

Synthesis and *In Situ* Transformation of Poly(oxybutylene)amides by Butoxylation

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ABSTRACT: A family of gasoline detergents was prepared by a two-step process—(1) preparation of amide initiators by reacting hydrophilic amines with ethyl acetate at high temperature; (2) consecutive butoxylation of the initiators with 1,2-epoxybutane (BO) to obtain oil-soluble products. The process led to the preparation of amide-initiated butoxylates, which were characterized by FTIR, NMR, and amine titration. During the butoxylation, it was found that the unexpected ester by-products were generated via an amide/ester exchange. The reaction profile was studied. The amide/ester exchange reaction, characterized by IR absorption of amide (1650 cm^{-1}) vs. ester (1735 cm^{-1}), reached equilibrium during the process of butoxylation to $1600 M_w$. Steric hindrance of the amide structures is an important factor controlling the formation of these ester byproducts. Selective hydrolysis to remove the ester by-products is necessary to render the final product with an improved engine performance of octane requirement. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 435–445, 2001

Key words: gasoline additive; detergent; poly(oxybutylene)amide; ester; amide; butoxylation

INTRODUCTION

Oil companies achieve their product differentiation by demonstrating special features of fuel additives.^{1–5} Particularly, the use of polymeric surfactants as fuel additives can prevent the deposits of intake valve and combustion chamber, and consequently reduce octane requirement of automobile engines and air pollution.^{6–11} Adding polymeric organic compounds into gasoline to enhance engine performance becomes an important research topics. One of the newly developed gasoline additives is known as polyether amines,

having a specific structure of poly(oxyalkylene)-aminocarbamate.^{12–14} Although the polyether amines had various chemical functionalities as disclosed in patents,^{12–15} their syntheses commonly involved the construction of a polymer backbone by the butoxylation of initiators with 1,2-epoxybutane. Recently, the butoxylation of hydrophilic amides to oil soluble surfactants was revealed to be an excellent polymeric surfactant by Shell Development Co.^{16–21} These polyether amides differed from the conventional polyether amines in several performance aspects. Particularly, the engine requirement for an octane number of gasoline can be reduced by adding these polyether amides in very low concentration. This performance is considered as a significant technology advance in gasoline additive research. In our recent study on the synthesis of new gasoline

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detergents, various polyether amides were prepared from several water-soluble amides and 1,2-epoxybutane to compare their performances. During the preparation of these additive compounds, unexpected poly(oxybutylene)ester by-products were detected. The later engine tests concluded these poly(oxybutylene)esters had a detrimental effect on the engine octane requirement tests. Hence, it became necessary to minimize this by-product formation.

This article reveals our study on the butoxylation profile, particularly with respect to side-product formation and the mechanism leading to amide/ester interchange. A selective hydrolysis to remove the harmful ester by-products and to upgrade the product purity was also studied.

EXPERIMENTAL

Materials

The poly(oxyalkylene)diamines, including poly(propylene glycol) bis(2-aminopropyl ether) at an average M_w of 230 (Jeffamine® D-230), and triethyleneglycoldiamine at an M_w of 148 (Jeffamine EDR-148) were obtained from Huntsman Co. or Aldrich Chemical Co. These polyether amines included poly(oxyalkylene)triamines such as trimethyl propane-initiated poly(propylene glycol)-tri(2-aminopropyl ether) at an M_w of 400, known as Jeffamine, T-403). Diethylenetriamine (DETA) and ϵ -caprolactam were purchased from Aldrich Chemical Co.

Preparation of Amide Initiators

Jeffamine D-230 Diamide 4

A mixture of Jeffamine D-230 (59.0 g, 0.26 mol) and ethyl acetate (91.0 g, 1.04 mol) was added into a 1-L autoclave. The autoclave was sealed and purged of air by pressurizing and depressurizing with nitrogen at 500 psi several times. With stirring and under initial nitrogen pressure of 200 psi, the mixture was heated slowly to 180°C and held at this temperature for 15 h. During the process, a maximum pressure at 320 psi was recorded. After the reaction completed, the reactor was cool to room temperature. The crude product was transferred to a flask and subjected to a rotary evaporator to remove the unreacted ethyl acetate. The crude product (74.0 g) was recovered. The product showed IR absorption of 1650 cm^{-1}

(carbonyl) and 1560 cm^{-1} (NH) amide, and total amine content of 0.25 mEq/g.

Jeffamine EDR-148 Diamide 2

A mixture of Jeffamine EDR-148 (50.0 g, 0.34 mol) and ethyl acetate (175.0 g, 1.70 mol) was added into a 1-L autoclave. The procedures were similar to the preparation of by Jeffamine D-230 diamide. The crude product (220.0 g) was recovered. The product had IR absorption of 1650 cm^{-1} (carbonyl) and 1560 cm^{-1} (NH) amide, and total amine content of 0.25 mEq/g.

DETA Triamide 6

A mixture of DETA (35.0 g, 0.34 mol) and ethyl acetate (176.0 g, 1.70 mol) was subjected to the procedures described above. The crude product (207.0 g) was recovered. The product had characteristic IR absorption of 1650 cm^{-1} (carbonyl) and 1560 cm^{-1} (NH) amide, and total amine content of 0.35 mEq/g.

