

Synthesis and Characterization of TRITON™ X-Based Surfactants with Carboxylic or Amino Groups in the Oxyethylene Chain End

Don-Ik Lee,^{1,2} Jae-Young Choi,¹ Eun Sung Lee,¹ Chang-Suk Ha,² Myounghee Han,² Jin-Young Bae²

¹Materials Laboratory, Samsung Advanced Institute of Technology, Nongseo-Ri, Giheung-Eup, Yongin-Si, Kyunggi-Do 449-712, South Korea

²Department of Polymer Science and Engineering, Polymer Technology Institute, Sungkyunkwan University, Suwon, Kyunggi-Do 440-746, South Korea

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ABSTRACT: This paper describes the synthesis and characterization of a series of TRITON™ X-based surfactants with a predominantly alkyl phenol ethoxylate (APE) backbone and carboxylic or amino chain ends. Three carboxylic acid-containing TRITON X (or APE)-derivatives, [OPE2-COOH], [OPE5-COOH], and [OPE10-COOH], were prepared from commercially available octyl phenol ethoxylate (OPE) of different oxyethylene units (i.e., $n = 2, 5,$ and 10) and ethyl bromoacetate via a simple etherification reaction followed by saponification. Two amine-containing TRITON X -derivatives, [NPE10-NH₂] and [NPE10-imidazole], were

prepared based on modifications of mesylate of nonyl phenol ethoxylate (NPE) of 10 oxyethylene units reacted with ammonia and imidazole, respectively. Depending on their composition and chain length of oxyethylene units used in the reaction, the surfactants show different thermal degradation behaviors. The carboxylic acid-containing surfactants give no char at high temperatures under air condition. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 162–170, 2007

Key words: TRITON™ X; surfactant; carboxylic acid; amine; char

INTRODUCTION

Hydroxyl-terminated alkyl phenol ethoxylates (APEs, Scheme 1), TRITON™ X series surfactants manufactured by Dow Co., are versatile nonionic surfactants, which are well known for their wetting, detergency, superior hard surface, metal cleaning, and excellent emulsification performance.^{1–4} These surfactants are used in almost every type of liquid, paste, and powdered cleaning compound, ranging from heavy-duty industrial products to gentle detergents. They are important ingredients of primary emulsifier mixtures used in the manufacture of emulsion polymers and stabilizers in latex polymers. APEs are also recognized for pigment wetting and stabilization in coatings, and are offered in a range of HLB to match specific wetting and dispersing requirements.⁴

Over 500 million pounds of APEs are produced today. Nonyl phenol ethoxylates (NPEs) and octyl phenol ethoxylates (OPEs) account for ~ 85 and 15%,

respectively, of the total volume. Dodecyl phenol ethoxylates (DPEs) and other APEs account for < 1% of the total volume.

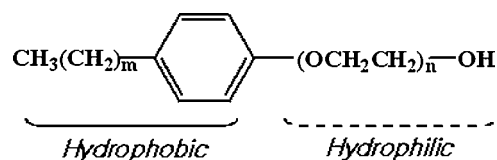
Technical synthesis of APEs starts with phenol which is alkylated by trimethylpentene, producing octyl phenol (OP) or with nonene isomers which forms nonyl phenol (NP) in an acid catalyzed process. Ethoxylation is performed by using KOH/ethanol as a catalyst with a known ratio of ethylene oxide to the alkyl phenol. The reaction results in an oligomeric mixture of the alkyl phenol containing an ethoxylate chain of varying lengths.¹

Several surfactants which have combinations of polyoxyethylene segments and alkyl chains having acidic groups (carboxylic acid or phosphoric acid) were reported in many patents.^{5–8} However, the study on the synthesis and characterization of acid (or amine)-terminated APEs has not been well documented. In addition, a systematic study on the dependence of thermal property on the composition and chain length of oxyethylene units in acid (or amine)-terminated APEs has not been reported so far, although it is expected that the APEs show high thermal behaviors with a relatively large content of oxyethylene segments in the backbone.

In this study, we attempted to introduce the carboxylic acid group (or amino and imidazole groups)

Correspondence to: E. S. Lee or J.-Y. Bae (b521@skku.edu or e.lee@samsung.com).

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Scheme 1 A typical structure of alkyl phenol ethoxylates (APEs).

into the oxyethylene chain end of various APEs such as OPEs and NPEs to establish the structure-thermal property relationship of APEs which have an acidic (or basic) functionality. Their synthesis and characterization were determined by $^1\text{H-NMR}$, FT-IR, solubility test, and TGA analysis. The effect of the oxyethylene chain length of the APEs on their thermal properties was investigated in detail.

