Effects and Measurements of Polyoxyethylene Block Length in Polyoxyethylene-Polyoxybutylene Copolymers

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Block copolymer surfactants, made from 1,2-butylene oxide (BO), propylene oxide (PO) and ethylene oxide (EO), exhibit wide ranges of properties and performance. In particular, BO/EO block copolymers exhibit improved surfactant performance with respect to PO/EO analogs. One interesting difference between these two classes of surfactants is the EO capping efficiency of polyoxypropylene (POP) vs. polyoxybutylene (POB) hydrophobe secondary hydroxyl groups. In this regard, nuclear magnetic resonance measurements have shown that POP secondary diols react more readily with EO than POB diols. For the case of ethoxylated POB polymers, the amount of unethoxylated secondary hydroxyl is proportional to the average length of the polyoxyethylene (POE) blocks. Differential scanning calorimetry was used to observe crystallinity of POE blocks. For a given POB hydrophobe molecular weight and weight percentage EO, surfactant performance properties can be augmented by affecting POE block length in the ethoxylation process.

KEY WORDS: **Average block length, block copolymer, ethoxylation, melting point, molecular weight distribution, nonionic surfactant, polyoxybutylene, polyoxypropylene, surfactant performance properties.**

Block copolymer nonionic surfactants are widely used in consumer and industrial applications. In particular, polyalkylene oxide block copolymers made from propylene oxide (PO), 1,2-butylene oxide (BO) and ethylene oxide (EO) comprise a major class of nonionic surfactants presently in use (1–5).

Nonionic surfactants in use today typically contain a polyoxyethylene (POE) moiety as the hydrophile. The hydrophobic block can be derived from a larger set of possible materials, examples of which are alkylated phenols, fatty alcohols and acids, polyoxypropylene (POP) and polyoxybutylene (POB). Each hydrophobe type imparts unique performance attributes to the class of nonionic surfactants in which it is utilized.

Nonionic surfactant hydrophobes can be compared with each other by observing their relative water and oil solubility. This comparison also leads to a ranking of the hydrophobicity of the hydrophobe types. In this ranking, a long-chain fatty alcohol or alkyl phenol hydrophobe is more nonpolar than POB. POB is less hydrophobic because of its polyether nature, but it is, however, soluble in mineral oils in all proportions. POP is the least hydrophobic of the class and exhibits higher water solubility and greatly decreased oil solubility.

Because of the increased hydrophobicity of the POB block, POB/POE block copolymer surfactants show a greater level of performance when compared to the POP/POE analogs in terms of surface and interfacial tension lowering and wetting.

This paper discusses the syntheses of POB/POE and POP/POE block copolymer nonionic surfactants. In particular, the EO capping reaction and POE block length variability will be covered in detail, and data will be presented that show how this variability can affect surfactant performance.

EXPERIMENTAL PROCEDURES

Synthesis of POB/POE and POP/POE block copolymers. The following describes a typical synthesis of a POB/POE block copolymer diol. The same procedure was used to produce POP/POE copolymers, except that PO was used instead of BO for making the central hydrophobe block:

Into a closed-system steel reaction vessel was charged 656 g of 1,2-propylene glycol (The Dow Chemical Company, Freeport, TX), containing 6% (w/w) solid KOH (Fisher Scientific Company, Fairlawn, NJ). The reactor was sealed, and the temperature was increased to 130°C, at which time 5645 g of BO was fed at such a rate that an internal pressure of below 70 PSIA was maintained. All oxides were obtained from the Dow Chemical Company. Following the addition of BO, the reaction temperature was maintained at 130°C until the pressure drop over a one-hour period was less than 0.5 PSIA (PSI absolute). After the BO digestion period was complete, the reactor contents were sampled. Hydroxyl analysis determined the diol polymer to have a molecular weight of 730. To allow room for the feeding of the next oxide, 3767 g of the intermediate diol was removed. This amount of material included small samples for hydroxyl analysis. To the remaining contents of the reactor was fed 597 g of EO at the same pressure and feed rate boundaries as in the BO feed step. The final product was analyzed to have a molecular weight of 902. The product was then hot-filtered through a proprietary agent suitable to remove the residual alkalinity of the KOH catalyst.