Jeffamine T-403 Triamide 8

A mixture of Jeffamine T-403 (75.0 g, 0.95 mol) and ethyl acetate (97.0 g, 0.95 mol) was subjected to the procedures described above. The crude product (168.0 g) was recovered. The product showed IR absorption of 1650 cm^{-1} (carbonyl), and 3100 and cm^{-1} (NH) amide, and total amine content of 0.33 mEq/g.

Butoxylation of ϵ -Caprolactam

A mixture of ϵ -caprolactam (17.6 g, 0.016 mol) and potassium hydroxide (0.7 g, 0.013 mol) were subjected to a rotary evaporator under a reduced pressure to remove the water generated. The mixture was then added along with 1,2-epoxybutane (BO) (232.0 g, 3.22 mol) to an autoclave. The autoclave was sealed and purged of air by pressurizing and depressurizing with nitrogen at 500 psi several times. With stirring and an initial nitrogen pressure of 200 psi, the mixture was heated slowly to 120°C and held at this temperature for 10 h. During the process, a maximum pressure of 607 psi was recorded. The pressure dropped during the process until the end of the reaction. The reactor was cool to room temperature. The crude product was transferred to a flask, subjected to a rotary evaporator to remove the unreacted BO. The crude product (245.0 g) was recovered in 98% yield. The product showed

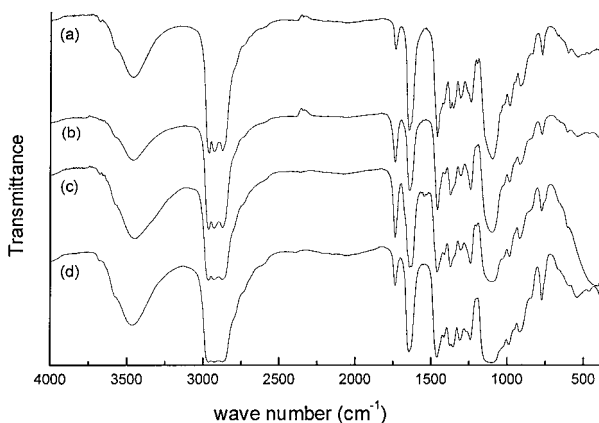


Figure 1 Relative ester-amine IR absorption of various butoxylation: (a) EDR 148-diamide-BO; (b) D230-diamide-BO; (c) DETA-triamide-BO; (d) T403-triamide-BO after 12-h reaction time at approximately 1600 M_w .

IR 1650 cm^{-1} (amide carbonyl) and 1100 cm^{-1} (C—O—C) absorption.

Butoxylation of D230-Diamide 4 to Butoxylates 5 at a Target M_w of 1600

A mixture of D230-diamide 4 (19.5 g, 0.06 mol) and potassium hydroxide (0.3 g, 0.005 mol) was subjected to a rotary evaporator to remove water and then charged into an autoclave with 1,2-epoxybutane(BO) (81.0 g, 1.1 mol). The autoclave was sealed and purged of air by nitrogen. With stirring and nitrogen pressure of 500 psi, the mixture was heated to 120°C for 17 h. The pressure reached to 640 psi, but decreased with time because of gradually consuming BO. When the pressure ceased to drop, the reactor was cool to room temperature. Crude product was transferred to a

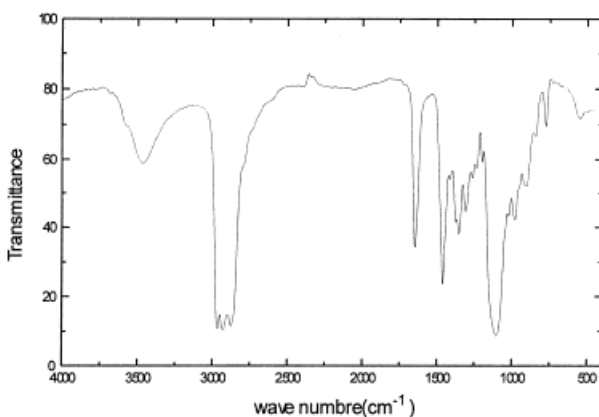


Figure 2 IR spectrum of ϵ -caprolactam butoxylates.

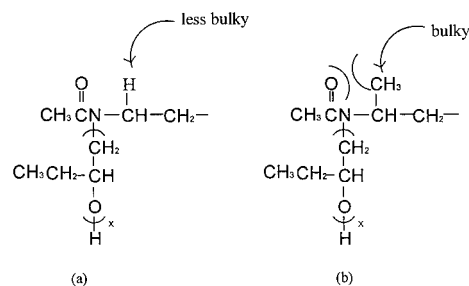


Figure 3 Steric hindrance of (a) ethyl- vs. (b) Propyl-amine.

flask and subjected to a rotary evaporator to remove unreacted BO. Approximately 95.0 g of crude product was recovered, indicating nearly 96% yield. Crude product was extracted by water. The gel permeation chromatography (GPC) analysis showed an average molecular weight of $M_w = 1521$ Daltons and polydispersity of 1.10 and FTIR: 1735 cm^{-1} (ester carbonyl), 1650 cm^{-1} (amide carbonyl), and 1100 cm^{-1} (ether) and $^1\text{H-NMR}$: 2.1 PPM (amide acetyl) and 2.0 PPM (ester acetyl). Total amine was 0.20 mEq/g. Other butoxylation of EDR-148 Diamide, DETA triamide, and T-403 triamide to the corresponding butoxylates 3, 7, and 9 at various molecular weights were carried out in the similar manner.

