

## Newly designed polysiloxane-graft-poly (oxyethylene) copolymeric surfactants: preparation, surface activity and emulsification properties

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*Abstract:* Two sets of comb-grafted polymeric surfactants based on poly(methylhydrogen siloxane) (PHMS) and/or poly(dimethylsiloxane) (PHMS-PDMS) were prepared by silylation of the active Si-H group with an active omega-vinyl group of specially designed undecenoic-polyethyleneglycol esters (UPEG) to form “newly-designed” polysiloxane-grafted-polyethyleneglycol comb-copolymeric surfactants.

The hydrophilic moieties are hooked to the hydrophobic backbone through a “spacer” (undecenoic acid). The variations in the surfactants’ structures were in the length and density of the grafted hydrophilic moieties, the chain length (DP) and nature of the hydrophobic backbone.

The first 12 different polymeric surfactants (set 1), termed PHMS-UPEG, were found to be ineffective emulsifiers with limited ability to stabilize oil-in-water emulsions. The second set of surfactants, named PHMS-PDMS-UPEG comb-grafted copolymers, significantly reduced the oil-water interfacial tension and effectively stabilized several types of oil-in-water emulsions. The best emulsifier of this set (PHMS-PDMS-52-UPEG-45), seems to be the one whose anchor backbone (PHMS-PDMS) dissolves (rather than spreads) in the oil phase, and whose stabilizing moieties are sufficiently long (45 EO units) and “hooked” to the silicone backbone at high density (52% substitution).

*Key words:* Polymeric surfactants – siliconic emulsifiers – surface activity – emulsification

### Introduction

Over a period of 20 years, the concept of steric stabilization by solvated polymer chains anchored to a particle surface has grown from an academic novelty to commercial exploration. Graft and block copolymers with different solubility characteristics can now be synthesized to match many combinations of particles and media [1–3].

The steric stabilization of aqueous dispersions by graft and block copolymers has been utilized extensively. The stabilizers are amphiphatic in nature, containing separate hydrophilic and hydrophobic units [4]. The variation can be in the chain length of the blocks (“Pluronics”) or in the case of graft polymers, in the length and frequency of

grafted chains and the chain length of the backbone [2, 3].

March and Napper [5] published results on the flocculation stability of sterically stabilized aqueous emulsions. They used well-characterized graft copolymers in water-toluene systems and concluded that in order to achieve optimal stability the anchor polymer had to be soluble in the dispersion phase. They established that in an amphiphatic polymeric surfactant the anchor stabilizer mass ratio (in their case 0.4) is of great importance in achieving stability.

On the basis of this pioneer work, several copolymers have been prepared and tested both as surfactants and as emulsifiers [6]. The most recent examples include poly(p-methylstyrene)-graft-poly(oxyethylene) copolymers [6]. Several

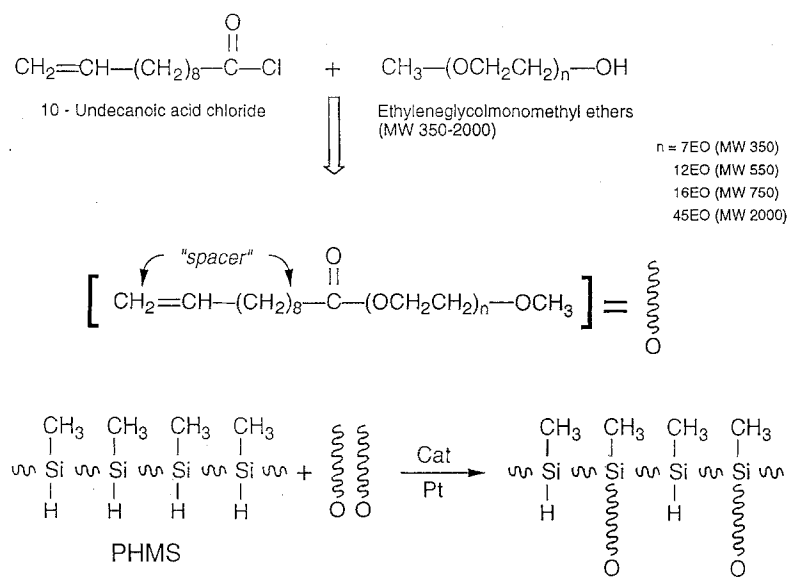


Fig. 1. Schematic illustration of the nature of the polysiloxane-graft poly(oxyethylene) copolymers.