Molecular weight analysis of intermediate diols and final products. Number-averaged molecular weights of intermediate and final products were determined indirectly by the imidazole-catalyzed phthalic anhydride method, ASTM D4Z 74-88, Method D (Potentiometric endpoint) (6). The weight percent hydroxyl value obtained is divided into 3400 (for diols) to obtain the number-averaged molecular weight. Titration end points were determined by potentiometry.

Differential scanning calorimetry (DSC). DSC analyses were carried out with a Mettler TA-4000 thermal analysis system (Hightstown, NJ), equipped with a DSC-30 low temperature attachment and GraphWare (Mettler) TA-72 data processing software. The sample (15–35 mg) was carefully weighed and placed in an aluminum-enclosed cell. Sample conditioning was done by heating from ambient temperature to 140°C, followed by cooling to −120°C. Pertinent data were taken during a secondary heating step from −120 to 200°C. Heating and cooling rates were 20°C per minute. All tests were run under nitrogen.

Nuclear magnetic resonance (NMR) analysis. Weight percentage EO and mole percentage primary hydroxyl were determined with a JEOL GX-400 carbon-13 NMR spectrometer (JEOL Inc., Peabody, MA), operating under

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the following parameters: d-6 acetone solvent (Aldrich Chemical Company, Inc., Milwaukee, WI); ambient temperature; observation frequency 100 MHz; irradiation frequency, 400 MHz; experimental mode, SGBCM; spectral width, 22 KHz; data points, 64K; flip angle, 90°; repeat sequence, 10 s. Mole percentage of secondary hydroxyl groups was obtained by subtracting the mole percentage primary hydroxyl value from 100.

Draves wetting time. ASTM Method D2281-68 (7) was used with a 3.00-g copper hook. Skeins were obtained from Testfabrics Inc. (Middlesex, NJ).

Ross-Miles foam testing. For ASTM Method D1173-53 (8), the jacketed foam receiver was first thoroughly washed with NOCHROMIX (registered trademark of Godax Laboratories, Inc., Pawling, NY) and rinsed three times with tap water, followed by deionized water. A temperature-controlled bath was used to maintain the temperature at 25°C.

Cloud point. Approximately 80 mL of a 1.0% (wt/vol) surfactant/deionized water solution was added to a 100-mL beaker. A magnetic stir bar was added. The solution was placed atop a heater/stirrer unit. A red alcohol thermometer bulb was immersed fully into the solution and secured to a ring stand with a small clamp. The stirrer was started, and the temperature controller was gradually increased to give a solution temperature rise of approximately 2°C per min. The temperature at which the solution started to become turbid was recorded.

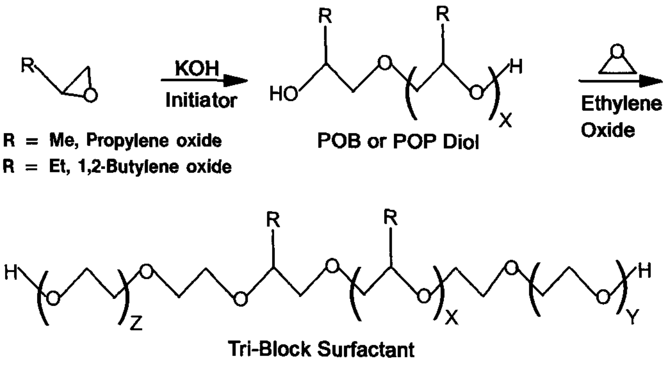
Interfacial tension measurement. A Krüss model K-12 computer-automated tensiometer (Krüss USA, Charlotte, NC) was used to measure interfacial tension. Accessories included a constant-temperature circulating bath, which held the temperature at 25°C plus or minus 0.1°C. Light mineral oil was used as the low-density phase. The Du Nouy ring method was used.

RESULTS AND DISCUSSION

Surfactant structure and synthetic ramifications. The hydrophobic portions of the surfactants were made by polymerizing PO or BO to give a POP diol or a POB diol. The resulting polymers were then ethoxylated to form the hydrophilic end blocks.

