Evaluation of novel synthetic conditioning polymers for shampoos

S. L. JORDAN, X. ZHANG, J. AMOS, D. FRANK, R. MENON,

R. GALLEY, C. DAVIS, T. KALANTAR, and M. LADIKA, *Dow* Wolff Cellulosics, A Subsidiary of the Dow Chemical Company, 171 River Road, Piscataway, NJ 08854 (S.L.J, X.Z., J.A., D.F., R.M., R.G., C.D., M.L.), and the Dow Chemical Company, Building 1712, Midland, MI 48674.(T. K.).

Synopsis

Cationic polymers have traditionally been used in shampoo formulations to impart conditioning properties to hair. In this study, commercial synthetic cationic polymers were investigated using coacervate formation, objective wet comb analysis, silicone deposition and panel studies to determine structure function properties with the goal of developing novel conditioning polymers. New polymers were synthesized and, based on criteria determined in the first part of the study, found to have marginal improvement over existing synthetic cationic conditioning polymers. A novel experimental polymer developed for a different industry was also investigated for conditioning properties. This polymer showed significant enhancement of silicone deposition over current commercial polymers, including cationic guar, even at significantly reduced silicone and polymer concentrations. The experimental polymer exhibited parity or improvement over benchmark polymers in panel studies, and similar performance to other synthetic polymers in objective wet comb studies.

BACKGROUND

For over thirty years cationic conditioning polymers have been used in anionic shampoo formulations to impart improved look, feel comb properties (1,2). These polymers are also used as deposition aids for benefit agents such as silicone. Two naturally derived cationic polymers, cationic hydroxyethyl cellulose (polyquaternium 10 or PQ10) and guar hydroxypropyltrimonium chloride (cationic guar) are used extensively in the market today. Hydrophobically modified PQ10 (PQ67) was recently introduced as well. Less widely used are various synthetic conditioning polymers including acrylamide and dimethyl diallyl ammonium chloride (polyquaternium 7 or, PQ7) and polyvinyl pyrrolidone and dimethyl aminoethylmethacrylate, (polyquaternium 11 or PQ11) (3). In general, cationic conditioning polymers coexist in shampoos with anionic surfactants in a single phase. As the shampoo is diluted during use and the surfactant approaches the critical micelle concentration (CMC), the cationic polymer forms a complex with the surfactant monomers that phase separates from the bulk solution. This phase separation, or coacervation, is known as the Lochhead effect (4–7). The gel-like coacervate contains a high concentration of the cationic polymer which is then deposited onto the negatively charged hair, forming a clear film. Insoluble actives (e.g. silicones) are effectively trapped in the coacervate and deposited along with the polymer.

While PQ10 and cationic guar are the most widely used conditioning polymers, the large variety of monomers available to make synthetic polymers has led to an explosion in the development of synthetic cationic polymers. Previous work with PQ10 and the hydrophobe modified PQ24 and PQ67 showed significant effects of changing parameters such as molecular weight, charge density and hydrophobic substitution on polymer performance (Figure 1) (4,8,9). Using these structure function relationships, polymers can be fine tuned to obtain customized efficacy for deposition, wet comb and dry conditioning properties. In the case of the naturally derived polymers, the structural changes are limited by the polymer backbone provided by nature. In contrast, the backbone for synthetic polymers can be changed and is limited only by the availability of monomers, giving the synthetic chemist additional "levers" to alter polymer performance. One of the key differences between natural and synthetic polymers is backbone flexibility in solution. Natural polymers tend to have a more rigid backbone while synthetic polymers are more flexible. While polymer performance is related to the ability to form coacervate and subsequently deposit on hair, the conformation of the polymer on the substrate and the surface properties it imparts to the hair are of equal, if not greater, importance to overall conditioning properties. It is unclear how backbone flexibility affects polymer conformation and properties on the substrate.