EXPERIMENTAL

Materials

Four kinds of APEs were used in this study. Three kinds of OPEs (TRITON™ X series) differing in oxyethylene units were Igepal™ CA-210 ($n \cong 2$, OPE2), TRITON X-45 ($n \cong 5$, OPE5), and TRITON X-100 ($n \cong 10$, OPE10) from Aldrich (St. Louis, MO). NPE10 (Tergitol™ NP-9, $n \cong 10$) was supplied from Aldrich (St. Louis, MO). Ethyl bromoacetate and sodium hydride were supplied from Aldrich (St. Louis, MO). The chemical structures of APEs, ethyl bromoacetate,

and sodium hydride are presented in Table I. All other reagents were purchased from commercial sources (Aldrich) and used without further purifications unless otherwise noted. Tetrahydrofuran (THF) was dried over CaH_2 and distilled. APEs were dried in vacuum before use.

The products are coded for example OPE10-COOH. The codes of OPE10 and COOH represent octyl phenol ethoxylate with 10 oxyethylene units and terminal carboxylic acid, respectively, (Table II).

Sample characterization

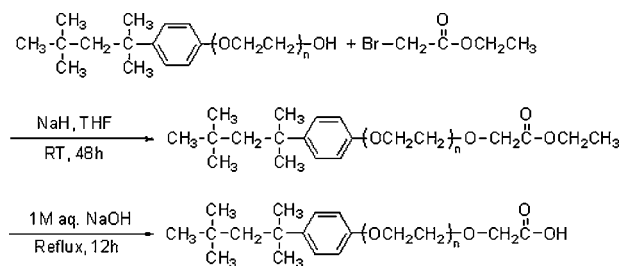
$^1\text{H-NMR}$ (500-MHz) spectra were recorded on a Varian Unity Inova Spectrometer (Palo Alto, CA) in CDCl_3 and with tetramethylsilane (TMS) as an internal standard except when reported. The IR spectra of the samples were recorded on a Unicam Mattson 500 FTIR spectrometer (Wellesley, MA) using a KBr plate technique. Thin layer chromatograph (TLC) analyses were performed on polyester sheets precoated with 0.25-mm thick silica gel containing a 254-nm indicator (Kodak 13,181, Tokyo, Japan). Thermogravimetric analyses (TGAs) were carried out both in nitrogen and air at a heating rate of $10^\circ\text{C}/\text{min}$ using a TGA 2050 (TA instruments, New Castle, DE). The flow rates for both cases were maintained at 10 and 90 cc/min for the balance part and for the furnace area, respectively. In each case, samples weighed ~ 100 mg.

TABLE I
Materials Employed in This Study

Chemical name	CAS no.	Chemical structure	Vender
Sodium hydride	7646-69-7	NaH	Aldrich
Ethyl bromoacetate	105-36-2	$\text{Br}-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{OCH}_2\text{CH}_3$	Aldrich
Igepal CA-210	68987-90-6	$\text{CH}_3-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}-\text{CH}_2-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}-\text{C}_6\text{H}_4-(\text{OCH}_2\text{CH}_2)_2\text{OH}$	Aldrich
Triton X-45	9002-93-1	$\text{CH}_3-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}-\text{CH}_2-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}-\text{C}_6\text{H}_4-(\text{OCH}_2\text{CH}_2)_5\text{OH}$	Aldrich
Triton X-100	9002-93-1	$\text{CH}_3-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}-\text{CH}_2-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}-\text{C}_6\text{H}_4-(\text{OCH}_2\text{CH}_2)_{10}\text{OH}$	Aldrich
Tergitol NP-9	68987-90-6	$\text{CH}_3(\text{CH}_2)_8-\text{C}_6\text{H}_4-(\text{OCH}_2\text{CH}_2)_{10}\text{OH}$	Aldrich

TABLE II
Codes for Various Materials Used in This Study

Code	Chemical structure
OPE2-OH	
OPE2-OCH ₂ CO ₂ Et	
OPE2-OCH ₂ CO ₂ H	
OPE5-OH	
OPE5-OCH ₂ CO ₂ Et	
OPE5-OCH ₂ CO ₂ H	
OPE10-OH	
OPE10-OCH ₂ CO ₂ Et	
OPE10-OCH ₂ CO ₂ H	
NPE10-OH	
NPE10-NH ₂	
NPE10-imidazole	



Scheme 2 Preparation of OPE-COOH.

Synthesis of OPE-ethyl carboxylate: OPE10-COOEt

The synthetic routes to OPE-COOH of different oxyethylene units are shown in Scheme 2, and only a representative example (i.e., OPE10-COOH) is given here.

Sodium hydride (0.9 g, 37.5 mmol) was added slowly to a solution of TRITON X-100 (OPE10, 16.07 g, 25 mmol) in dry THF (50 mL) at 25°C. The solution was stirred for 2 h. Ethyl bromoacetate (6.26 g, 37.5 mmol) was added dropwise to the mixture over 2 h at 0°C and stirred for 12 h at 25°C under nitrogen condition. The reaction mixture was then poured into ice-cold water. The organic layer was separated and washed with aq. HCl and water, respectively. The solvent was evaporated yielding yellowish viscous oil. The resulting oil was purified by column chromatography using silica gel as the stationary phase and CH₂Cl₂/methanol (7:3) as the eluent. The solvent was removed *in vacuo* to yield the product: yield = 14.24 g (78%); ¹H-NMR (500 MHz, CDCl₃), δ 7.20–6.84 (m, —Ar—), 4.30 (s, —OCH₂COOCH₂CH₃), 4.13 (q, —OCH₂COOCH₂CH₃), 4.11 (t, —Ar—OCH₂CH₂—), 3.84 (t, —Ar—OCH₂CH₂—), 3.73 (t, —OCH₂CH₂OCH₂COOCH₂CH₃), 3.66 (br s, —(OCH₂CH₂)_n—), 1.7 (s, —C(CH₃)₂CH₂C(CH₃)₃), 1.35 (s, —C(CH₃)₂CH₂C(CH₃)₃), 1.25 (t, —OCH₂COO—CH₂CH₃), 0.72 (s, —C(CH₃)₂CH₂C(CH₃)₃).