copolymers have been prepared that vary in hydrophobic backbone chain lengths, hydrophilic branch length and frequency of branches. The copolymers were found to reduce surface tension and stabilize oil-in-water emulsions [6]. The unusual and interesting properties of silicone poly(ethyleneglycol) copolymers manifested themselves in a broad spectrum of applications [7], mainly in cosmetic formulations in which silicone has been used for more than 30 years [8]. The silicone polyethyleneglycol copolymers are known also as silicone poly(oxyalkylene oxide), silicone oxyethylene copolymers, and dimethicone copolymers [9]. These polymers, when dissolved in water, are able to significantly reduce surface tensions of aqueous systems (20–25 dyne/cm) [10, 11]. The incorporation of the polyalkylene ether groups into the silicone polymeric backbone modifies the hydrophilic properties of the dimethylsilicone oils and contributes significant hydrophilic properties. The proper balance between the oil-like backbone and the hydrophilic polyethyleneglycol groups determines its surface activity.

Silicone polyether polymers act as surfactants, foam promoters, and dispersants in aqueous solutions, as well as defoamers in non-aqueous or organic systems. Most of these polymers also showed inversed temperature solubility in water [12]. In most cases grafted copolymers were

prepared via hydrosilation on Si-H active groups, of  $\Omega$ -olefines as shown in Fig. 1. As a result, the hydrosilation leads to the formation of hydrolytically stable polymers.

Pioneering in the field of preparation of siliconic surfactants are the Finkelmanns [13, 14], who designed and prepared silicone-based copolymers as hydrotropic liquid crystals. Vick [9] also designed and prepared some silicone-based surfactants and examined their surface activity in water.

The present study is an attempt to redesign new and well-defined poly(ethyleneglycol) siliconic copolymers to serve as polymeric emulsifiers. The well-characterized comb copolymers, given an appropriate balance between the oxyethylene groups and the silicone backbone, should show improved surface activity and emulsification power. These polymers were tested as emulsifiers for various O/W emulsions, while their ability to stabilize emulsions was correlated to their structure.

## Experimental

### Materials

Poly(hydrogenmethylsiloxane) (PHMS) MW 2165, was purchased from Aldrich USA and used

Table 1. Molecular weight of backbone and composition of the two sets of polymers. Set 1 consists of PHMS-UPEG and set 2 is block copolymer of PDMS-PHMS-UPEG.

Set #	MW of backbone	wt% of PHMS	# of EO units
1	2165	10	7,12,16,45
	2165	50	7,12,16,45
	2165	90	7,12,16,45
2	2250	16.5	7,12,16,45
	2050	32.5	7,12,16,45
	950	52.5	7,12,16,45

without any further purification (see Table 1). Poly(hydrogenmethyl siloxane) coupled to poly(dimethylsiloxane) (PHMS-PDMS) block copolymers consisting of 16.5, 32.5, and 52.5% of active Si-H groups and molecular weight of 950 and 2250 respectively have been obtained from Hüll's Petrach Systems, USA, and also used as received (see Table 1).

Oligomeric surfactants with 7, 12, 16, and 45 ethyleneglycol (EO) units attached to undecenoic acid (UPEG) were prepared in our lab according to procedure described elsewhere [15]. The materials were well characterized by NMR, FTIR, and other analytical methods prior to attaching them to the siliconic polymers.

The catalyst for the hydrosilation reaction was *cis*-dichlorobis(diethylsulfide) platinum (II) (Stream Chemicals, USA). The use of this catalyst allows us to carry out the hydrosilation reaction without the need for careful temperature control and elimination of moisture.

