

Designing new functional cosmetic ingredients from polyglycerol, a versatile bio-based platform for improved sustainability

MICHAEL J. FEVOLA, FRANK C. SUN, and STACEY E. YORK,
Johnson & Johnson Consumer Inc., Skillman, NJ 08558 (M.J.F., F.C.S.)
and University of Oregon, Eugene, OR 97403 (S.E.Y.).

Synopsis

Polyglycerol (PG) is a well-known cosmetic ingredient and important precursor for the synthesis of a variety of cosmetic ingredients, such as surfactants, emulsifiers, and conditioning agents for hair and skin. When derived from renewable resources, PG can provide a more sustainable platform for the development of new ingredients with improved performance in cosmetic applications. This paper will discuss recent advances in the utilization of bio-based PG ingredients as alternatives to traditional ethoxylate chemistries for mild nonionic surfactants, substantive humectants, and micellar thickeners.

INTRODUCTION: POLYGLYCEROL AS A BIO-BASED CHEMICAL PLATFORM

In addition to being one of the most widely used cosmetic ingredients, glycerin also serves as a feedstock for the synthesis of a variety of surfactants, emulsifiers, conditioning agents, and other cosmetic ingredients (1). Plant-derived glycerin is an abundant bio-based coproduct resulting from the oleochemical production of fatty acids and soap; it is the preferred source of glycerin for cosmetics, and it is an attractive platform for the development of new cosmetic ingredients with improved functionalities.

Polyglycerol (PG) is a complex, polydisperse, low molecular weight polyether composed of repeat units that are based on dehydrated three-carbon glycerol groups, which can be linear, branched, or cyclic in nature (2). PG is extremely hydrophilic due to the presence of many pendant hydroxyl groups in primary and secondary positions; however, the hydroxyl values and hydrophilicity of PG decreases with increasing cyclic repeat unit content, as each cyclic repeat unit formed effectively consumes one pendant hydroxyl group.

Bio-based PG may be produced via the direct condensation polymerization of glycerol (purified glycerin) with water as the by-product, or via ring-opening polymerization of glyceryl carbonate (GC), a cyclic carbonate monomer synthesized from glycerol (Figure 1). Other routes to PG exist, e.g., via polymerization of glycidol or epichlorohydrin; however, these routes are less preferred, since most glycidol and epichlorohydrin are derived from nonrenewable feedstocks, and these monomers present significant health and safety hazards.

Address all correspondence to Michael Fevola at mfevola@its.jnj.com.

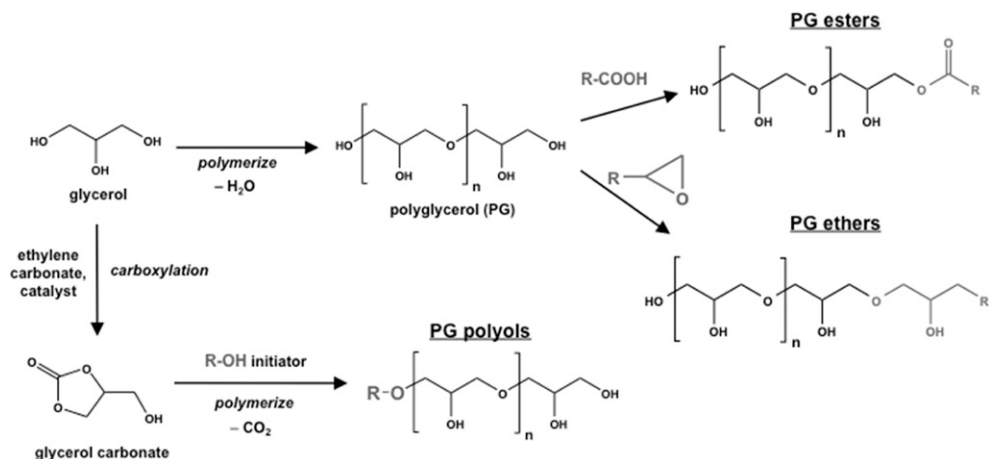


Figure 1. Synthetic versatility of PG chemistry as a platform for cosmetic ingredients.

Although PG has been known for over a century, this material offers a plurality of benefits that continue to make it a practical platform for the development of cosmetic ingredients. PG is nontoxic and biodegradable, and polyglyceryl esters (PGEs) have been safely used as ingredients in food and cosmetics for several decades. The extreme hydrophilicity of PG renders it highly biocompatible and makes PG a good candidate for the synthesis of hydrophilic moieties in nonionic amphiphilic molecules.