Synthesis of OPE10-COOH

OPE10-COOEt (13.14 g, 18 mmol) was added to the mixture of 1M aqueous NaOH (100 mL) and methanol (10 mL). The solution was refluxed for 12 h. The reaction mixture was adjusted to pH 2 using aqueous HCl. The organic layer was extracted by methylene chloride. And then, the solvent was evaporated to give yellowish viscous oil. The resulting oil was purified by column chromatography using silica gel as the stationary phase and CH₂Cl₂/methanol (7 : 3) as the eluent. The solvent was removed *in vacuo* to yield the product: yield = 10.61 g (84%); ¹H-NMR (500 MHz, CDCl₃), δ 7.20–6.84 (m, —Ar—), 4.18 (s, —OCH₂COOH), 4.11 (t, —Ar—OCH₂CH₂—), 3.84 (t, —Ar—OCH₂CH₂—), 3.73 (t, —OCH₂CH₂—OCH₂COOH), 3.64 (br s, —(OCH₂CH₂)_n—), 1.7 (s, —C(CH₃)₂CH₂

C(CH₃)₃), 1.35 (s, —C(CH₃)₂CH₂C(CH₃)₃), 0.72 (s, —C(CH₃)₂CH₂C(CH₃)₃).

Synthesis of NPE10-mesylate: NPE10-OSO₂CH₃

The synthetic routes to NPE10-NH₂ and NPE10-imidazole are shown in Scheme 3.

Triethyl amine (20.76 g, 205 mmol) was added slowly to a solution of Tergitol NP-9 (NPE10, 25.29 g, 41 mmol) in CH₂Cl₂ (50 mL) at 25°C. The solution was stirred for 15 min. Methanesulfonyl chloride (22.55 g, 205 mmol) was added dropwise to the mixture over 2 h at 0°C and stirred for 12 h at 25°C under nitrogen condition. The reaction mixture was then poured into ice-cold water. The organic layer was separated and washed with brine and water, respectively. The solvent was evaporated yielding yellowish viscous oil. The resulting oil was purified by column chromatography using silica gel as the stationary phase and CH₂Cl₂/methanol (7 : 3) as the eluent. The solvent was removed *in vacuo* to yield the product: yield = 27.82 g (98%); ¹H-NMR (500 MHz, CDCl₃), δ 7.20–6.84 (m, —Ar—), 4.38 (t, —OCH₂CH₂OSO₂CH₃), 4.11 (t, —Ar—OCH₂CH₂—), 3.84 (t, —Ar—OCH₂CH₂—), 3.77 (t, —OCH₂CH₂OSO₂CH₃), 3.66 (br s, —(OCH₂CH₂)_n—), 3.08 (s, —OSO₂—CH₃), 0.5–1.7 (m, C₉H₁₉—Ar—).

Synthesis of NPE10-NH₂

Ammonia solution (2.0M in ethanol), (47.52 g, 120 mmol) was added to a solution of NPE10-mesylate (16.72 g, 24 mmol) in ethanol (50 mL). The solution was refluxed for 12 h. The reaction mixture was then poured into ice-cold water. The organic layer was separated and washed with brine and water, respectively. The solvent was evaporated yielding yellowish viscous oil. The resulting oil was purified by column chromatography using silica gel as the stationary phase and CH₂Cl₂/methanol (7:3) as the eluent. The solvent was removed *in vacuo* to yield the product: yield = 12.89 g (85%); ¹H-NMR (500 MHz, CDCl₃), δ 7.20–6.84 (m, —Ar—), 4.11 (t, —Ar—OCH₂CH₂—), 3.84 (t, —Ar—OCH₂CH₂—), 3.75 (t, —OCH₂CH₂—NH₂), 3.72 (t, —OCH₂CH₂—NH₂), 3.66 (br s, —(OCH₂CH₂)_n—), 0.5–1.7 (m, C₉H₁₉—Ar—).

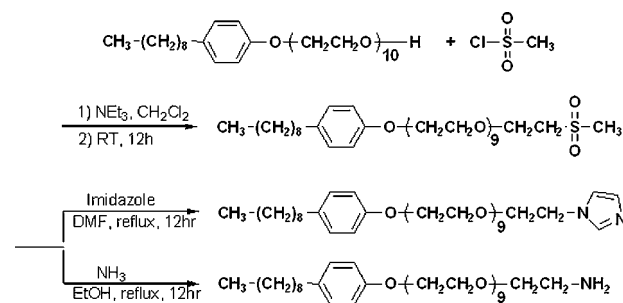
Scheme 3 Preparation of NPE10-imidazole and NPE10-NH₂.