Toluene and hexane (Analytical Solvents) served as reaction medium and purification solvent, respectively. It should be noted that the silicone surfactants produced were mostly free of unreacted UPEG's.

The organic phase (oil phase) used in the emulsification procedure was one of the following: Silicone oil F-10 (Aidchim, Israel), toluene, dodecane (Aldrich, USA), analytical and purified soybean oil (Olivex, Israel). All oils were used without further purification.

#### Surface activity

Surface (water/air) and interfacial (organic phase/water) tensions were measured using the Wilhelm technique (Lauda Tensiometer). Sam-

ples were equilibrated for a minimum of 24 h in the instrument cell to reach constant readings.

#### Emulsification

Oil-in-water emulsions (1 wt% polymeric surfactant, 30 wt% organic phase – "oils") were prepared using the Ultra Turrax homogenizer (Janke & Kunkel, IKA Labor Technik, T25 model, FRG). Emulsification time was 20 min at 9500 rpm. Emulsion stability was evaluated by visual observations (measurements of percent of oil separation, creaming layer or flocculation), microscopic examination (Nikon AFX-IIA, Japan) and droplet size measurements (Coulter counter TA II, USA) to determine droplet size distribution at time intervals within 30 days.

## Results and discussion

### 1. PHMS-UPEG block copolymer surfactants

*Surface activity and emulsification:* Surface activities of the 12 prepared PHMS-UPEG type surfactants, which have the same backbone MW (2165) have been measured and characterized. The equilibrium surface tensions (0.1 wt% PHMS-UPEG) are shown in Fig. 2. These copolymeric surfactants, in contrast to other polymeric surfactants (such as poly(*p*-methylstyrene-graft poly(oxyethylene)) [16], are quite effective in reducing surface tension of water. The surface tension increases with the increase of the degree of substitution, at any poly(ethyleneglycol) chain length. Moreover, the longer the PEG chain length, the higher the surface tension. These results are in good agreement with other surfactants [16–21].

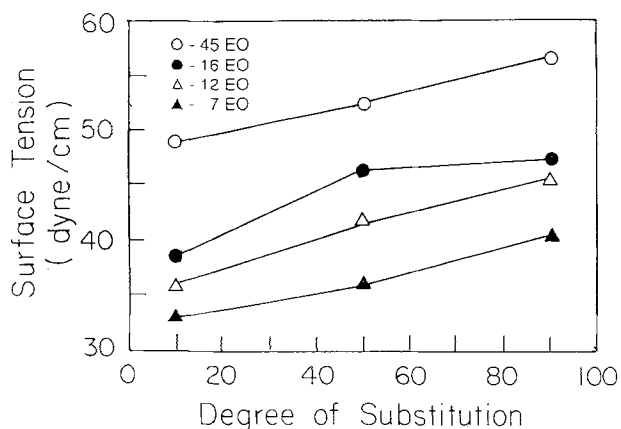


Fig. 2. Surface tensions of block copolymers of PHMS-UPEG type solutions (0.1 wt%) as a function of the degree of substitution of the UPEG on the backbone for various EO units.

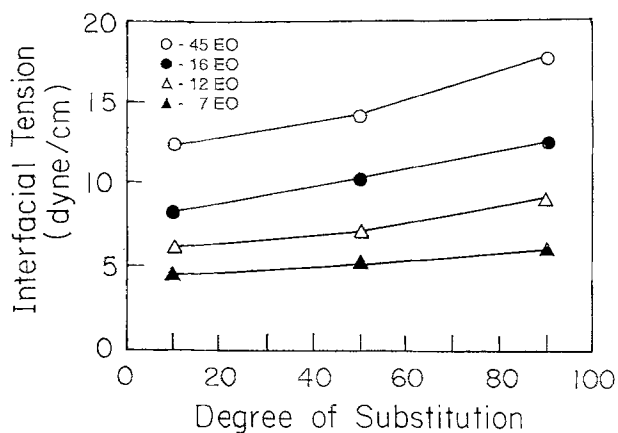


Fig. 3. Interfacial tensions of dodecane-water in the presence of PHMS-UPEG (0.1 wt%) as a function of the degree of substitution of the UPEG on the backbone.