Hydrolysis of Amide/Ester Oligomers

Partial Hydrolysis

To a 250-mL round-bottomed flask, equipped with heating devise, mechanical stirrer, and reflux condenser were placed DETA-triamide butoxylates 7 (20 g, $M_w = 1680$, amine content 0.6 mg/g)

Table I Average Value of Polydispersity of GPC

Butoxylates	Polydispersity (M_w/M_n)	Average of Two Duplicated Runs
D230-diamide-BO	1.12 1.10	1.11
EDR148-diamide-BO	1.06 1.08	1.07
T403-triamide-BO	1.15 1.14	1.15
DETA-triamide-BO	1.08 1.09	1.09

Table II Reaction Profiles of D230-Diamide and 1,2-Epoxybutane [D230-Diamide (40.0 g), 1,2-Epoxybutane (160.0 g), and KOH (0.6 g); Conditions: N₂ 500 psi, 120°C]

Time (h)	Basicity (mEq/g)	M_w (GPC)	IR Relative Intensity:Area Ratio of 1650 cm ⁻¹ (amide) to 1735 cm ⁻¹ (Ester)
0	0.25	—	0
6	0.34	—	0.01
7	0.50	—	0.02
8	0.73	—	0.19
9	0.77	950	0.27
11	0.67	1270	0.44
24	0.36	2600	0.45

and 10 wt % aqueous HCl (80.0 g). The mixture was heated to 90°C for 6 h with refluxing. After 6 h, product was cool to room temperature. Crude product was transferred to a separation funnel, extracted with 50 mL of deionized water twice, and neutralized with 40 mL of 3 N NaOH for three times, and finally extracted with 100 mL of deionized water for four times. The final product was 12.5 g after being subjected to a rotary evaporator to remove the light materials. The product had IR absorption of 1650 cm⁻¹ (amide carbonyl) and the absence of 1735 cm⁻¹ (ester carbonyl). Total amine was found to be 0.6 mEq/g.

Complete Hydrolysis

In similar manner, the mixture of DETA-tri- amide butoxylates 7 (20.0 g, $M_w = 1680$) and 20 wt % HCl (80.0 g) was heated to 100°C for 6 h. The product was cooled to room temperature and transferred to a separation funnel, extracted in the same manner as above. After several times of water extraction, the product was subjected to the vacuum and then recovered (12.5 g). It was found

that the absorption of 1735 cm⁻¹ (ester carbonyl) and 1650 cm⁻¹ (amide carbonyl) was hardly observed in the IR spectrum, indicating the absence of amide and ester functionalities.

Instrumentation

¹H-NMR characterization was carried out by a Varian Uity Inova FT-NMR (300 MHz) spectrometer using CDCl₃ as the solvent. FTIR spectra were obtained using a Perkin-Elmer Paragon 500 FTIR spectrometer. Gel permeation chromatography (GPC) analyses were performed on a Waters 410 differential refractometer and Styragel® HR1 column (Waters Co.) using THF as eluent, calibrated by polystyrene standards. Total amines were estimated according to the method of ASTM (D2073).

RESULTS AND DISCUSSION

Amide Butoxylation to Poly(oxybutylene)-Backboned Amido Alcohols

The alkoxylation of amides has been seldom reported.²² The amide-functionalized polyethers are

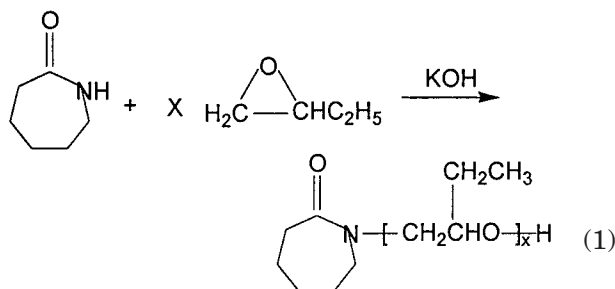
Table III Reaction Profiles of Diethylenetriamine (DETA) and 1,2-Epoxybutane [Diethylenetriamine (29.0 g), 1,2-Epoxybutane (171.0 g), and KOH (0.6 g) Conditions: N₂ 500 psi, 120°C]

Time (h)	Basicity (mEq/g)	M_w (GPC)	IR Relative Intensity:Area Ratio of 1650 cm ⁻¹ (Amide) to 1735 cm ⁻¹ (Ester)
0	0.24	—	0
1	0.45	449	0.01
2	0.32	770	0.04
3	0.29	849	0.05
5	0.25	1143	0.05
7	0.21	1294	0.05
9	0.21	1301	0.06
11	0.20	1308	0.06
24	0.22	1358	0.06

structurally different from the poly(oxybutylene)-glycols, which are known to have practical applications such as oil lubricants.^{23,24} From the synthetic point of view, the preparation of these products always involves the reaction of alkoxylation.^{25,26} The variations in chemical structures and functional groups could affect the product properties such as viscosity, lubricity, and subsequently their broad applications.^{27,28} In this study, we have screened and compared several amides as initiators to understand the nature of this reaction. The butoxylation of amides generally produced butoxylates comprising of poly(oxybutylene) backbone, amide, and hydroxyl termini in the same molecule. Three types of amides were used as initiators to produce the butoxylates.