According to the Personal Care Product Council website (http://www.personalcarecouncil. org/), there were 88 polyquaternium polymers with INCI names in 2008 compared with 42



Figure 1. Cationic hydroxyethyl cellulose (PQ10, PQ24, and PQ67) can be modified via molecular weight, charge density and hydrophobic substitution. Backbone composition can be designed for synthetic polymers.

in 1999, more than doubling in ten years. This total does not include cationic polymers and blends that do not have "polyquaternium" in the INCI name. Most of these polymers are synthetic derivatives. The large number of polymers is a reflection of the wide variety of monomers available and the numerous combinations that can be synthesized and variables that can be changed within a polymer family (e.g. molecular weight, charge density, monomer ratios, hydrophobic substitution, etc) (3,10,11). Several cationic polymers, particularly those that contain polyvinyl pyrrolidone, are designed for styling while others are designed for conditioning properties and still others for a combination of properties. In this study, about one hundred polymers were synthesized in an effort to develop structure function relationships of synthetic cationic polymers as conditioning agents. Variables such as monomer content and ratios, molecular weight and charge density were evaluated. In addition, an experimental cationic polymer designed for a different industrial application was found to have significantly improved deposition characteristics compared with current commercial polymers.

EXPERIMENTAL

MATERIALS

All materials were used as received:

Cationic polymers. PQ10 was from Amerchol Corporation (Piscataway, NJ). Experimental synthetic polymers were synthesized by Dow Wolff Cellulosics and The Dow Chemical Company to specifications. Commercial synthetic polymers were obtained from Nalco (Tarrytown, NY), BASF (Florham Park, NJ), Rhodia (Cranbury, NJ), and CIBA (Tarrytown, NY).

Surfactants. Sodium laureth sulfate, SLES-2, cocoamidopropyl betaine, CAPB, disodium cocamphodiacetate, and DSCADA were all from Cognis (Cincinnati, OH).

Silicone. Silicone emulsion (particle size ~200 nm) was from Dow Corning (Midland, MI)

Hair. Hair was from International Hair Importers and Products (White Plains, NY).

METHODS

Wet combing. Wet combing was measured using a Dia-Stron Miniature Tensile Tester. The force required to pull a comb through a wet hair tress treated with surfactant alone and then surfactant plus polymer was measured. Five grams of hair was washed with 0.5 grams of a shampoo, and rinsed at constant temperature. The difference in force required to comb the hair tress before and after treatment was reported as the wet comb reduction.

Coacervate study. Haze measurements were performed using a hazemeter two minutes after diluting the test formulation 2.5 to 20 times with water and mixing at room temperature.

Silicone deposition. The amount of silicone deposited on hair after shampooing was measured. Five grams of hair was washed with 1 gram of a shampoo, and rinsed at constant temperature. Hair was extracted with a 1:1 mixture of methyl butyl ketone and toluene. Atomic absorption spectroscopy was used to measure silicone content; reporting µg silicone/g hair. *Panel studies.* Five grams European brown hair was washed with 1 gram of shampoo (sample A) with the test product while five grams of hair was washed with 1 gram of a control shampoo (sample B). For each panel study, two tresses of hair were washed with sample A and two tresses were washed with sample B. One tress of each sample (A and B) was hung side by side in two sets of two. Panelists were asked to compare each set separately for feel and ease of comb wet in a forced choice test. Five panelists were asked to do the evaluation, giving a total of 10 evaluations. The test was repeated on separate hair tresses prepared as described and then dried. Panelists were asked to compare each set for dry feel and comb.

Polymer substantivity. Each tress was wetted and washed with 1 g of shampoo for 1 minute and rinsed with tap water. The tress was rewashed as needed for the dye build up test. After the completion of the washes, the tress was placed in a beaker with 50 mL of 0.05%red dye 80 (Jos. H. Lowenstein Sons, Inc., Brooklyn, NY) in deionized water (pH 3.0) for one minute (gently shaken). The tress was removed and rinsed under tap water to remove unattached dye. Excess water was squeezed from the tress and the hair was placed in a beaker containing 50 ml isopropanol/water (50/50 by volume) solution (pH=12.5) for 5 minutes with occasional gentle shaking. Hair was removed from the solution, rinsed, dried, and weighed. Absorbance of the extraction solution was measured at 533 nm and the amount of dye calculated using a calibration curve for dye concentration and equation 1:

$$\mu g \, dye/g \, hair = (abs + 0.0013) * (5 \times 10^4) / (wt \text{ of hair, } g) \tag{1}$$