These observations result from the change of the hydrophilic nature of the surfactants: increasing hydrophilicity by increasing PEG chain length, or degree of substitution, leads to increased water solubility, hence, decreased surface activity. The same general behavior is observed for the interfacial tensions between water and dodecane (0.1 wt% surfactant), as presented in Fig. 3. The reduction in interfacial tension is very significant, especially for the short ethyleneglycol chain length (7 EO), which reduces the interfacial tension from 45 to 4 dyne/cm.

The role of the polyethyleneglycol fraction on the surface and interfacial tensions was evaluated by plotting these values against EO weight percentage of all 12 polymers (Fig. 4). It is obvious that the surface activity of the PHMS-UPEG surfactants generally depends on their relative EO content and is not specifically related to the frequency of grafting or length of the hydrophilic moiety.

Silicone-based poly(ethyleneglycol) copolymer, like many common low-molecular weight surfactants, exhibits inverse temperature solubility characteristics. As the solution temperature is raised the surfactant solubility decreases to a point at which the material is no longer soluble and tends to form a new phase (cloud point) [9]. Similar phenomenon is observed with the present copolymers: hydrogen bonding and hydration water molecules around the PEG chains are responsible for the improved solubility of the siloxane polymeric moieties at room temperature in water. As the temperature is raised the hydrogen bonds tend to break due to thermal vibrations and at a given point (cloud point) the silicone molecule separates from the solution. It is therefore important to note that very hydrophobic copolymers (low EO content) will have cloud points close to room temperature, while others that are more hydrophilic (70–75% EO) have cloud points of approximately 80 °C (Fig. 5). The most hydrophilic polymers (> 85% EO) will have very high cloud points (95–100 °C). This information is important to consider when preparing emulsions from those surfactants. The general dependence on the EO fraction, and not on the chain length or degree of substitution alone is also observed here.

*Emulsification:* Attempts were made to emulsify several oils with the PHMS-UPEG set of polymeric surfactants in order to correlate the emulsification ability (efficiency) with surface activity. To our disappointment, most emulsions prepared with any of the given surfactants, and with most tested oils, were very unstable. The emulsions were prepared with 1 wt% polymeric surfactant (0.1 wt% was sufficient concentration to reduce interfacial tensions to 5–18 dynes/cm), and it was concluded that even this high concentration was not sufficient for the surfactant to provide suitable steric stabilization. It has been

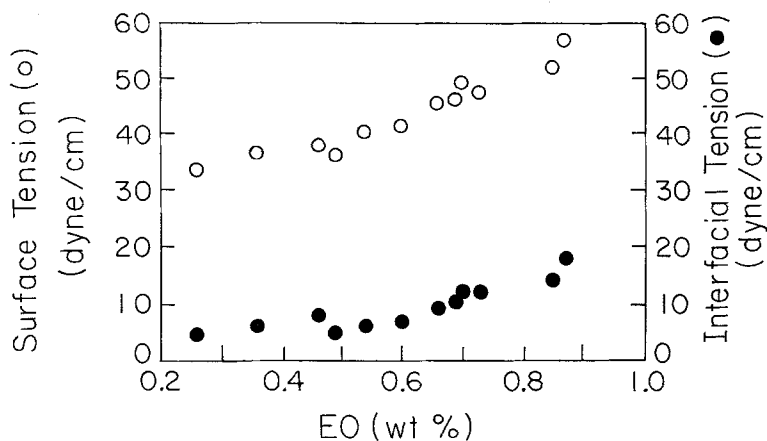


Fig. 4. Surface and interfacial tensions of PHMS-UPEG block copolymers as a function of wt% of EO units in the polymer.