TABLE III
Solubility Tests of Various APE Derivatives

Sample	Aq. HCl	Aq. NaOH	H ₂ O	MeOH	Acetone	MC	THF	Toluene	Hexane
OPE2-OH	×	×	×	○	○	○	○	○	○
OPE5-OH	Δ	Δ	Δ	○	○	○	○	○	Δ
OPE10-OH	○	Δ	○	○	○	○	○	○	×
NPE10-OH	○	Δ	○	○	○	○	○	○	×
OPE2-COOH	×	Δ	Δ	○	○	○	○	○	Δ
OPE5-COOH	×	○	Δ	○	○	○	○	○	×
OPE10-COOH	Δ	○	○	○	○	○	○	○	×
NPE10-NH ₂	○	×	○	○	○	○	○	○	×
NPE10-imidazole	○	×	○	○	○	○	○	○	×

×, insoluble; ○, soluble; Δ, partly soluble.

Synthesis of NPE10-imidazole

Imidazole (7.49 g, 110 mmol) was added to a solution of NPE10-mesylate (15.33 g, 22 mmol) in DMF (50 mL). The solution was refluxed for 12 h. The reaction mixture was then poured into ice-cold water. The organic layer was separated and washed with brine and water, respectively. The solvent was evaporated yielding yellowish viscous oil. The resulting oil was purified by column chromatography using silica gel as the stationary phase and CH₂Cl₂/methanol (7:3) as the eluent. The solvent was removed *in vacuo* to yield the product: yield = 13.67 g (91%); ¹H-NMR (500 MHz, CDCl₃), δ 7.6–7.02 (m, —Imidazole), 7.20–6.84 (m, —Ar—), 4.16 (t, —OCH₂CH₂O—imidazole), 4.11 (t, —Ar—OCH₂CH₂—), 3.84 (t, —Ar—OCH₂CH₂—), 3.70 (t, —OCH₂CH₂O—imidazole), 3.66 (br s, —(OCH₂CH₂)_n—), 0.5–1.7 (m, C₉H₁₉—Ar—).

RESULTS AND DISCUSSION

Synthesis and characterization of APE-COOH, APE-NH₂, and APE-imidazole

The hydroxyl group can be converted to an acid moiety by reacting it with a suitable modifying agent. In this study, hydroxyl functionalities of OPEs were reacted with ethyl bromoacetate in the presence of sodium hydride. Thus, ethyl carboxylates of OPEs were prepared in > 80% yield via a simple etherification reaction (Scheme 2). The corresponding carboxylate was converted quantitatively to the acid by saponification. Using three OPEs of different oxyethylene units as starting materials, we have prepared three TRITON X-based surfactants containing terminal carboxylic acid (i.e., OPE2-COOH, OPE5-COOH, and OPE10-COOH, Table II).

The hydroxyl group of APEs also can be converted to a sulfonate group by reacting it with a suitable sulfonating agent. In our case, hydroxyl functionalities of nonyl phenol ethoxylate (Tergitol NP-9, *n* = 10, coded as NPE10-OH) were reacted with methanesulfonyl chloride (or mesyl chloride) in the presence of triethylamine. Thus, mesylate of NPE10 was prepared in

> 95% yield via an esterification reaction (Scheme 3). The corresponding mesylate was converted almost quantitatively to NPE10-NH₂ and NPE10-imidazole using ammonia and imidazole, respectively (Table II).

Solubility test

The virgin APEs were soluble in various solvents including water, slightly acidic water and methanol, but less soluble in basic water (Table III). However, as expected, the resulting three APEs containing carboxylic acid (OPE2-COOH, OPE5-COOH, and OPE10-COOH) were soluble in basic water, but less soluble in acidic water and hexane. This confirms the introduction of acidic moiety into the terminal hydroxyl group of APEs. And, the polar-nature of APEs is significantly increased due to the reaction.

In cases of NPE10-NH₂ and NPE10-imidazole, they are both soluble in acidic water as expected, but less soluble in basic water (Table III).

FTIR study

FTIR spectra of OPE10-OH and OPE10-COOH were recorded using a FTIR unit in KBr pellets, and OPE10-

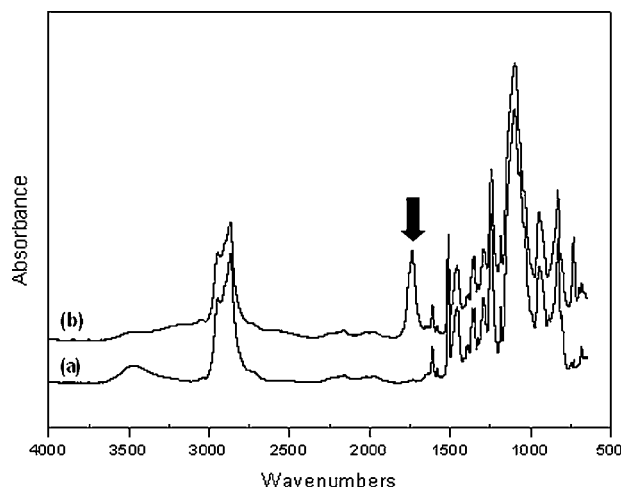


Figure 1 FTIR spectra of (a) OPE10-OH and (b) OPE10-COOH.