RESULTS AND DISCUSSION

EVALUATION OF COMMERCIAL SYNTHETIC POLYMERS

Several commercial synthetic polymers were evaluated for coacervate formation, objective wet comb and silicone deposition. The study included 11 commercial polymers (Table I). Not all polymers were tested for each performance characteristic. Coacervate studies were performed as a screen to determine if the polymer phase separates from the formulation on dilution and was performed on all samples. Wet combing is a good measure of overall conditioning on damaged hair and was used to screen six of the polymers. Only two polymers were screened for silicone deposition. In all cases, cationic guar and PQ10 polymers were used as positive controls for these studies.

Figure 2 shows the coacervate curves of 0.5% polymer in 15.5% sodium laureth sulfate-2 (SLES-2) & 2.6% disodium cocoamphodiacetate (DSCADA). Several of the polymers, including Blend A, Blend B, and PQ47 did not form coacervates. Others, such as PQ11, had variable results depending on the manufacturer. Some were not compatible with the formulation, in which case coacervates could not be detected. These differences may be related to the molecular weight, residual monomer levels or cationic substitution of the polymer. For the samples that did form coacervates, they tended to form early in the dilution process, similar to one PQ10 (high molecular weight/high charge density, Amerchol Corp.) and cationic guar (Rhodia). In contrast, the second PQ10 (high molecular weight/ medium charge density, Amerchol Corp.), formed coacervate at later dilution. It has been shown that this later coacervate, which forms at higher dilution, tends to lead to softer conditioning properties (1,4).

The best coacervate forming polymers were chosen for further analysis. Objective wet combing studies are shown in Table II. Polymers (0.5%) were formulated into 15.5% SLES-2 and 2.6% DSCADA. Of the six synthetic polymers evaluated, only PQ7 and Blend A exhibited significant wet combing reduction, and neither was as effective as either PQ10 or at least one of the cationic guar polymers. It should be noted that objective

INCI name (composition)	Structure
PQ-11	Ожистийной аррокатог об йтэрэртовобого үлёй аний облаебораллогиоваца говораалаава ДАНЕСНАР, их аруссан ожисого,
 (polyvinyl pyrrolidone and dimethyl aminoethylmethacrylate— DMAEMA) 2 manufacturers 	
PO-47	Chemical Structure
(acrylic acid, methyl acrylate and methacrylamidopropyltrimonium chloride—MAPTAC)	Sur-op- For- For-
PQ-7	CHEMICAL STRUCTURE
(acrylamide and dimethyl diallyl ammonium chloride— DADMAC) 3 manufacturers	
PO-6	CHEMICAL STRUCTURE
(dimethyl diallyl ammonium chloride— DADMAC) 2 manufacturers	
Acrylamidopropylatrimonium chloride/acrylamide copolymer Blend A	
PQ7 + Acrylamidopropyltrimonium chloride – APTAC/acrylamide copolymer Blend B	

 Table I

 List of Commercial Polymers Evaluated for Conditioning on Hair.

Polymer	% Combing reduction
PQ11a	8
PQ6	0
PQ47	0
PQ7a	29
PQ7b	16
Blend A	38
Blend B	19
PQ10 (LMW)	70
PQ10 (HMW)	63
Cartionic guar	54
Cartionic guar	31
-	

 Table II

 Objective Wet-Comb Analysis on 8-Hour Bleached Hair.

All polymers were tested at 0.5% active in 15.5% sodium laureth sulfate-2 (SLES-2) and 2.6% disodium cocoamphodiacetate (DSCADA).