Simple Hydrophilic-Hydrophobic Type

The use of a simple amide as initiator for butoxylation-generated oil-soluble polyether backboned poly(oxybutylene)amides. To produce simple "one head-one tail" structures, cyclic amides were preferred to primary amides ($-\text{CONH}_2$). This can be exemplified by the ϵ -caprolactam butoxylates.



The oligomers, consisting of a hydrophilic amide head and a poly(oxybutylene) backbone with the oxybutylene units larger than 6 or the molecular

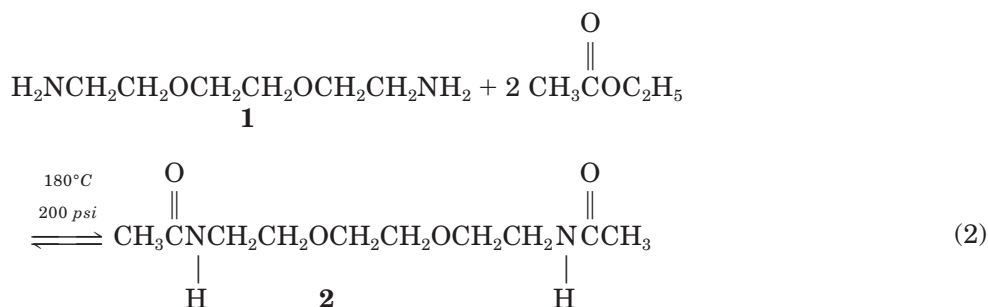
weight over 600, were oil soluble. The single carbonyl absorption at 1650 cm^{-1} of FTIR analysis and 174.4 ppm ($\text{C}=\text{O}$) of ^{13}C -NMR clearly indicated the existence of the cyclic amide. The butoxylation underwent anionic polymerization to give a narrow range of product distribution. In one example, the GPC analysis indicated an average molecular weight of $M_w = 1230$ Daltons and a polydispersity of 1.1.

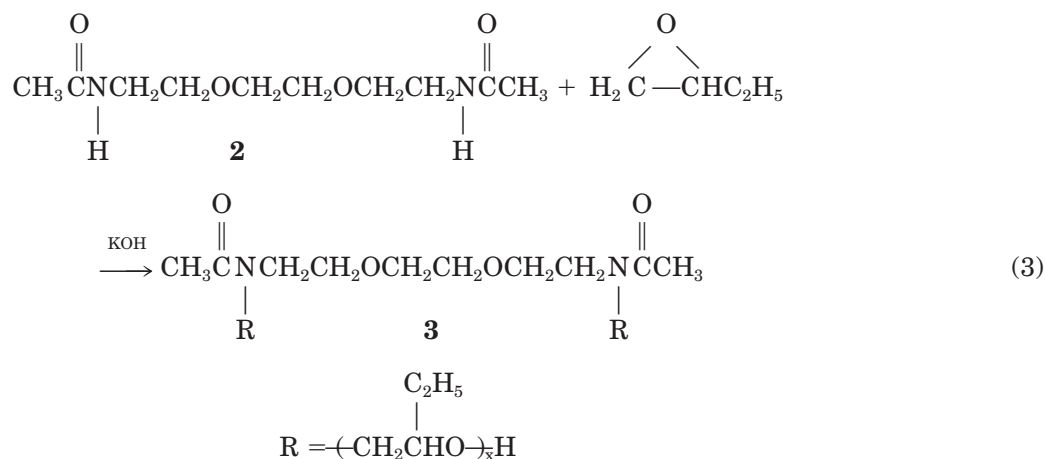
Preparation of Amide Initiators

Besides the commercially available ϵ -caprolactam as the initiator, the other requisite amide initiators used in this study were prepared by the amidation of amine and ethyl acetate according to eq. (2). The same reaction can be extended to poly(propyleneglycol)-bis(2-aminopropyl ether) (D-230), diethylenetriamine (DETA), trifunctional poly(propyleneglycol)-tri(2-aminopropyl ether) (T-403) as the starting amines, affording the corresponding amides in high yield. These products can be easily monitored by the characteristic IR absorption at 1650 cm^{-1} (amide) and the disappearance of amine basicity during the reaction.

Butoxylates of Gemini Type

Starting with a symmetric diamide such as triethyleneglycol diacetamide (2), the butoxylation afforded a twin-tail structural detergent. The structure is similar to the reported Gemini surfactants.²⁹ The symmetric diamide was conveniently prepared from the triethyleneglycol diamine (i.e., Jeffamine EDR-148) and ethyl acetate as described in eq. (2). Followed by the butoxylation, a symmetric *N,N*-bis-poly(oxybutylene)amidoalcohol was generated.