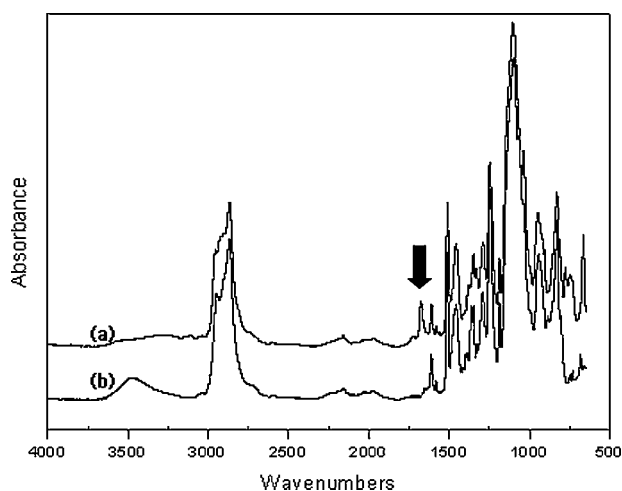


Figure 2 FTIR spectra of (a) NPE10-imidazole and (b) NPE10-OH.

COOH showed carbonyl ($-\text{CO}-$) absorption band at $\sim 1725 \text{ cm}^{-1}$ (Fig. 1), and this indicated the introduction of the carboxylic group into the octyl phenol ethoxylate structure. A stretching vibration band at 3500 cm^{-1} also showed the presence of $-\text{OH}$ combined with $-\text{CO}-$ in the spectrum.

IR spectra of NPE10-OH and NPE10-imidazole were recorded in KBr pellets, and NPE10-imidazole showed alkene ($-\text{C}=\text{C}-$) absorption band due to the aromatic moiety at $\sim 1650 \text{ cm}^{-1}$ (Fig. 2), and this

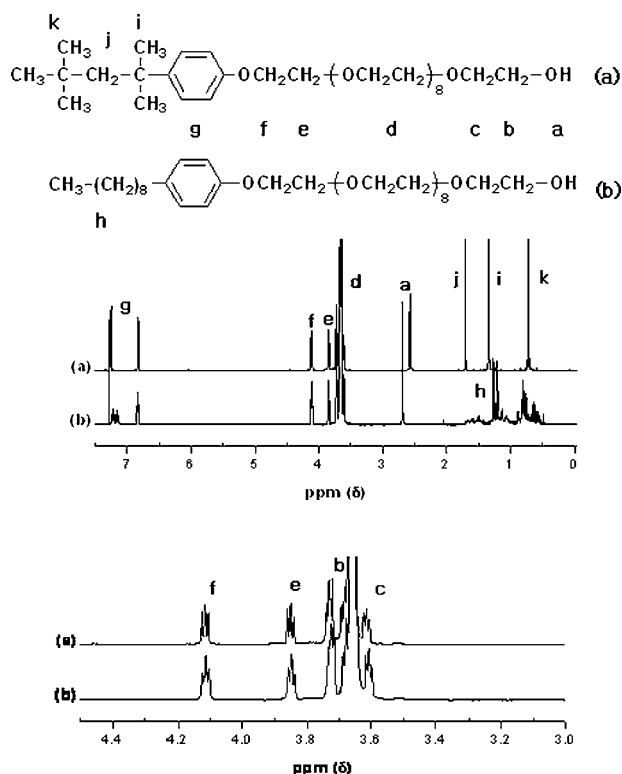


Figure 3 $^1\text{H-NMR}$ spectra of (a) OPE10-OH and (b) NPE10-OH in CDCl_3 .

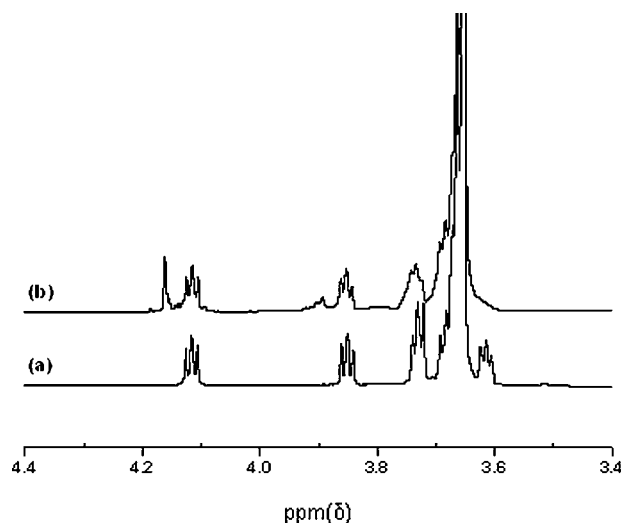


Figure 4 $^1\text{H-NMR}$ spectra of (a) OPE10-OH and (b) OPE10-COOH.

indicated the introduction of the imidazole group into the NPE10-OH structure. The stretching vibration band at 3500 cm^{-1} due to $-\text{OH}$ disappeared after the reaction.