PG is especially attractive as an alternative to traditional polyethylene glycol (PEG) chemistry. While the majority of PEG is derived from nonrenewable feedstocks (e.g., natural gas), PG is 100% renewable when derived from bio-based glycerol. PG does not contain or give rise to 1,4-dioxane, a controversial trace by-product that has led to a negative public perception of PEG-based ingredients (despite the fact that they are recognized as safe by regulatory agencies and independent scientific panels). PG is significantly more hydrophilic than PEG due to its higher hydroxyl values at equivalent molecular weights, and it is more amenable to chemical modification compared to PEG due to its greater number of free hydroxyl groups as sites for substitution. Figure 1 demonstrates various synthetic routes that can be employed when using PG as a synthetic platform; this versatility enables PG to be derivatized in a variety of ways to achieve specific functional benefits.

HIGH HLB PGEs AS ALTERNATIVES TO ETHOXYLATED SORBITAN ESTERS IN MILD CLEANSERS

Highly ethoxylated sorbitan esters, e.g., PEG-80 sorbitan laurate and polysorbate 20, have traditionally been utilized to enhance the mildness of gentle cleansing products, such as baby shampoos and adult facial cleansers (3,4). Recently, high HLB polyglyceryl nonionic surfactants, in particular PGEs, have received renewed attention as ethoxylate alternatives for this application and have proven successful at delivering mildness without compromising on performance (5).

Table I shows examples of such surfactant blends based on a combination of polyglyceryl-10 oleate, polyglyceryl-10 laurate, zwitterionic surfactants, and sulfate-free anionic surfactants

Table I
Low pH, Mild Cleansing Formulations Based on High HLB PGEs

Ingredient (INCI name)	Example 2 (wt% active)	Example 7 (wt% active)
Polyglyceryl-10 oleate	3.60	3.60
Polyglyceryl-10 laurate	1.00	1.00
Coco-betaine	5.63	–
Sodium lauroamphohydroxypropylsulfonate	–	5.63
Sodium cocoyl glutamate	4.05	–
Sodium methyl 2-sulfolaurate (and) disodium 2-sulfolaurate	–	4.05
Sodium benzoate	0.5	0.5
Sodium chloride	4.00	–
Citric acid	Q.S. to pH 4.5	Q.S. to pH 4.9
Water	Q.S. to 100 wt%	Q.S. to 100 wt%

preserved using sodium benzoate at a pH < 5. These formulations exhibited outstanding mildness, foaming, and clarity and also demonstrated thickening at low pH values (Figure 2) that could contribute to product viscosity. Additionally, by employing 100% bio-based PGEs instead of highly ethoxylated sorbitan esters, the renewable carbon content in the formulations was increased dramatically.

CATIONIC ETHERS OF PG AND PGEs AS NOVEL CONDITIONING AGENTS FOR SKIN AND HAIR

Both PG and PGEs may be substituted with quaternary ammonium groups via reaction with 2,3-epoxypropylalkyldimethylammonium chloride or 3-chloro-2-hydroxypropylalkyldimethylammonium chloride reagents in aqueous media to yield cationic hydroxypropyl PG ethers (6). The cationic groups may be either hydrophilic or hydrophobic in nature, e.g., trimethylammonium versus C₁₂–C₁₈ alkyldimethylammonium, and combinations of cationic groups may also be employed. Cationic amphiphilic molecules demonstrating surface activity can be achieved by either modifying PG with long chain alkyl (e.g., lauryl

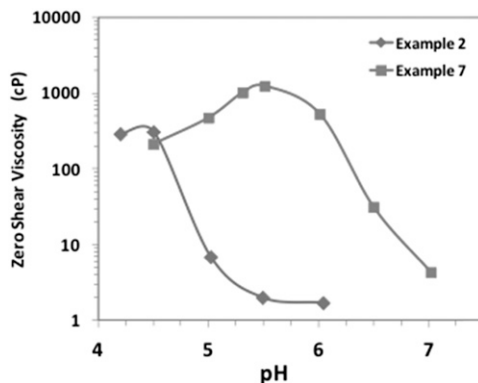


Figure 2. Zero-shear viscosity as a function of pH for the formulations in Table I. pH adjusted via addition of concentrated citric acid solution.

or stearyl) quaternary ammonium groups or by modifying PGEs with trimethylammonium groups. The properties of cationic PG and PGE derivatives can be tuned by controlling multiple synthetic variables, i.e., PG degree of polymerization (DP), PGE acyl chain length, PGE degree of acyl substitution, degree of cationic substitution, and the ratio of hydrophilic/amphiphilic cationic groups, enabling the synthesis of ingredients with performance targeted to specific applications. Figure 3 shows schematic examples of the design flexibility afforded by this chemistry.

