to dissolve and be expanded in a shampoo formulation and upon dilution during a rinsing stage, the hydrophobic part and the oppositely charged ionic groups on the polymer would cause the polymer to collapse and phase separate. If this were the case, why would such a polymer show less tendency to build up than the more conventional hydrophilic cationic polymers? It has been theorized that polyampholytes adsorb on anionic surfaces in a much more loopy conformation than cationic polyelectrolytes because the attraction between ionic groups in the polymer would compete with the ionic attraction between the polymer and the substrate.²⁴ The loopy conformation would be expected to be more easily removed especially when it was exposed to high ionic strength micellar shampoo.

Geary, Hughes, Brown, Coffindaffer; Asante and Wells of Procter & Gamble broadened the field by disclosing a wide range of cationic conditioning polymers for use in shampoos.²⁵ Homopolymers are required to have a cationic charge density from about 2 meq/gm to about 4 meq/gm and an average molecular weight of at least 500,000 and the copolymers described include amphoteric polymers, under the condition that the overall polymer charge is cationic. It is interesting that Geary et al claim that the cationic polymer can promote the formation of a microscopic-phase separation of lyotropic liquid crystals.

Niemec, Yeh, Gallagher and Hoe of Johnson & Johnson show more uniform deposition if more than one cationic polymer [Poly (acrylamide-co- acrylamidopropyltrimonium) chloride (Salcare SC 60 from Ciba), hydroxy-propylguartrimonium chloride] and a quaternary silicone are included in the formulation (silicone quaternium-13).²⁶ They conducted a set of tests to provide support for their claims:

- Multiple Attribute Consumer Assessment Study against Pantene Pro-V for normal hair and J&J's pH5.5 regular shampoo for cleaning, wet-combing, dry combing,

hair softness, lather amount and creaminess;

- Secondary Ion Mass spectrometry to detect Si on the hair surface;
 - X-Ray photoelectron Spectroscopy (XPS) to measure thickness of silicone polymer layer on hair from Si:C:O ratios and
 - Instron Ring Compression for combing/detangling.
- These instrumental tests can be conducted by the Textile Research Institute in Princeton, NJ.

Associative Thickeners

Associative thickeners are hydrophobically-modified hydrophilic polymers. They can roughly be classified as hydrophobically-modified alkali swellable thickeners (for example Aculyn polymers from Rohm & Haas), Hydrophobically-modified polysaccharides (such as Natrosol Plus from Hercules) and hydrophobically-modified ethoxylated urethanes (such as the RM series from Rohm & Haas). They are increasingly being used in two-part oxidative hair dye systems, and in hair bleaching compositions where it seems that the precise structure of the associative thickener is important in determining the quality of the color imparted to the hair.²⁷

Polymeric Emulsifiers

Pemulen polymeric emulsifiers are cross-linked hydrophobically-modified polyacrylates.^{28,29} They offer the advantage of almost ubiquitous emulsification properties and triggered release of the oil phase upon application to the substrate. The triggered release can be driven by the ions of perspiration or by depletion coalescence as water evaporates from the formulation after application to the substrate. However, in some formulations, the texture of these emulsions requires improvement. L'Alloret of L'Oréal teaches the use of styrene/sodium polyacrylate diblock copolymers as polymeric emulsifiers with improved textures.³⁰

When skin is exposed to water for extended periods, the stratum corneum can absorb up to five times its own weight of water and its function as a protective barrier is compromised. Deckner et al reasoned that it is important to deposit a barrier film of oil on the skin during showering or bathing in order to maintain the barrier function. They teach that they achieve this by applying high internal oil-in-water emulsions as rinsable, skin-conditioning compositions.³¹ The emulsions are stabilized by polymeric emulsifiers that exhibit a minimum surface tension of 60 mN m⁻¹. Suitable stabilizers are listed as Pemulen TR-1, Pemulen TR-2, ETD 2020, Carbopol 1382 (Acrylates/C10-30 alkyl acrylate crosspolymer-Noveon), Natrosol CS Plus 330, 430, Polysurf 67 (cetyl hydroxyethyl cellulose-Hercules), Aculyn 22 (acrylates /steareth-20 methacrylate copolymer-Rohm & Haas) Aculyn 25 (acrylates /laureth-25 methacrylate copolymer-Rohm & Haas), Aculyn 28 (acrylates /beheneth-25 methacrylate copolymer-Rohm & Haas), Aculyn 46 (PRG-150/stearyl alcohol/SMDI copolymer-Rohm & Haas) Stabylen 30 (acrylates/vinyl isodecanoate-3V), Structure 2001 (acrylates/steareth-20 itaconate copolymer-National Starch), Structure 3001 (acrylates/ceteth-20 itaconate copolymer-National Starch), Structure Plus (acrylates/aminoacrylates/C10-30 alkyl PEG 20 itaconate copolymer-National Starch), Quatrisoft LM-200 (polyquaternium-24), and also metal oxides titanium, zinc, iron, zirconium, silicon, manganese, aluminium and cerium, polycarbonates, polyethers, polyethylenes, polypropylenes, polyvinyl chloride, polystyrene, polyamides, polyacrylates and cyclodextrins.

The stabilization of high internal phase emulsions is not a trivial matter. These systems are so crowded that there is little space left for the polymeric emulsifier in the aqueous phase. As a consequence, the composition lies on the verge of depletion coalescence. However, having the ability to formulate in this region offers the advantages of high, shear-thinning viscosities, lubricious feel of the product and a high probability of coalescence and deposition of the oil phase on the skin during rinsing in the shower.

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