Figure 2. Coacervate curves of various cationic polymers. All polymers were tested at 0.5% active in 15.5% sodium Laureth Sulfate-2 (SLES-2) and 2.6% disodium cocoamphodiacetate (DSCADA).

wet combing is typically performed on damaged (bleached) hair and is therefore a measure of strong conditioning. Silicone deposition studies were performed on the best performing polymers (PQ7 and Blend A). Both polymers showed silicone deposition after two washes when formulated in 15.5% SLES-2 & 2.6% DSCADA. Blend A deposited a significant amount of silicone (~3200 mg/kg) while PQ7 deposited silicone at a level similar to that of cationic guar (~500 mg/kg). Previous studies had shown significant differences in deposition of silicone based on polymer type and silicone particle size (12). For example, cationic guar tends to deposit high amounts of small particle size silicone (~200 nm) while PQ10 is more efficient at depositing large particle size silicone (~30 μ). Efficiency of deposition of varying particle size silicone may similarly be affected by synthetic polymer type, but was not investigated in this study. A final study was performed to measure polymer build up on hair. Using the dye method, relative concentration of polymer was measured on hair tresses after 1, 3, 5 and 10 washes. The dye method is qualitative rather than quantitative, so only relative build up can be determined, not total amount of polymer deposited. Using these criteria, PQ7 and PQ11 show similar build up as PQ10 and significantly less than cationic guar, Blend A and Blend B (data not shown).

Based on the various studies performed with commercial polymers, several showed:

- good coacervate formation, but some sensitivity to surfactant base and a narrow zone of coacervation at low dilution levels (PQ11)
- minor objective wet comb reduction (PQ7 & Blend A)
- medium (PQ7) to very high (Blend A) silicone deposition
- low (PQ7) to high (Blend A) polymer build up

PQ7 was chosen as a model polymer for synthetic studies to improve conditioning performance.

EVALUATION OF EXPERIMENTAL, SYNTHETIC CATIONIC POLYMERS

Several polymers were synthesized based on the PQ7 monomers (acrylamide & diallyldimethylammonium chloride, DADMAC). These polymers included additional monomers (e.g. dimethylaminoethyl methacrylate) and various molecular weight, monomer ratios, and charge density. The relative performance of these polymers in objective wet comb, silicone deposition and panel studies lead to several generalizations, including higher MW polymers yield higher silicone deposition and higher charge density yields higher silicone deposition. The specific addition of dimethylaminoethyl methacrylate as a third monomer in particular showed significant improvement in silicone deposition (from 500 mg/kg for PQ7 to 1000 mg/kg for the tertiary polymer) but did not show significant improvement in panel studies, particularly as compared to either PQ10 or cationic guar (data not shown). The data generated from the experimental polymers, confirms earlier work with natural polymers that indicated improved conditioning and silicone deposition with increasing molecular weight and charge density. The overall low level of perceived conditioning benefit for the more complex derivatives did not justify continued investigation.

EVALUATION OF EXPERIMENTAL CATIONIC POLYMERS PRODUCED FOR OTHER INDUSTRIES:

Cationic polymers are useful in industries aside from personal care for general flocculation and deposition. An experimental polymer was identified from another industry and evaluated for conditioning properties. The polymer was successfully formulated in several shampoo bases, but most tests were performed in 15.5% SLES-2/2.6% DSCADA. As observed with other synthetic polymers, this polymer was not able to form clear shampoo formulations. Therefore, coacervate formation was not measured. Similar to PQ7, the wet comb reduction (Figure 3) of this polymer was not as high as either cationic guar or PQ10, while the polymer build up was comparable to cationic guar. The new polymer, however, was used at half the polymer is as effective as typical use levels for other conditioning polymers. Figure 4 shows silicone deposition of the polymer at 0.1% compared to benchmark polymers at 0.25% after five washes. Even at less than half the polymer concentration, significantly more silicone was deposited as compared with cationic guar (>5000 mg/kg, experimental polymer & ~700 mg/kg, cationic guar). This high level of silicone deposition gives formulators flexibility in formulation, potentially reducing silicone and polymer in shampoos while maintaining performance.

Several panel studies were performed to determine consumer preference. These studies were primarily performed using cationic guar (JaguarTM C13S) as control. Cationic guar was chosen since it exhibits high levels of silicone depositon with this particular silicone particle size and also does not normally formulate clear shampoos. The panel studies in Figure 5 show panelist preference for the experimental polymer as compared to cationic



Figure 3. Wet comb reduction of experimental polymers compared with PQ7, PQ10 and cationic guar. All polymers were used at 0.3% except experimental polymer, which was used at 0.15%. Surfactant base: 15.5% SLES-2/2.6% DSCADA.



