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Synthesis of Poly(glycerol-succinic acid)-dithiocarbamate and Poly(glycerol-succinic acid)-1,3,4-thiadiazole Dendrimers and Their Use as Anti-Wear Oil Additives

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A series of poly(glycerol-succinic acid) dithiocarbamate and 1,3,4-thiadiazole dendrimers, which have potential as anti-wear oil additives, were synthesized. Their anti-wear properties in three different oils (100N, DB-51, and soybean) were evaluated using a four-ball wear tester. The results indicated that thiocarbamate dendrimers have moderate anti-wear properties in DB-51 oil, and 1,3,4-thiadiazole dendrimers exhibited good anti-wear properties in 100N and DB-51 oils. However, dithiocarbamate and 1,3,4-thiadiazole dendrimers were not effective anti-wear additives in soybean oil.

Key Words : Dendrimer, Lubricant additives, Dithiocarbamate, 1,3,4-Thiadiazole, Anti-wear

Introduction

Many different lubricant additives have been investigated and developed. Two widely used oil additives, ZDDPs and Mo-DTC, are shown in Figure 1.[1-3] Typical oil additives are compounds that usually contain sulfur, phosphorous, nitrogen, and some heavy metals as the active elements for imparting lubricating properties.[4,5] However, because of the recently increased attention to environmental and toxicological considerations, lubricating oil compositions that do not contain phosphorus or heavy metals are now sought.[6-11] It has been reported that dithiocarbamate and some heterocyclic compounds, such as 1,3,4-thiadiazole, benzothiazole, and triazine derivatives, have good tribological properties and are potential candidates for environmentally friendly oil additives.[12-19]

Dendrimers are defined as monodisperse, highly branched macromolecules; they have specific properties because of their large surface area-to-volume ratio with well-defined interior and exterior structures. As the dendrimer generation increases, the larger number of terminal groups influences various properties such as solubility, miscibility and adhesive properties of the dendrimer.[20,21] Over the past few years, a number of dendrimers have been synthesized and investigated for many applications, including sensors,[22] catalysis,[23,24] gene delivery,[25] and drug delivery.[26] Some biodendrimers, composed of biocompatible monomers such as glycerol and succinic acid, have also been developed and used as molecular capsules and materials for biotechnology applications.[27-30]

We designed dendrimers composed of poly(glycerol-succinic acid) dendrimers with two different terminal groups. These new materials are expected to be applicable as environmentally friendly anti-wear oil additives and are expected to be particularly compatible with ester base oils such as DB-51 and soybean oil.

In this study, several generations of dendrimers were synthesized, and their tribological behavior in three different oils (100N, DB-51, and soybean oil) was evaluated using a four-ball wear tester, which is unprecedented, as far as we know. We set out to determine whether higher generation dendrimers have better anti-wear properties due to the greater number of active functional groups per molecule compared to mono-branched structures.

Experimental Section

General. All of the starting chemicals were used as received from Aldrich or TCI Chemical. Ultra-low sulfur diesel (ULSD) and 100N oil were purchased from the SK Corporation of Korea. Ester oil DB-51 and soybean oil were received from Exxon Mobil Corporation and CJ Cheil Jedang Corporation of Korea, respectively. Nuclear magnetic resonance (NMR) spectra were recorded on a JEOL JNM-AL400 spectrometer. Mass (MALDI-TOF) spectra were obtained using the Bruker autoflex III model.

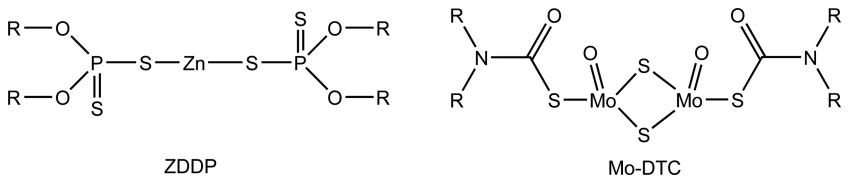


Figure 1. Two widely used oil additives.