$^1\text{H-NMR}$ study

Figure 3(a) shows the 500 MHz $^1\text{H-NMR}$ spectrum of OPE10-OH, as it is, for comparison. Figure 4 shows the $^1\text{H-NMR}$ spectrum of OPE10-COOH. It can be noticed that the main OPE10-OH structure remains in the product spectrum; also, the methylene singlet peak at 4.18 ppm due to $-\text{OCH}_2-\text{COOH}$ moiety can be detected. Since the hydroxyl terminal group of OPE10-OH is consumed during the reaction, the methylene triplet peak at 3.72 ppm due to $-\text{OCH}_2\text{CH}_2-\text{OH}$ is shifted downfield.

Figure 3(b) shows the 500 MHz $^1\text{H-NMR}$ spectrum of NPE10-OH, and Figure 5 shows the spectrum of

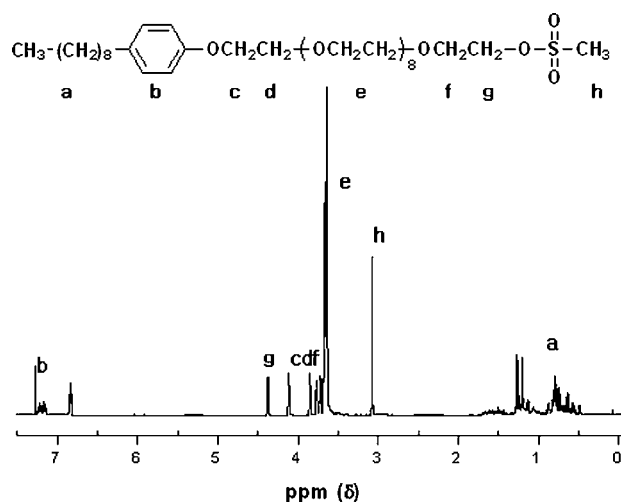


Figure 5 $^1\text{H-NMR}$ spectrum of NPE10- OSO_2CH_3 in CDCl_3 .

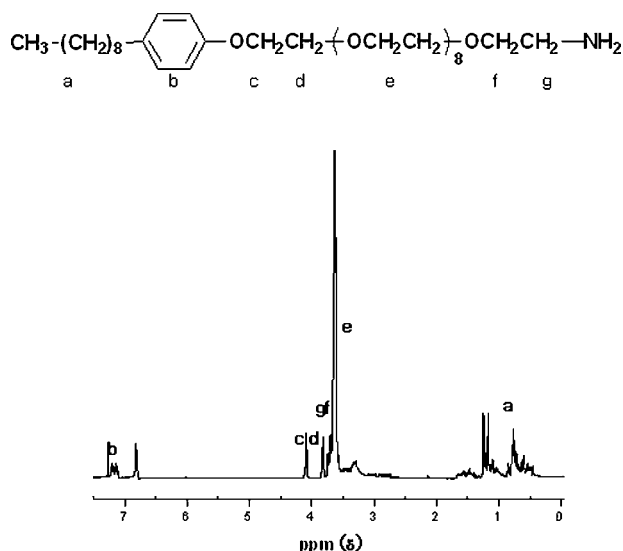


Figure 6 $^1\text{H-NMR}$ spectrum of NPE10-NH₂ in CDCl₃.

NPE10-OSO₂CH₃. It can be noticed that the main NPE10-OH structure remains in the product spectrum; also, the methylene singlet peak at 3.08 ppm due to —O—SO₂—CH₃ moiety can be detected. In the $^1\text{H-NMR}$ spectrum of NPE10-NH₂ (Fig. 6), the methylene singlet peak at 3.08 ppm due to —O—SO₂—CH₃ moiety disappeared, and the methylene triplet peak at 4.38 ppm due to —OCH₂CH₂—OSO₂CH₃ was shifted upfield.

In the $^1\text{H-NMR}$ spectrum of NPE10-imidazole (Fig. 7), the aromatic singlet peak at 7.6 ppm and the two doublet peaks at 7.02 ppm due to the imidazole moiety can be detected.