Figure 4. Silicone deposition of experimental polymer, cationic guar, PQ7 and PQ10. All polymers were at 0.25% except experimental polymers, which was used at 0.1%. Silicone concentration: 1%, surfactant base: 15.5% SLES-2/2.6% DSCADA.

guar in 15.5% SLES-/DSCADA/1% silicone at less than half the polymer concentration (0.1% experimental polymer; 0.25% cationic guar) for both wet and dry properties. As can be seen in Figure 6, even after up to 10 washes, the experimental polymer performs at least as well as cationic guar, indicating an increased level of silicone deposition does not affect performance after many wash cycles. To confirm the benefits of 2-in-1 shampoos formulated with the new polymer, an additional study was done to compare the conditioning performance with PQ7. As with cationic guar, the experimental polymer was used at 0.1% vs. 0.25% for PQ7. Figure 7 shows similar or better performance of the experimental polymer (4967 mg/kg silicone deposited) vs. PQ7 (1091 mg/kg silicone deposited), ruling out a general panel bias against cationic guar in the first series of studies.

While it was established that the experimental polymer can deposit large amounts of silicone on hair, it is unclear whether this level of silicone is needed to obtain good conditioning properties. As with most cationic conditioning polymers, the experimental



Figure 5. Panel study comparing experimental polymer with cationic guar in 15.5% SLES-2/2.6% DSCADA/1% silicone. Wet and dry comb and feel was evaluated. Black: 0.25% cationic guar; gray: 0.1% experimental polymer.



Figure 6. Panel study comparing experimental polymer with cationic guar after 10 washes in 15.5% SLES-2/2.6% DSCADA/1% silicone base. Wet and dry comb and feel was evaluated. Black: 0.25% cationic guar; gray: 0.1% experimental polymer.

polymer likely binds to the hair to impart its own conditioning properties. The 2-in-1 shampoos give extra conditioning with silicone, but in essence the polymer and silicone work together to maximize performance. There is also a continued need in the competitive shampoo market to reduce overall formulation cost while maintaining product performance. Several studies were done to evaluate the effectiveness of silicone deposition and wet and dry comb and feel with reduced concentrations of silicone in the formulation. The panel study shown in Figure 8 indicates that even at 1/10 the silicone concentrations.



Figure 7. Panel study comparing experimental polymer with PQ7 in 15.5% SLES-2/2.6% DSCADA/1% silicone base. Wet and dry comb and feel was evaluated. Black: 0.25% PQ7; gray: 0.1% experimental polymer.



Figure 8. Panel study comparing experimental polymer with cationic guar in 15.5% SLES-2/2.6% DSCADA base. Wet and dry comb and feel was evaluated. Black: 0.25% cationic guar, 1% silicone; gray: 0.1% experimental polymer, 0.1% silicone.



Figure 9. Panel study comparing experimental polymer with PQ7 in 15.5% SLES-2/2.6% DSCADA base. Wet and dry comb and feel was evaluated. Black: 0.25% PQ7; gray: 0.1% experimental polymer.

tration (0.1%) and low polymer concentration (0.1%), the experimental polymer performs well vs. the benchmark. As would be expected, the concentration of silicone deposited on the hair is less than at 1% silicone (534 mg/kg at 0.1% silicone and 5400 mg/kg at 1% silicone) and similar to that deposited from the formulation containing cationic guar (523 mg/kg at 1% silicone). This wide range of silicone and polymer concentrations available to the formulator increases flexibility in formulation design.

The data presented indicate the experimental polymer can be used in 2-in-1 formulations to deposit silicone and improve hair conditioning performance. Not all shampoos, however, contain silicone. Therefore, the polymer was evaluated against cationic guar, PQ10 and PQ7 in shampoos without silicone. As mentioned earlier, the experimental polymer is not able to form clear shampoos. Of the four polymers tested (15.5% SLES-2/2.6% DSCADA), only PQ10 formed clear formulations. In each case , the experimental polymer performed as well or better than the commercial polymers in panel studies. The data for comparison vs. PQ7 is shown in Figure 9. This data shows the largest improvement in wet comb properties with 100% of the panelists preferring the experimental polymer over PQ7. The comparison to PQ10, on the other hand, showed parity (data not shown).