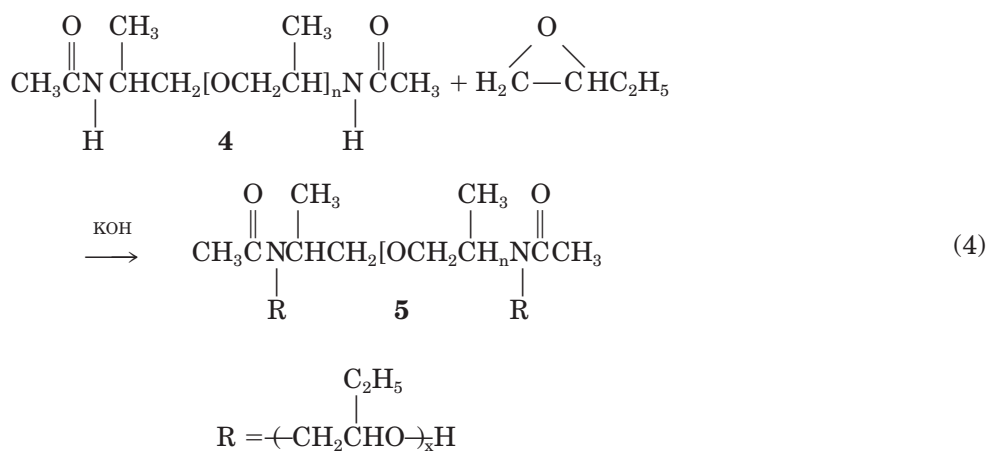




The oil-soluble Gemini butoxylates were identified by IR and NMR. The infrared absorption at 1650 cm^{-1} (amide), 1100 cm^{-1} (ether), and 1735 cm^{-1} was observed, as shown in Figure 1(a). Similar spec-

tra were obtained for this family of different molecular weights that were determined by GPC.

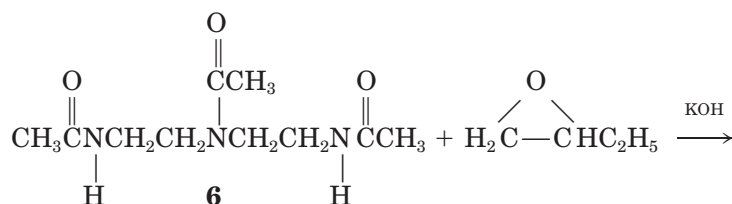
Similarly, the poly(oxypropylene)diamide was converted into the corresponding butoxylates.

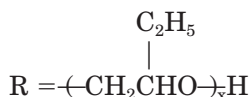
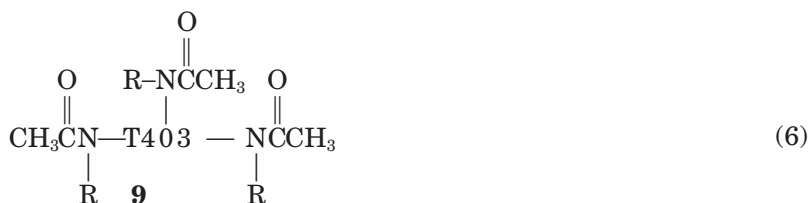
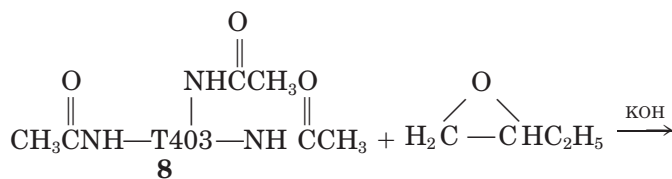
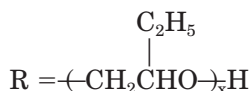
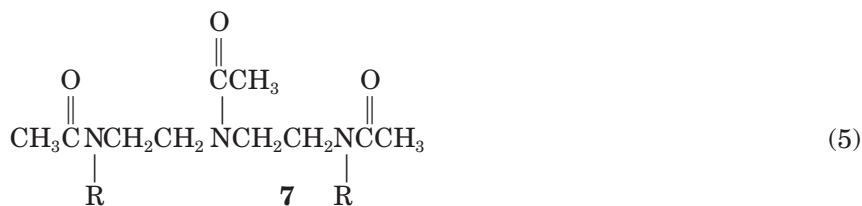


Butoxylates of Symmetric and Multiple Amide Type

The hydrophilic amide moiety in the structure is believed to be the essential functionality that is responsible for the detergency and the engine octane requirement. For comparison, diethylenetri-

amine (DETA) was allowed to react with 1,2-epoxybutane (BO) to form a structure of triamide dibutoxylates, as described in eq. (5). Similarly, other analogous oligomers were prepared according to eq. (6), where T-403 represents the backbone of Jeffamine T-403, as described in the attached figure.