The anti-wear properties of the dendrimer additives were evaluated by 4-ball WSD (ASTM D4172) which were examined on a 4-ball tester (SETASHELL 4-BALL LUBRICATION TESTER 19800-4 STANHOPE-SETA Co.). The additive concentration was 1 wt % in all oils. The testing conditions were as follows: rotating speed of 1200 rpm, 20 kgf pressure, and testing duration of 60 min at room temperature. All balls used in the test were 12.7 mm in diameter and made of GCr15-bearing steel (C, 0.95-1.05%; Si, 0.15-0.35%; Mn, 0.20-0.40%; P, < 0.027%; S, < 0.020%; Cr, 1.30-1.65%; Ni, < 0.30%; Cu, < 0.25%) with an HRc of 59-61.

Synthetic Procedures. Compounds **1**, **2**, **3**, **4**, **5**, and **6** were prepared according to known procedures.[31-33]

2-Hydroxypropyl Dibutylcarbamodithioate (9): Chloroacetone (3.7 g, 40 mmol) was added to a solution of compound **6** (10.23 g, 42 mmol) in THF (100 mL). The reaction mixture was stirred at room temperature for 2 h. The mixture was washed with a 1 M aqueous $NaHCO_3$ solution (100 mL) and then extracted with ether (3 × 50 mL). The combined organic layer was washed with brine, dried with anhydrous Na_2SO_4, and then concentrated by rotary evaporation to afford 10.45 g of light yellow oil. Next, this oil was dissolved in a THF (40 mL) and MeOH (40 mL) mixture. Then, sodium borohydride (1 g, 26.7 mmol) was added at 0 °C over 30 min, and the mixture was stirred at room temperature for 2 h. A solution of 1 M NH_4Cl (100 mL) was added at a temperature below 20 °C, and the mixture was stirred at room temperature for 0.5 h and then extracted with ether (3 × 50 mL). The combined organic layer was washed with brine, dried with anhydrous Na_2SO_4, and then concentrated by rotary evaporation to afford 10.3 g of light yellow oil (97.7% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 0.95 (m, J = 7.3, 6H), 1.32 (d, J = 6.8, 3H), 1.34 (m, 4H), 1.70 (m, 4H), 2.89 (s, 1H), 3.38 (q, J = 7.3, 1H), 3.60-3.76 (m, 3H), 3.98 (m, 2H), 4.11 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 13.57, 13.68, 19.96, 22.37, 28.21, 29.16, 44.83, 52.61, 55.41, 66.99, 196.11.

4-(1-(Dibutylcarbamothioylthio)propan-2-yloxy)-4-oxobutanoic acid (7): Succinic anhydride (4.96 g, 50 mmol) was added to a solution of 2-hydroxypropyl dibutylcarbamodithioate (20 g, 76 mmol) and DBU (0.755 g) in toluene. The reaction mixture was heated at reflux temperature for 8 h. The mixture was washed three times with 1 N NH_4Cl and then dried over $MgSO_4$. After filtration, the crude product was purified by silica gel chromatography, eluting with 1:1 ethyl acetate:hexane. Following vacuum filtration, 7.5 g of oil were collected (42% yield). ^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ 0.94 (t, J = 7.3, 3H), 0.98 (t, J = 7.3, 3H), 1.33 (d, J = 6.5, 3H), 1.35 (m, 4H), 1.7 (m, 4H), 2.6 (m, 4H), 3.45 (q, J = 7.1, 1H), 3.7 (m, 3H), 3.94 (t, J = 6.9, 2H), 5.17 (m, 1H).

5-(Decylthio)-1,3,4-thiadiazole-2-thiol: 1,3,4-Thiadiazole-2,5-dithiol (2.25 g, 15 mmol) and 1-bromodecane (2.21 g, 10 mmol) were added to a round-bottom flask containing DMF (30 mL). After 10 min, K_2CO_3 (1.38 g, 10 mmol) was added to the mixture, and then the mixture was stirred for 12 h at room temperature. Water (30 mL) was poured into the reaction mixture, and the organic phase was extracted with diethyl ether (50 mL) and washed three times with 1 N $NaHCO_3$. The residual solution was dried over $MgSO_4$. After filtration, solvent was removed under reduced pressure, and crude product was purified by flash column chromatography (ethyl acetate:hexane 1:10) to afford 2.6 g of white powder (89% yield). The melting point was 71 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 0.88 (t, J = 7.3, 3H), 1.26 (broad, s, 12H), 1.42 (m, 2H), 1.76 (m, J = 7.5, 2H), 3.12 (t, J = 7.3, 2H), 11.30 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 14.09, 22.65, 28.58, 28.94, 28.97, 29.25, 29.39, 29.46, 31.84, 33.68, 159.99, 188.83.