Cationic amphiphilic PGs are particularly well suited for application as ethoxylate-free alternatives to substantive humectants such as lauryl methyl gluceth-10 hydroxypropyltrimonium chloride (7). The nonionic, hydrophilic character of PG provides similar humectancy, mildness, and formulation compatibility analogous to that of PEG, whereas the cationic quaternary ammonium groups enable substantivity to keratinaceous substrates, i.e., hair and skin, and provide antistatic benefits on hair. Cationic amphiphilic PG derivatives demonstrate good foaming behavior due to their surface activity and do not negatively impact foam performance in surfactant-based cleansers. These compounds have also shown potential to act as micellar thickeners in surfactant systems, although the viscosity building ability is highly dependent on the exact molecular structure of the derivative (6).

MICELLAR THICKENERS DERIVED FROM PG-MODIFIED METHYL GLUCOSIDE OR SORBITAN DIESTERS

Although most PG is derived via condensation polymerization of glycerol, PG may also be prepared via base-catalyzed ring-opening polymerization of GC initiated by any substrate bearing an alcohol group (2,8). In contrast to the postpolymerization reactions where functional groups are “reacted to” PG, this addition polymerization route enables PG chains to be “grown from” a variety of hydroxyl functional starting materials.

In an effort to synthesize PG-based alternatives to highly ethoxylated micellar thickeners, e.g., PEG-120 methyl glucose dioleate and PEG-150 distearate, GC polymerization initiated by hydrophobic diesters, such as methyl glucose dioleate (MGD) or sorbitan dioleate, was used to prepare a series of polyglyceryl polyol esters for evaluation as thickeners for surfactant systems, as illustrated by the example in Figure 4. GC and acetylated GC were also copolymerized from MGD in an effort to limit branching in the PG chains by blocking some of the hydroxyl groups where PG branching can occur.

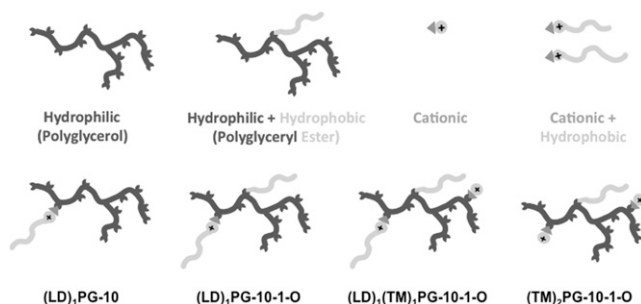


Figure 3. Schematic representation depicting synthetic design flexibility of cationic amphiphilic PG derivatives. LD: laurdimoniumhydroxypropyl; TM: hydroxypropyltrimonium; PG-10: polyglycerin-10; PG-10-1-O: polyglyceryl-10 oleate.

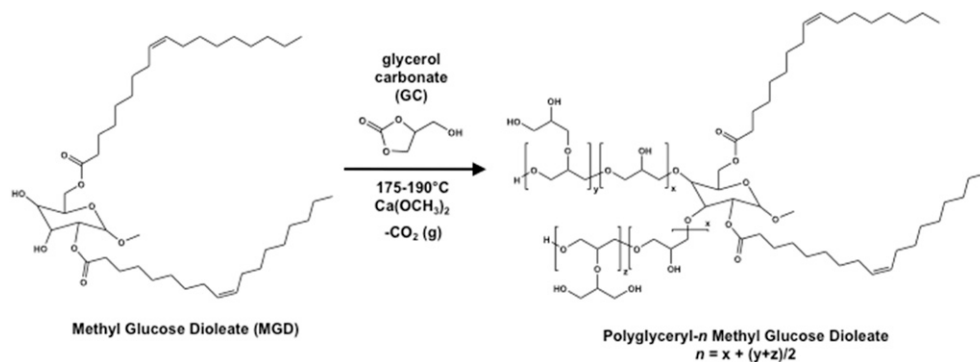


Figure 4. Synthesis of polyglyceryl-*n*-methyl glucose dioleate via base-catalyzed ring-opening polymerization of GC initiated by MGD.