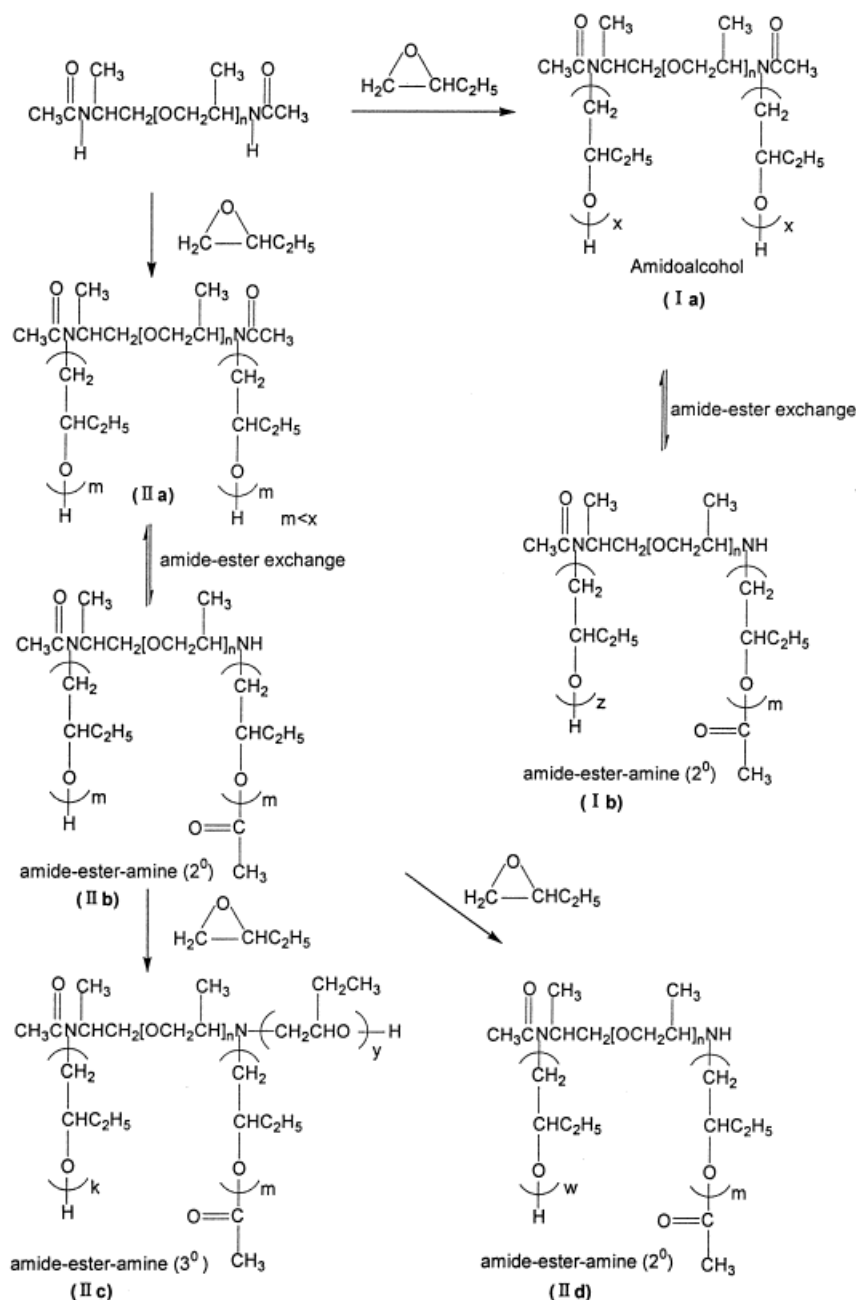
In Situ Amide/Ester Exchange

The butoxylation of amide with 1,2-epoxybutane was expected to selectively produce poly(oxybutylene)amidoalcohol. However, among three types of butoxylation described above, the ϵ -caprolactam butoxylate was the only series of compounds obtained in high selectivity (Fig. 2). This was indicated by a single IR absorption at 1650 cm^{-1} . For the Gemini and multiple amide reaction products, there was a predominant 1650 cm^{-1} amide absorption and a minor 1735 cm^{-1} ester absorption, as shown in Figure 1. Products derived from different initiators showed different degree of the ester absorption. The observation of ester formation in butoxylation was unexpected and perhaps unprecedented. Among many amide initiators, it is possible to classify them in two classes. Butoxylates derived from the class (b) of initiators had higher intensive absorption for T-403-triamide-BO and D-230-diamide-BO than another class (a) of DETA-triamide-BO and EDR-148-diamide-BO. Figure 3 states the structural differences between these two series of products. Accordingly, the following trend was observed. When

the α -carbon position next to the amides such as EDR-148 and DETA was primary carbon, less amide/ester exchange was obtained according to the IR absorption. On the other hand, the α -carbon position of amides such as T-403 and D-230 being the secondary carbon led to much amide/ester exchange. The difference in steric hindrance on the α -carbon is accounted for the observation. Summarized in Table I, the GPC polydispersity of products under the same reaction conditions of temperature, pressure, and amount of catalyst have the following average values: EDR-148 (1.07), DETA (1.09), D-230 (1.11), and T-403 (1.15). The polydispersity of EDR-148 and DETA was smaller than that of T-403 and D-230. Presumably, the broader distribution of polydispersity resulted from the reaction of amide/ester exchange. It is concluded that, by the judicious choice of a proper amine as initiators, the reaction of amide/ester exchange can be minimized.

Mechanism for Amide/Ester Exchange

The reaction of poly(propylene glycol)bis(2-aminopropyl ether) ($M_w = 230$) and ethyl acetate



Scheme 1 Possible reaction pathways.

afforded the corresponding diamide with the characteristic at IR absorption at 1650 cm^{-1} . The absorption of carbonyl ester (1735 cm^{-1}) was absent in the amide initiator. After the process of butoxylation, the polyetheramide showed IR absorption of amide (1650 cm^{-1}) and ester (1735 cm^{-1}), and $^1\text{H-NMR}$ spectra of amide acetyl (2.1 ppm) and ester acetyl (2.0 ppm). In Scheme 1, a possible mechanism involving amide/ester exchange during butoxylation is illustrated. There

were shown not only amide and hydroxyl functional groups but also ester, secondary (2°) amine, and tertiary (3°) amine. The main pathway is the reaction of the amide proton with BO to form amidoalcohol. Based on the product analyses, it was found that both of the IR absorption of amide/ester and the total amine content in the crude product mixture increased. The amide-ester exchange could occur intramolecularly or intermolecularly, accompanied with the secondary amine