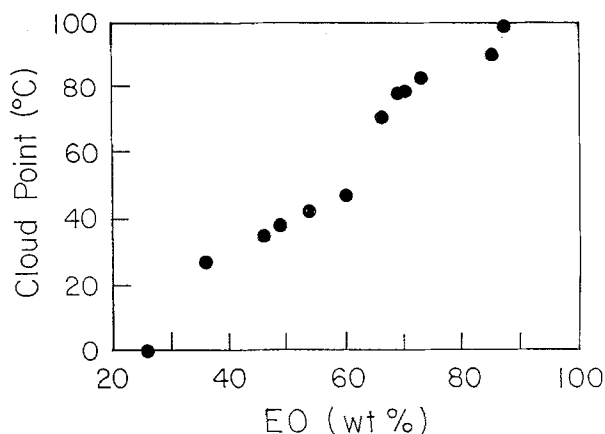


Fig. 5. Cloud points (°C) of PHMS-UPEG block copolymers as a function of wt% of EO units in the polymer.

assumed, as will later be discussed, that the hydrophobic portion of the surfactant (PHMS) did not provide efficient anchoring in the oil phase.

## 2. PHMS-PDMS-UPEG comb grafted copolymer surfactants

**Surface properties:** The PHMS was replaced by two PHMS-PDMS block copolymer backbones (with various molecular weights) as a basis for another set of graft copolymeric surfactants. Twelve new polymeric surfactants termed PHMS-PDMS-UPEG were designed and prepared. The differences between the various compounds being the frequency of substitution (anchoring density) and the length of the PEG chains (number of EO units). Surface tension values of the solutions

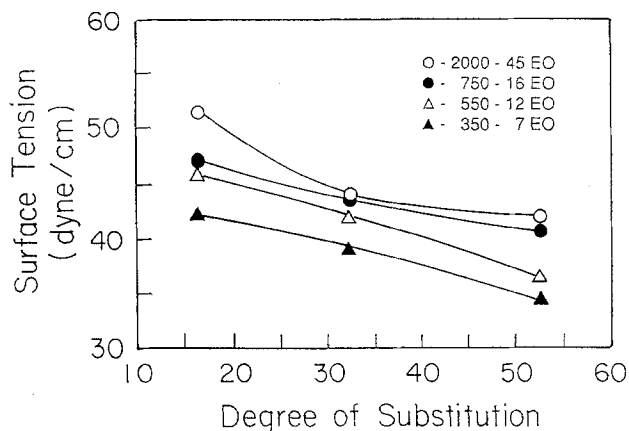


Fig. 6. Surface tensions of water-air interface in the presence of 0.1 wt% PHMS-PDMS-UPEG graft copolymers as a function of the degree of substitution of UPEG for 7-45 EO units.

containing surfactants (0.1 wt%) are presented in Fig. 6. As expected, it was found that the surface tension of PHMS-PDMS-UPEG polymers tends to increase with the increase of the PEG chain length. However, surprisingly, the surface tension tends to decrease with the increase of the oligomers' degree of substitution, a trend opposite to what was observed for the PHMS-based surfactants. A possible explanation for this anomaly is that the surface tension is directly related to the length and organization of the siliconic hydrophobic backbone at the water/air interface. It is known that the most dominant factor to effect the surface tension of water-polymeric surfactants (block copolymers) is the molecular weight of the

backbone. It was found in Vick's work [9], that in every series of silicic surfactants the surface tensions of the aqueous solutions are dependent on the length of the silicic backbone and on the hydrophilicity of the anchoring PEG side chains. From his work (and ours), it seems that the lowest surface tensions were reached in the silicic surfactants with the shortest silicic backbones. In the present work, as seen in Table 1, the PHMS-UPEG surfactants have a constant, comparatively high M.W. (2165), whereas the M.W. of PHMS-PDMS-UPEG surfactants varied (950, 2050, 2250). Clearly, it is apparent that the surface tensions of the highly substituted PHMS-PDMS-UPEG surfactants (52.5% substitution, M.W. of 950) are lower than the 50% substituted PHMS-UPEG surfactant (M.W. = 2165).