A suitable initiator for these reaction types contains at least one reactive hydrogen atom. Typically, a hydroxyl-functional initiator is used in the presence of sodium or potassium hydroxide. In this work, copolymers made from initiators that contained two reactive hydrogens were studied. The following are simplified block structures of these two classes of surfactants, POP/POE block copolymer diol $HO(C_2H_4O)_y(C_3H_6O)_x(C_2H_4O)_zH$ and POB/POE block copolymer diol $HO(C_2H_4O)_y(C_4H_8O)_x(C_2H_4O)_zH$.

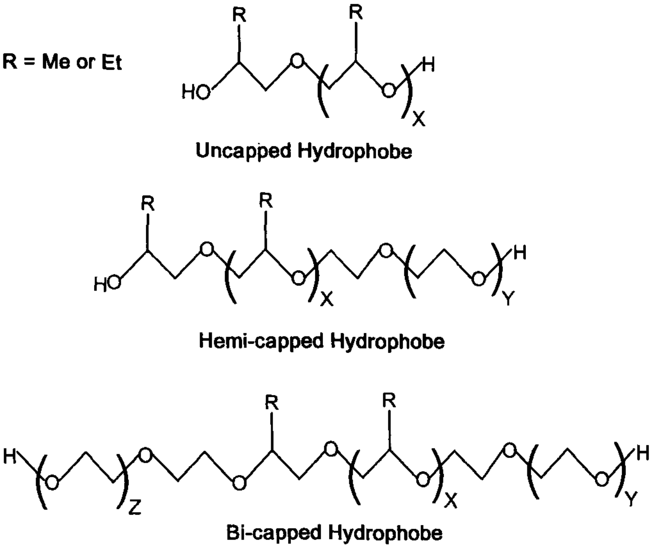
Scheme 1 shows an idealized reaction sequence for making a POB/POE or POP/POE block copolymer surfactant. In such alkylene oxide polymerizations, a host of possible courses of reaction exist, depending on the initiator functionality, order of oxide feed, and whether the oxide feed is random (using a mixture of oxide types) or homogeneous (using only one oxide type per feed). The polymers of interest here are made with homogeneous alkylene oxide feeds, starting with PO or BO and finishing (capping) with EO.



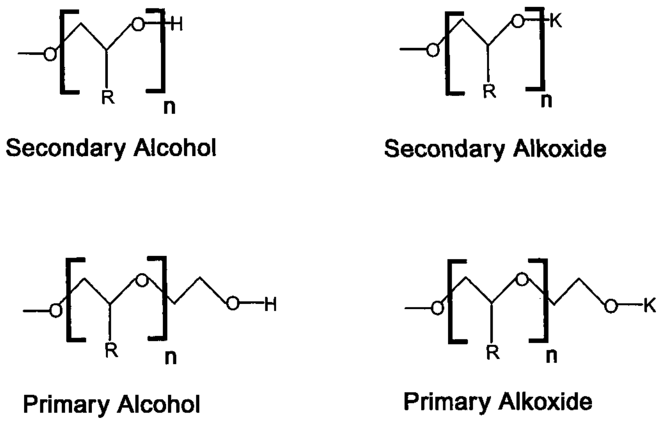
SCHEME 1

Hyroxyl end group reactivity. For this work, it is important to draw attention to the secondary hydroxyl (OH) groups at each end of the hydrophobic polymer intermediate (Scheme 1). At the end of the ethoxylation step, a significant percentage of the secondary OH groups remain. This effect illustrates why the typical tri-block structures, shown above (see second paragraph of Results and Discussion section of this paper) and in Scheme 1, are not truly descriptive of the polymers of interest. In practice, a typical surfactant matrix includes totally uncapped hydrophobe diol, hemi-capped hydrophobe, and bi-capped hydrophobe, as shown in Scheme 2. The relative amounts of these three species will depend on the extent of hydrophobe ethoxylation. The unreacted secondary OH groups are analogous to the unreacted fatty alcohol moiety found in common alcohol ethoxylate nonionic surfactants.