Figure 5 shows zero-shear viscosity data for the polyglyceryl methyl glucose dioleate (PGMGD) thickeners as a function of PG repeat unit DP when used at 5 wt% in an adult shampoo surfactant base consisting of ammonium laureth sulfate (ALES), ammonium lauryl sulfate (ALS), and cocamide MEA (CMEA). The data reveal that as the DP of the PG chains initially increases from 4 to 10 repeat units, the viscosity building ability of the molecules increases dramatically; however, as the DP increases beyond 10 repeat units, the viscosity building decreases precipitously, and molecules having DP greater than *ca.* 20 repeat units actual cause the surfactant blend to lose viscosity. This behavior is the result of the changing molecular geometry of the PGMGD with increasing PG DP: as the hydrophilic PG chains of the head group become progressively larger relative to the hydrophobic MGD tail group, the PGMGD will become more hydrophilic and the critical packing parameter (CPP) of the molecule will decrease. The initial increase in hydrophilicity and decrease in CPP enable PGMGD to have favorable solubility in the surfactant system and cause the net radius of curvature in the system to decrease, leading to the formation of longer rod-like micelles and higher viscosities in the surfactant system tested (10). However, as the PG DP continues to increase beyond 10 repeat units, the excess hydrophilicity and continually decreasing CPP will eventually cause the net radius

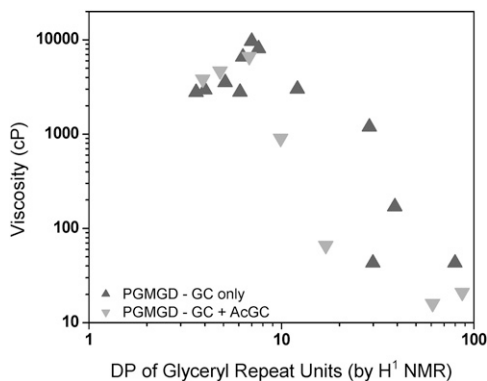


Figure 5. Zero-shear viscosity data for PGMGD thickeners at in an adult shampoo surfactant base (ALES/ALS/CMEA). PGMGD concentration = 5 wt%.

of curvature to begin increasing, resulting in shorter rod-like micelles and eventually a transition from rod-like to spherical micellar geometry, all of which coincide with the observed decreasing viscosities.

Based on these findings, the polyglyceryl polyol ester thickeners are considered to function more effectively as hydrophobic core thickeners and not like highly ethoxylated hydrophilic corona-type thickeners, e.g., PEG-120 methyl glucose dioleate.¹⁰ These PG-based thickeners are best suited for surfactant systems that build viscosity via rod-like micelle formation, e.g., blends containing high concentrations of anionic surfactants. The GC polymerization approach enables effective control of the PG DP, in turn offering the potential to synthesize thickeners with CPPs tailored to provide the most efficient radius of curvature for maximizing rod-like micelle formation in a given surfactant system.

CONCLUSION

PG is a versatile bio-based platform that can be exploited for the development of a broad range of functional cosmetic ingredients, including surfactants, conditioning agents, and thickeners. When utilized with green chemistry and sustainable design principles in mind, PG offers ingredient manufacturers and formulators yet another alternative to increase biorenewable content in their products without sacrificing on functional or aesthetic benefits. The synthetic flexibility of PG ingredient platforms enables ingredients to be tailored to specific applications and for maximum performance.

REFERENCES

- (1) M. J. Fevola, *Cosmetics & Toiletries*, 126(8), 548 (2011).
- (2) G. Rokicki, P. Rakoczy, P. Parzuchowski, and M. Sobiecki, Hyperbranched aliphatic polyethers obtained from environmentally benign monomer: Glycerol carbonate, *Green Chem.*, 7, 529–539 (2005).
- (3) J. N. Masci and N. A. Poirier, *Detergent compositions*, US Patent 3,055, 836 (1962).
- (4) R. J. Verdicchio and J. M. Walts, High-lathering non-irritating detergent compositions, US Patent 3,950,417 (1976).
- (5) M. J. Fevola, Compositions comprising a polyglyceryl nonionic surfactant and a zwitterionic surfactant, US Patent 8,227,393 B2, (2012).
- (6) M. J. Fevola, F. C. Sun, and S. E. York, Cationic polyglyceryl compounds and compositions, US Patent 8,961,945 B2 (2015).
- (7) S. B. Polovsky, H. L. Moshel, J. P. Pavlichko, and A. Friedman, Alkoxyated alkyl glucoside ether quaternaries useful in personal care, US Patent 5,138,043 (1992).
- (8) H. S. Bevinakatti, A. G. Waite, and J. Frank, Polyglycerol ethers of sorbitan carboxylic acid esters, Patent WO2009016375A2 (2009).
- (9) S. Andjelic, M. Erneta, M. J. Fevola, and F. C. Sun, Polyglyceryl compounds comprising a methyl glucoside or sorbitan remnant and compositions comprising the same, US Patent 8,455,418 B2 (2013).
- (10) U. Kortemeier, J. Venzmer, A. Howe, B. Grüning, and S. Herrwerth, *SOFW J.*, 136(3), 30–38 (2010).