CONCLUSIONS

Synthetic cationic polymers were evaluated for conditioning performance in shampoos. The commercial polymer, PQ7, showed some conditioning performance and silicone deposition compared to benchmark PQ10 and cationic guar polymers. Additional modifications to PQ7 had only minor affects on performance. A new, experimental cationic polymer designed for a different industry was found to improve silicone deposition up to ten fold at significantly lower polymer concentrations than typically used in shampoo formulations. In addition, these polymers performed well in panel studies vs. benchmark polymers, even at 1/10 the silicone concentration. The improved efficiency of deposition gives formulators formulation flexibility and could reduce overall formulation cost.

REFERENCES

- W. Li and S. L. P. Jordan, Cationic cellulosic polymers with multifunctional and outstanding performance for personal care, *Cosmet. Toiletr.*, 1, 1–4 (2003).
- (2) R. Schueller and P. Romanowski, "Introduction to Conditioning Agents for Hair and Skin", in *Conditioning Agents for Hair and Skin*, R. Schueller and P. Romanowski, Eds. (Marcel Dekker, New York, 1999), pp. 1–12.
- (3) B. Idson, "Polymers as Conditioning Agents for Hair and Skin," in *Conditioning Agents for Hair and Skin*, R. Schueller and P. Romanowski, Eds. (Marcel Dekker, New York, 1999), pp. 251–280.
- (4) S. L. Jordan, R. L. Kreeger, X. Zhang, T. V. Drovetskaya, C. B. Davis, J. L. Amos, S. E. Gabelnick, S. Zhou, W. Li, E. F. DiAntonio, and A. A. Protonentis, "Effect of Hydrophobic Substitution on Cationic Conditioning Polymers," in *Cosmetic Nanotechnology Polymers and Colloids in Cosmetics*, S. E. Morgan, K. O. Havelka, and R. Y. Lochhead, Eds. (ACS Symposium Series, 2007), pp. 59–71.
- (5) R. Y. Lochhead, "Shampoos," in *The Chemistry and Manufacture of Cosmetics*, 3rd ed., M. L. Schlossman, Ed. (Allured Publishing Corporation, Carol Stream, IL, 2002), vol. 2, pp. 277–326.
- (6) R. Y. Lochhead, Conditioning shampoo, Soap, Cosmet. Chem. Spec., 42-49 (October 1992).
- (7) E. D. Goddard, "Polymer/Surfactant Interaction in Applied Systems," in *Principles of Polymer Science and Technology in Cosmetics and Personal Care*, E. D. Goddard and J. V. Grubber, Eds. (Marcel Dekker, New York, 1999), pp. 181.
- (8) T. V. Drovetskaya, R. L. Kreeger, J. L. Amos, C. B. Davis, and S. Zhou, Effects of low-level hydrophobic substitution on conditioning properties of cationic cellulosic polymers in shampoo systems, *J. Cosmet. Sci.*, 55(Suppl.), S195–S205 (2004).
- (9) T. V. Drovetskaya, E. F. DiAntonio, R. L. Kreeger, J. L. Amos, and D. P. Frank, New high-charge density hydrophobically modified cationic HEC polymers for improved co-deposition of benefit agents and serious conditioning for problem hair, J. Cosmet. Sci., 58, 421–434 (2007).
- (10) R. Y. Lochhead and J. V. Gruber, "Appendix: Encyclopedia of Polymers and Thickeners for Cosmetics," in *Principles of Polymer Science and Technology in Cosmetics and Personal Care*, E. D. Goddard and J. V. Grubber, Eds. (Marcel Dekker, New York, 1999), pp. 571–655.
- (11) J. V. Gruber, "Synthetic Polymers in Cosmetics," in *Principles of Polymer Science and Technology in Cosmetics and Personal Care*, E. D. Goddard and J. V. Grubber, Eds. (Marcel Dekker, New York, 1999), pp. 217–274.
- (12) W. Li, J. Amos, S. Jordan, A. Theis, and C. Davis, Selecting the optimum silicone particle size/cationic polymer structure to maximize shampoo conditioning performance, *J. Cosmet. Sci.*, 57(2), 178–180 (2006).