The residual secondary OH groups are the result of an equilibrium, established after the first EO units are reacted with the hydrophobe, to form primary OH end groups (Scheme 3). The equilibrium between secondary and primary OH lies more heavily toward the primary alkoxide species due to the higher acidity of the primary alcohol in the presence of alkoxide anion. For this reason, the secondary alcohol exhibits a relative decrease in reactivity toward ethoxylation with respect to the more highly ionized primary alcohol sites. This effect has been studied



SCHEME 2



SCHEME 3

extensively for alcohol ethoxylates and other ethoxylate systems (9–11). The molecular weight distribution of the POE block has been explained most notably by Weibull and Nycander (12) (Equations 1 and 2) with supporting work by Gold (13):

$$V = c[\ln(n_{oo}/n_o)] - (c-1)[1-(n_o/n_{oo})] \qquad [1]$$

$$n_i/n_{oo} = [c^{i-1}/(c-1)^i]\{(n_o/n_{oo}) - (n_o/n_{oo})^c \sum_{j=0}^{i-1} (1/j!)[(c-1)\ln(n_{oo}/n_o)]^j\} \qquad [2]$$

From their work, equations based on the simple-case Flory distribution (14) (Equation 3) were developed for calculating the amount of unreacted starting alcohol and the relative molecular weight distribution of ethoxylate oligomers present in the final product.

$$\frac{n_i}{n_{oo}} = \frac{e^{-V}\,V^{i-1}}{(i-1)!} \qquad [3]$$

In the distribution equations above, V is the ratio of moles EO reacted per mole starting alcohol; n_{oo} is the number of moles of starting alcohol; and n_i is the number of moles of product containing i EO units. The Flory equation applies when the relative reactivities of competing alcohols (the initiator and the alkoxylated oligomers) are equivalent.

The Weibull and Nycander equations (12) are a special case of the Flory poisson distribution. Another variable, n_o, is present in these equations and represents the number of moles of unreacted starting alcohol. This set of equations is also somewhat more complex than Equation 3. The measurable variables in Equations 1, 2 and 3 are V, n_{oo} and n_o. Variable n_o is measured indirectly by C^{13} NMR as percent secondary OH in the final surfactant product. Variable C is calculated by rearranging Equation 1 and solving for C. C is a factor numerically greater than one, and its magnitude increases with an increasing difference in reactivity between the starting alcohol initiator and ethoxylated oligomers. We have calculated C values of 20 to 30 for the ethoxylation of POB diols and from 6 to 8 for POP diols. As evidenced by this difference in C values between POB and POP ethoxylates, the extent of EO capping for POP diols is higher than for the corresponding POB diols. This is due to the lower acidity of the POB terminal OH and to higher steric hindrance compared to the POP secondary OH. Lower amounts of unethoxylated secondary hydroxyl groups are directly associated with higher EO capping efficiency. Figure 1 shows representative primary hydroxyl mole percentages plotted against the log of the number of moles EO added per secondary OH group for POB and POP diols. The surfactant diols shown here have number-averaged molecular weights ranging from 500 to 4000.

The extent of EO capping can be improved by increasing the reactivity of the secondary OH end groups by increasing the KOH catalyst concentration. This leads to an overall increase in the concentration of reactive alkoxide end groups. Higher end-group reactivity effectively lowers the C value (Equations 1 and 2) and leads to a narrower average chainlength distribution for the POE blocks. As predicted by Equation 2, an increase in secondary OH-group EO capping leads to a decrease in the average POE block length, thus narrowing the POE molecular weight distribution and decreasing the POE block crystallinity. The decrease in crystallinity has a significant bearing on the physical and performance properties of the surfactant and is similar to "peaking" technology for alcohol ethoxylates.

EO block length observation by DSC. DSC was used to determine the relative average EO block length for POB/POE block copolymers. Figure 2 shows a representative DSC thermogram of a POB/POE copolymer.