Thermal Degradation Behaviors of OPE-COOH and NPE-amine: TGA study

In this experiment, first, thermal stabilities of three acidic surfactants, [OPE2-COOH], [OPE5-COOH] and

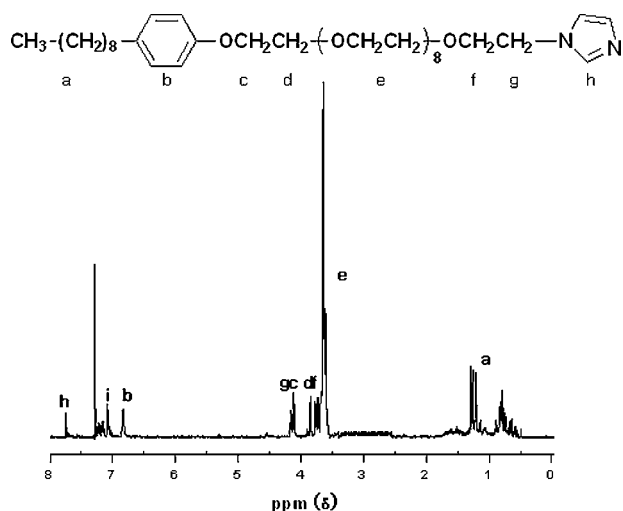


Figure 7 $^1\text{H-NMR}$ spectrum of NPE10-imidazole in CDCl₃.

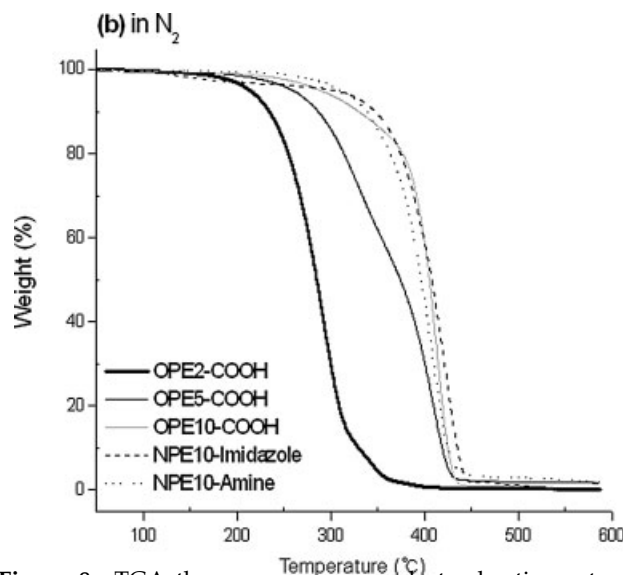


Figure 8 TGA thermograms scanned at a heating rate of 10°C/min under nitrogen condition: (a) OPE2-COOH, (b) OPE5-COOH, (c) OPE10-COOH, (d) NPE10-imidazole, and (e) NPE10-NH₂.

[OPE10-COOH], and their charring behaviors were investigated. Figure 8 shows the TGA thermograms of the three surfactants under nitrogen. Initial thermal degradation temperatures (T_i) are in order of OPE10-COOH (260°C) > OPE5-COOH (233°C) > OPE2-COOH (182°C) and the residue weights at 550°C are also in order of OPE10-COOH (0.82 wt %) > OPE5-COOH (0.55 wt %) > OPE2-COOH (0.45 wt %). This indicates that the higher the molecular weight (or number of oxyethylene units) of OPE-COOH, the higher the T_i and the char residue.

On the other hand, under air atmosphere, the presence of oxygen affect the T_i of the OPE10-COOH sig-

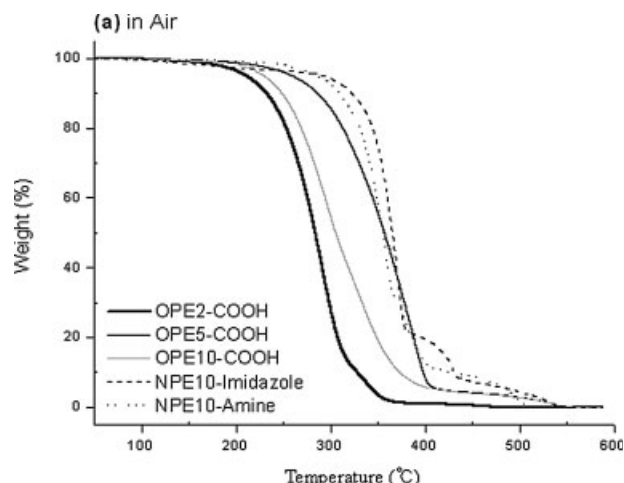


Figure 9 TGA thermograms scanned at a heating rate of 10°C/min under air condition: (a) OPE2-COOH, (b) OPE5-COOH, (c) OPE10-COOH, (d) NPE10-imidazole, and (e) NPE10-NH₂.

nificantly (200°C in air versus 260°C in nitrogen), and no char is observed in air at 550°C (Fig. 9). Initial thermal degradation temperatures are in order of OPE5-COOH (205°C) > OPE10-COOH (200°C) > OPE2-COOH (181°C) (i.e., the presence of oxygen does not affect the Ti of OPE2-COOH which has the lowest number of oxyethylene units ($n = 2$), but does affect the Ti of relatively long oxyethylene unit-containing OPE-COOH, e.g., OPE5-COOH and OPE10-COOH) although no char is observed for all three cases at 550°C (Fig. 9). Therefore, it can be concluded that the relatively thermally stable OPE5-COOH and OPE10-COOH are expected to be suitable as surfactant with relatively long hydrophilic anchoring block for high temperature purposes, where the surfactant should be burned-out completely in air, since they have relatively low Ti and no char formation at high temperatures in air.