The assumption is that the water-air interface is covered with a polymeric film consisting of hydrophilic groups that are completely soluble in water, and the silicic organic-like backbone spreads on the surface facing the air. As a result, the character of the interface changes to resemble the PDMS, which behaves like a third new phase. It is therefore expected that the surface tension of the water-air interface will be similar to that of PDMS-water, which is ca. 20 dyne/cm. The surface tension of the newly formed water-PDMS phase depends on the mixed copolymers PHMS-PDMS which, as opposed to PHMS copolymers, might exhibit a tendency (similar to that of the hydrophobic components) to be "pushed out" of the aqueous solution onto the "oil-like" phase. Thus, both dimethylsiloxanes and the substituted hydrogen siloxane will spread on the "oil-like" phase. The surface then becomes more like a mixture of dimethylsiloxane and polyethylene-glycol. As such, the surface tension is a combination of the two as opposed to PHMS-UPEG or UPEG alone.

The interfacial tension measurements reveal that, in general, the PHMS-PDMS-UPEG polymers tend to be more efficient surfactants than the previous PHMS-UPEG polymers, as can be seen in Fig. 7.

**Emulsification:** As previously described, emulsification was repeated with the present surfactants in the presence of a variety of oils under similar preparation conditions (1 wt% emulsifier, 30 wt% oil (organic phase), 20 min homogeniz-

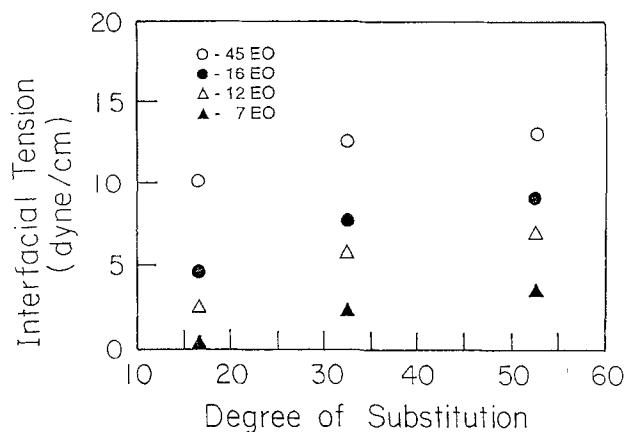


Fig. 7. Interfacial tensions of water-dodecane interface in the presence of 0.1 wt% PHMS-PDMS-UPEG graft copolymers as a function of the degree of substitution of UPEG for 7-45 units.

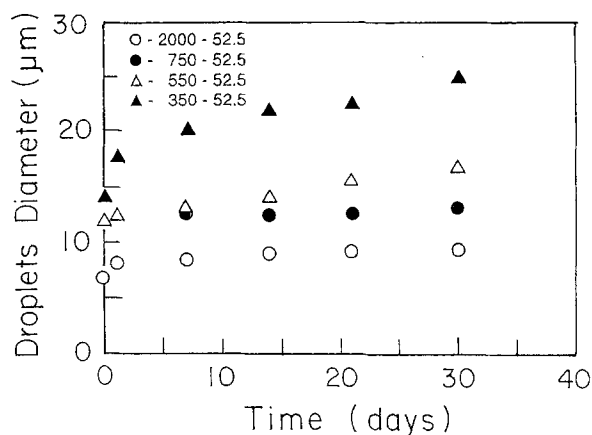


Fig. 8. Average droplet size vs. time of oil droplets in 5 wt% dodecane emulsions stabilized with 0.1 wt% of block copolymer for 16.5 to 52.5 wt% substitution and 16 EO units attached to UPEG.