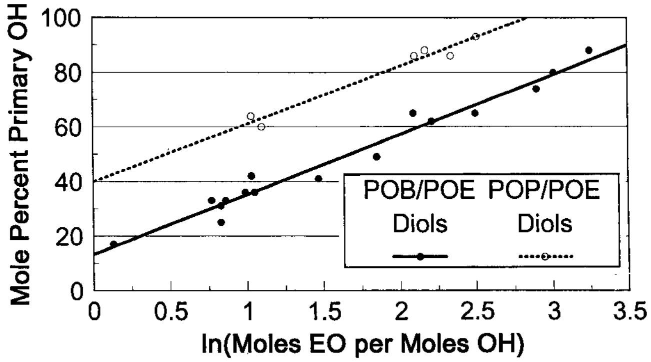


FIG. 1. Relationship between mole percent primary hydroxyl and number of moles ethylene oxide (EO) added per OH in the ethoxylation of polyoxypropylene (POP) and polyoxybutylene (POB) hydrophobe diols; POE, polyoxyethylene.

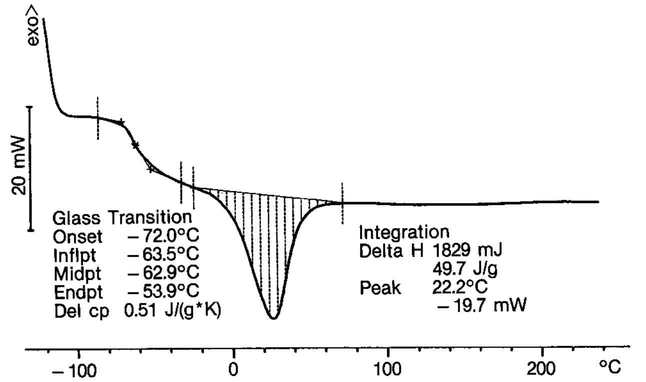


FIG. 2. Representative differential scanning calorimetry thermogram for a polyoxybutylene/polyoxyethylene block copolymer diol. Abbreviations: Infl pt, inflection point; Midpt, midpoint; Endpt, endpoint; Del cp, change in heat capacity; exo> represents the exotherm in the positive "y" direction.

During the heating process step, a glass transition for the POB block occurs near −65°C. At a higher temperature, an endothermic melting transition occurs, and the associated heat of fusion can be calculated. The peak temperature of the transition and the heat of fusion can be correlated with the percentage of POE in the polymer.

A first approach to studying the effects of POE block length and melting behavior was to analyze standard POE diols of varying average molecular weights. Figure 3 shows peak DSC melting points and heats of fusion vs. the reciprocal of molecular weight for five POE diols, ranging from 400 to 3200 average molecular weight. Linear equations for each of these variables are as follows:

$$Tm = (-524/EO\#) + 67 \qquad [4]$$

$$Hf = (-543/EO\#) + 178 \qquad [5]$$

where Tm = peak melting temperature in °C, Hf = heat of fusion in J/g, and $EO\#$ = the average number of EO monomer units in the POE diol.

Booth and others (15–17) have reported detailed findings on the subject of POE crystallinity and structure as related to homo- and block polymers. As the molecular weight (and average POE block length) increases, the weight percentage of hydroxyl end groups decreases proportionately. The terminal OH groups have the effect of decreasing the melting point and heat of fusion by lowering the crystallinity of the polymer matrix.

The peak melting behavior of ethoxylated POB diols was studied by DSC and found to be dependent on the two variables of EO percentage and the amount of KOH used in the ethoxylation reaction. As mentioned above, the secondary OH groups of the POB diol do not all react with EO in the EO capping reaction. A higher KOH catalyst level will increase the likelihood of more secondary OH groups reacting and thus narrow the distribution of the blocks. The resulting decrease in the PEO block length can be observed by DSC.