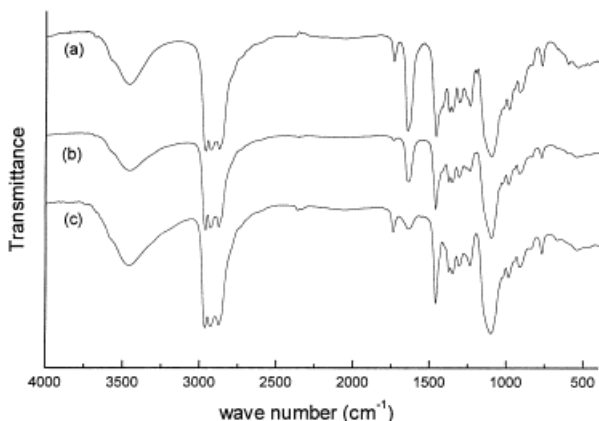


Figure 4 Hydrolysis of DETA-diamide-BO (a) before, (b) partial, and (c) complete.

formation. The consecutive butoxylation of 2° amine to form 3° amine may be possible but with a slower reaction rate. The D230-diamide and DETA-triamide reactions were chosen for the kinetic study by taking samples for analyses periodically. Table II summarizes the analyses of IR, basicity, and GPC. The relative intensity of IR absorption between the amide (1650 cm^{-1}) and the ester (1735 cm^{-1}) was estimated. The amine content was observed changing from 0.2 mEq/g to 0.8 mEq/g, and then to 0.4 mEq/g. The results implied the transformation of *in situ* amide/ester exchange. The reactions of amide/ester exchange and butoxylation proceeded simultaneously. In a relative sense, the amide/ester exchange was faster than the butoxylation. The amide/ester exchange reached equilibrium, and the amine content ceased to increase further. The relative intensity of amide to ester showed 0.01 at 6 h, 0.02 at 7 h, 0.19 at 8 h, 0.27 at 9 h, 0.44 at 11 h and 0.45 at 24 h. Those data are in good agreement with the *in situ* amide/ester exchange to form amines. While the amide/ester exchange was at equilibrium, the butoxylation was still proceeding and the product molecular weight was increasing as shown by GPC analysis. As a result, the amine content decreased. Table III showed the analytical results of DETA-triamidebutoxylation. A similar trend was obtained, but with a lower level of amide/ester exchange. Total amine increased in the beginning and subsided in the end of reaction. The amine content of the raw material was 0.2 mEq/g and increased to 0.4 mEq/g within the first hour. Molecular weight increased gradually in resulting the drop of amine content to 0.2 mEq/g. It addressed that amide/ester exchange proceeded

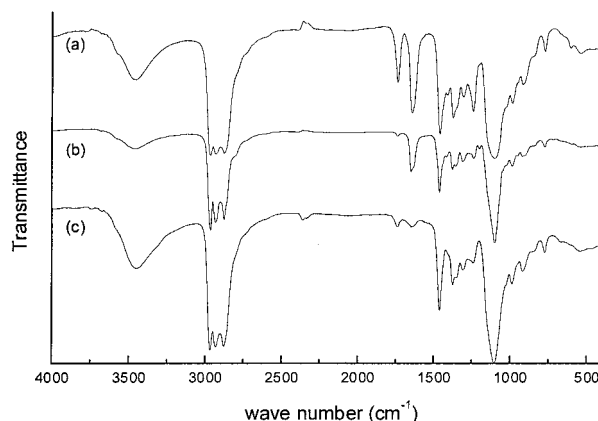


Figure 5 Hydrolysis of D230-diamide-BO (a) before, (b) partial, and (c) complete.

more quickly in this system. Furthermore, IR at 1650 and 1735 cm^{-1} reached equilibrium as expressed by the relative intensity, 0.45 in Table II and 0.06 in Table III. With the similar molecular weight at 1300 (GPC), total amine showed 0.7 mEq/g in D-230-diamide (Table II) and 0.2 mEq/g in DETA-triamide reactions (Table III). Overall, Scheme 1 exhibited the formation of the conventional amide butoxylates (1a) and the additional ester products, with second or tertiary amines (1b and 1c), via the amide/ester exchange. The exchange reaction occurred during the process of butoxylation (i.e., $2a \rightarrow 2b$). The intermediate 2b underwent both of OH and NH butoxylation to 2c

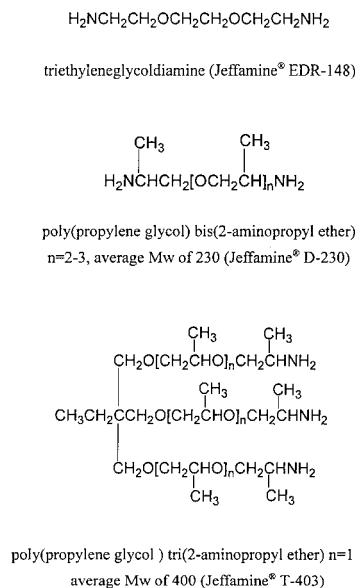


Figure 6 Chemical structures of various amine precursors.