When comparing thermal stabilities of OPE10-COOH, NPE10-NH₂ and NPE10-imidazole under nitrogen atmosphere, all three APE derivatives have similar initial thermal degradation temperatures (Ti) and char residues (Fig. 8). It is likely that the number of oxyethylene units of APEs affects the thermal degradation behaviors of the derivatives regardless of the chain ends in nitrogen. In air, both NPE10-NH₂ and NPE10-imidazole show the similar thermal degradation behaviors to those in nitrogen except for the temporary char residue at ~ 400°C due to the effect of oxygen in causing a temporary carbonization, which later gets oxidized. However, OPE10-COOH thermally degrades much faster than NPE10-NH₂ and NPE10-imidazole (Fig. 9). At the present time, although the reason why OPE10-COOH thermally degrades differently in air compared to both NPE10-NH₂ and NPE10-imidazole of the same number of oxyethylene units is not clear, the carboxylic acid terminal group of OPE10-COOH is likely to activate the thermal degradation of the backbone in air.

Next, this data was compared with those for other commercially available phosphorous-based surfactants (i.e., RE610 and BYK111; their exact chemical structures are not reported in literatures, but both they are well recognized as surfactants for high temperature purposes in industry) (Fig. 10). Both RE610 and BYK111 show one degradation step in the TGA curve at 262 and 160°C, respectively, both with ~ 7 wt % char residue under air. OPE10-COOH evaporates almost completely in one step (*vide supra*). It can be seen in Figure 10 that all the surfactants tested have similar thermal degradation behavior in air, however, much enhanced amount of char is observed at 600°C for the phosphorous-based compounds (up to 7.38 wt % of char yield) while no char is observed for OPE10-COOH.

Both RE610 and BYK111 produce negligible amount of char upon thermal degradation in nitrogen, but about 7 wt % charring residue is obtained at elevated temperatures in air indicating that an oxidative cross-

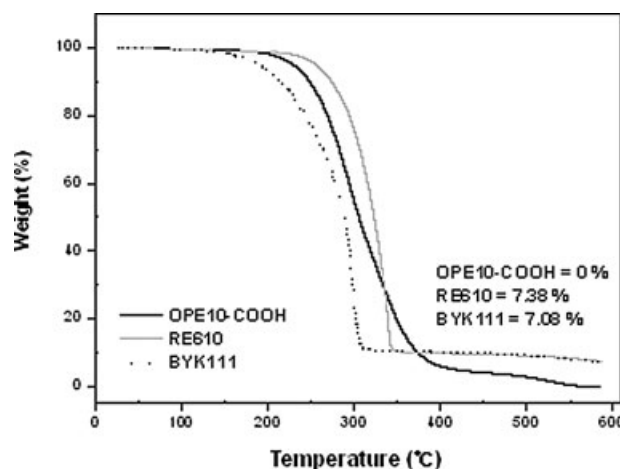


Figure 10 TGA thermograms scanned at a heating rate of 10°C/min under air condition: (a) OPE10-COOH, (b) RE610, and (c) BYK111.

linking in the condensed phase may account for the char formation. It is likely that the interaction of phosphoric acid terminal group with hydroxy groups generated in the course of air oxidation of RE610 and BYK111 at elevated temperatures leads to the formation of crosslinking (or esterification) yielding phosphorous-based chars. In contrast, OPE10-COOH produce a very small amount of char in nitrogen (0.82 wt %), and in air, it is completely burned-out. This indicates that there is no interaction leading to crosslinking between carboxylic acid and OPE10 backbone in the condensed phase at elevated temperatures.

However, it was shown that the number of oxyethylene units of OPE-COOH affects their thermal degradation behavior (esp. Ti, *vide supra*) in air. Among various OPE-COOH compounds we tested only OPE10-COOH shows the much enhanced thermal decomposition process in air, and gives no char. It is representative of an interacting behavior of carboxylic acid and oxyethylene units in the early stage of the degradation in air.

CONCLUSIONS

In this paper, we show that by reacting commercially available TRITON X-based surfactants with ethyl bromoacetate in the presence of sodium hydride followed by saponification, carboxylic acid-terminated TRITON X-derivatives (OPE2-COOH, OPE5-COOH and OPE10-COOH) are synthesized in high yields. TRITON X surfactants also can be converted to amino-terminated TRITON X-derivatives (NPE10-NH₂ and NPE10-imidazole) based on modifications of mesylates of TRITON X with amino nucleophiles such as ammonia and imidazole.

We also report the effects of the number of oxyethylene units of TRITON™ X used in the synthesis and

the kind of terminal groups on analytical characterizations and the thermal properties of the novel surfactants. OPE10-COOH which is composed of octyl phenol ethoxylate (TRITON X-100, $n = 10$) terminated a carboxylic acid as an anchoring group was one of the best candidate as dispersant for high temperature purposes (e.g., paste formulation) among the five synthesized surfactants through this study and two other commercially available surfactants, and showed no char after thermal decomposition in air.

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