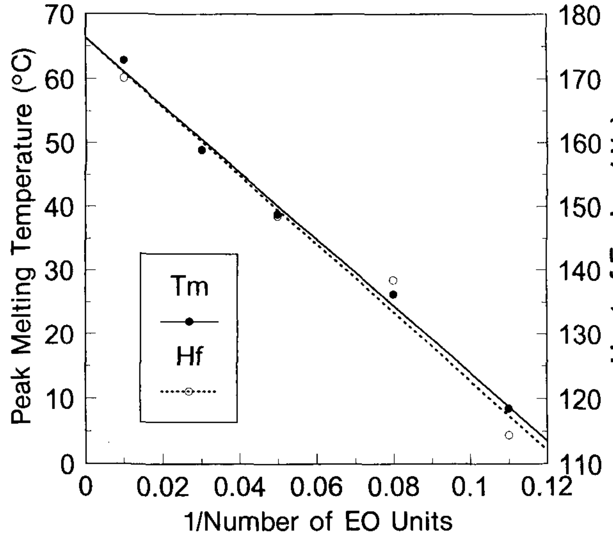


FIG. 3. Peak differential scanning calorimetry melting temperature and heat of fusion as a function of the reciprocal of the degree of ethoxylation for polyoxyethylene diols. EO, ethylene oxide; Hf, heat of fusion in J/g; Tm, peak melting temperature in °C.

An experiment was run in which two similar sets of POB/POE copolymers were synthesized. One set was made by ethoxylation of a POB diol of molecular weight 1000 in the presence of a lower amount of KOH catalyst. The second set was made with a POB hydrophobe of the same molecular weight but with three times the amount of KOH. Figure 4 shows the *Tm* vs. weight percentage of EO for the two sets of polymers. Notice that the copolymers made with higher KOH concentration have lower melting temperatures, indicating lower POE average block length. The two curves converge at higher percentages of EO due to the low level of secondary OH (<1%) and, therefore, similar POE block length.

Effects of POE block length on surfactant performance properties. The effect of POE block length on physical properties and surfactant performance was studied.

Differences in foaming, cloud point, interfacial tension and cotton wetting were seen between the two sets of POB/POE copolymers made with different amounts of KOH catalyst. Each material had a 1000-*Mw* POB diol hydrophobe, capped with 50 weight percentage of EO. The KOH levels differed by a factor of five. Table 1 lists data

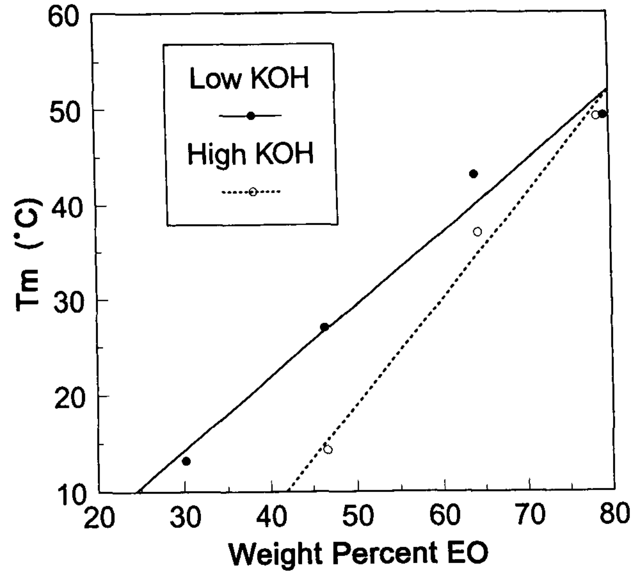


FIG. 4. Peak differential scanning calorimetry melting temperature vs. weight percent-ethylene oxide (EO) for polyoxybutylene/polyoxyethylene copolymers made with differing KOH catalyst levels. Tm, melting temperature in °C.

TABLE 1

Surfactant Performance Differences Among Polyoxybutylene/Polyoxyethylene Copolymers[a]

	Ross-Miles foam height 1% (mm)		Cloud point 1% aqueous (°C)	Interfacial tension 0.1% (dynes/cm)	Draves wetting time (s) 3 g, 0.125%
	$T^b = 0$	$T = 5$			
Higher catalyst	172	26	36	7.3	10
Lower catalyst	156	16	42	10.6	17

[a] The copolymers have identical hydrophobe molecular weights and weight percentages of ethylene oxide, but were made in the presence of different KOH catalyst levels.

[b] T, time in minutes.

that show the performance differences between the two surfactants. Interfacial tension and wetting performance were improved by using the higher KOH level, whereas the cloud point was depressed and foaming was enhanced. However, in other systems, these properties may be affected differently when catalyst level is changed, and performance may be degraded.

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