ation at 9500 rpm). The emulsions were easy to prepare and remained noncoalesced and stable for several months. Attempts were made to correlate emulsion stability with emulsifiers' character and structure. Stability was reflected through droplet size distribution measurements, using the Coulter counter. Figure 8 presents the change in droplet size with equal PEG chain length (16 EO units) but different frequency of substitution (16, 32, and 52%). It can be clearly seen that polymers with high frequency of substitution are better

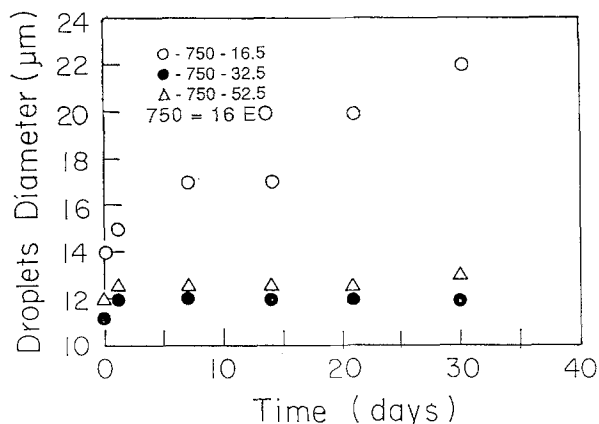


Fig. 9. Average droplet size of oil droplets in o/w emulsions prepared with 5 wt% dodecane and 0.1 wt% PHMS-PDMS-UPEG grafted block copolymer for 52.5% substitution of UPEG and various EO units (MW 350–2000) as a function of time.

steric stabilizers and exhibit less change in droplet size with time than those with low substitution.

Figure 9 shows the change in droplets size for emulsions prepared with polymers with equally high-frequency of substitution (52%) and various PEG chain lengths (7 to 45 EO units). It is clear, once again, that polymers with long stabilizing moieties will provide better steric protection on the oil droplets than those with short hydrophiles.

As a result of the trends seen in Figs. 8 and 9, it is possible to postulate that if the “anchoring moiety” (polymer) cannot spread and strongly adsorb onto the oil/water interface, the “stabilizing groups” will play the dominant role in controlling the emulsion stability. This suggests that long hydrophobic moieties spread at high surface density on the oil will be the most efficient surfactants, providing a thick covered film layer. The short-chain polymers or polymers with incompatible functional groups to the oil must consist of long and highly substituted hydrophilic moieties.

These findings indicate that the surface and interfacial tensions of a given copolymer are not sufficient criteria to predict emulsification ability and stability of the surfactant. A better understanding of the polymer spreading ability, together with its oil dissolution, are important factors to consider prior to examining their stabilizing activity in the dispersed phase.

These efficient surfactants were used to prepare oil-water emulsions of various oils (toluene, silicone and dodecane). They were found to form very stable emulsions, which proves the universality of the silconic comb-grafted copolymers in stabilizing many types of o/w emulsions. Their impressive stabilizing ability is attributed to their well balanced structure of the block copolymeric backbone and the hydrophilic moieties grafted at sufficient density and length.

## Conclusions

Polysiloxane-graft-poly(oxyethylene) hydrophilic copolymeric surfactants have been designed and prepared. It was clearly seen that block copolymers based on PHMS-PDMS are more efficient hydrophobic backbone (dangling moiety) than that of the homopolymer of PHMS.

Grafting the blockcopolymer with hydrophilic polymeric surfactant hooked to the backbone through a “spacer” of undecanoic moiety (UPEG) also have a beneficial effect on the ability of the surfactant to spread on the oil interface and to anchor stray with a number of sites. The proper balance between the length of the backbone, the degree of grafting (grafting density), and the chain length of the hydrophilic moieties led to the ideal polymeric surfactant with excellent steric stabilization ability and good interfacial properties. The ideal emulsifier – PHMS-PDMS-52%-45 UPEG (block copolymer of PHMS-PDMS of MW 950 grafted at 52% chain density with 45 UPEG units) – was selected as the best hydrophilic emulsifier for o/w emulsions.

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