Table IV Performance Tests of Gasoline Additives (Tests Were Performed on the Fuel Containing 200 ppm Additive Compound)

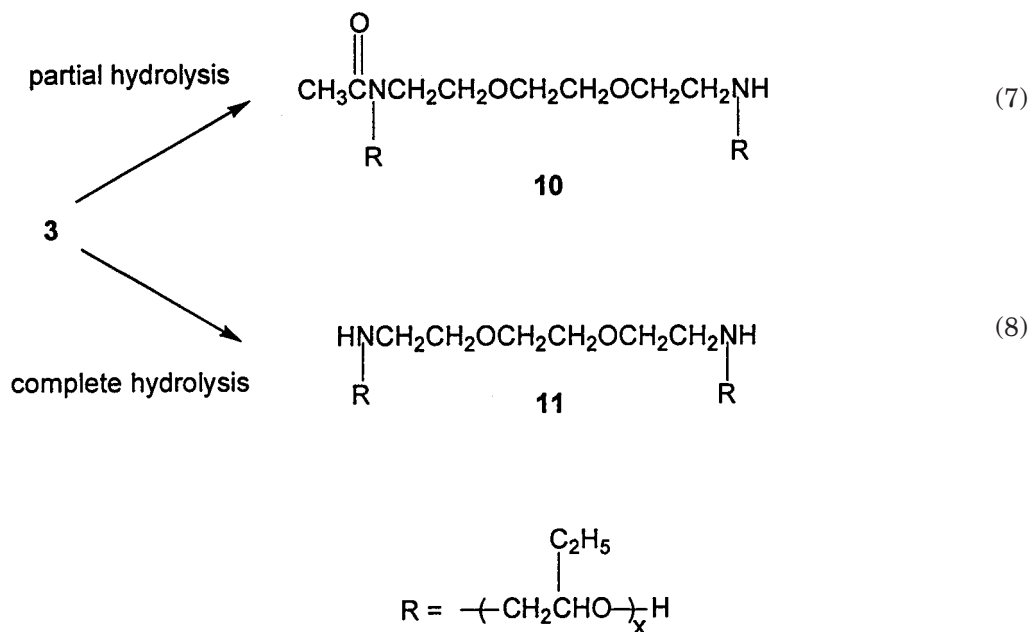
Additive	Intake Valve Coking Simulator (IVCS)	Combustion Chamber Deposit (CCD-OVEN)	Octane Requirement Reduction (ORR)
	mg/250 mL Gasoline	Residue (wt %) 300°C-60 min	Engine ONR (Δ RON)-60 hr
DETA-triamide-BO	15.8 (2.9)	2.0	-0.1
DETA-triamide-BO (partial hydrolysis)	20.5 (5.0)	4.2	2.1
Commercial product OGA480	1.0	2.5	0.4

until all BO was consumed. The analysis of 2° and 3° amines in the product implied the NH butoxylation was less favored than the OH butoxylation.

Selective Hydrolysis of Ester over Amide

The amide/ester exchange during butoxylation could not be avoided completely. Efforts on the selective hydrolysis were followed. Figure 4 shows the IR spectrum of products before and after the hydrolysis. In spectrum (b), DETA-triamide-BO product was hydrolyzed by 10 wt % of HCl. Selectively, the absorption at 1735 cm^{-1} disappeared

and amide group at 1650 cm^{-1} still remained in the IR analyses. The complete hydrolysis showed the total disappearance of ester (1735 cm^{-1}) and amide (1650 cm^{-1}) absorption (Spectrum c). Figure 5 shows the before and the after hydrolysis of D-230-amide-BO by using 10 wt % of HCl. Figure 5(b) showed D-230-amide-BO partially hydrolyzed by 10% NaOH. The NMR spectra indicated that 2.1 ppm (amide) still remained and 2.0 ppm (ester) disappeared. The partial or complete hydrolysis to poly(oxybutylene)amide-amine-alcohol were illustrated in eqs. (7) and (8).



Engine test

Our efforts on the removal of ester by-products can be justified by the product quality expressed by engine tests. The formation of ester cannot be

eliminated in the butoxylation due to the amide/ester exchange. The results of engine test using the hydrolyzed products and unhydrolyzed crude products is stated in Table IV. The octane requirement reduction (ORR) tests were used to

determine the octane number required (ONR) for the engine to run without knocking. The ORR of DETA-triamide-BO (200 ppm in based fuel) was -0.1 RON, less than the ORR of a leading brand of commercial product, OGA-480 (0.4). The partially hydrolyzed product significantly improved the octane requirement to 2.1 RON. The positive 2.1 RON means the significant performance difference between the additived and the base fuels. The existence of ester by-products gave a negative effect on ORR, while the ester-free amide butoxylates exhibited a positive effect. The results obtained by the partially hydrolyzed poly(oxybutylene)amides were significantly better than those of the commercially available additives, based on our own performance tests.

CONCLUSION

Three types of poly(oxybutylene)amides—simple, Gemini, and multiple butoxylates—were prepared by the reaction of amides and 1,2-epoxybutane. The butoxylation of amides is proven to be a viable process to produce oil soluble surfactants.

The IR and NMR analyses revealed the unexpected ester formation through the *in situ* exchange of amide and hydroxyl functional groups, in resulting the formation of secondary amine and tertiary amine. These byproducts adversely affected the engine performance. The ester formation can be subsided by designing a less hindered structure of amide initiators having a primary carbon next to amide nitrogen. Furthermore, a selective hydrolysis of ester from the product mixtures may remedy the by-product problem. It was shown that the poly(oxybutylene)amides were active components for the engine performance.

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