5-Decylthio-2-(2-hydroxyl)ethylthio-1,3,4-thiadiazole (10): 5-(Decylthio)-1,3,4-thiadiazole-2-thiol (5.8 g, 20 mmol) and 2-chloroethanol (2 g, 25 mmol) were added to a round-bottom flask containing DMF (30 mL). After 10 min, K_2CO_3 (4.1 g, 30 mmol) was added to the mixture, and then the mixture was stirred for 12 h at room temperature. Water (30 mL) was poured into the reaction mixture, and then the organic phase was extracted with diethyl ether (50 mL) and washed three times with 1 N $NaHCO_3$. The residual solution was dried over $MgSO_4$. After filtration, solvent was removed under reduced pressure, and the product was dried in a vacuum oven to afford 6 g of white powder (76% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 0.88 (t, J = 7.3, 3H), 1.25 (broad, s, 12H), 1.43 (m, 2H), 1.78 (m, 2H), 3.27 (t, J = 7.1, 2H), 3.46 (t, J = 7.3, 2H), 3.62 (broad, s, 1H), 3.99 (t, J = 7.0, 2H).

4-(2-(5-(Decylthio)-1,3,4-thiadiazol-2-ylthio)ethoxy)-4-oxobutanoic acid (8): Succinic anhydride was added (0.4 g, 4 mmol) to a solution of 5-decylthio-2-(2-hydroxyl)ethylthio-1,3,4-thiadiazole (0.6 g, 1.79 mmol) in pyridine (10 mL). The reaction mixture was stirred for 24 h at room temperature. Pyridine was removed *in vacuo*, and the residue was dissolved in ethyl acetate. The organic phase was washed three times with 1 N NH_4Cl (10 mL) and then dried over $MgSO_4$. The filtrate was removed under reduced pressure, and the crude product was purified by flash column chromatography (ethyl acetate:hexane, 2:1) to afford 0.56 g of white powder (72% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 0.88 (t, J = 7.1, 3H), 1.26 (broad, s, 12H), 1.43 (m, 2H), 1.78 (m, 2H), 2.68 (m, 4H), 3.27 (t, J = 7.3, 2H), 3.55 (t, J = 7.1, 2H), 4.46 (t, J = 7.0, 2H).

Bis(1-(dibutylcarbamothioylthio)propan-2-yl) succinate (G0-DTC): Succinic acid (0.22 g, 1.9 mmol), 2-hydroxypropyl dibutylcarbamodithioate (1 g, 3.8 mmol), and DMAP (0.68 g, 5.5 mmol) were dissolved in CH_2Cl_2 (20 mL). The reaction flask was flushed with nitrogen, and then DCC (1.15 g, 5.6 mmol) was added. The solution was stirred at room temperature for 14 h under a nitrogen atmosphere. Then, the resulting product dicyclohexylurea (DHU) was filtered and washed with a small amount of CH_2Cl_2 (10 mL). The organic phase was washed with 1 N $NaHCO_3$ and then dried over $MgSO_4$. After filtration, the crude product was purified by silica gel chromatography, eluting with 1:6 ethyl acetate:hexane. Following vacuum filtration, 0.95 g of colorless oil was collected (84% yield). ^{1}H-NMR (400 MHz, $CDCl_3$,

ppm) δ 0.94 (t, *J* = 7.3, 6H), 0.98 (t, *J* = 7.3, 6H), 1.35 (m, 14H), 1.7 (m, 8H), 2.61 (s, 4H), 3.45 (m, 2H), 3.7 (m, 6H), 3.95 (m, 4H), 5.17 (m, 2H).

First Generation Dithiocarbamate Dendrimers (G1-DTC): Mono acid **7** (4.91 g, 13.5 mmol), compound **3** (0.6 g, 2.3 mmol), and DMAP (1.21 g, 9.9 mmol) were dissolved in CH_2Cl_2 (100 mL). The reaction flask was flushed with nitrogen, and then DCC (3.09 g, 15 mmol) was added. The reaction was stirred at room temperature for 14 h under a nitrogen atmosphere. Upon reaction completion, DHU was filtered and washed with a small amount of CH_2Cl_2 (10 mL). The organic phase was washed with 1N $NaHCO_3$ and then dried over $MgSO_4$. After filtration, the crude product was purified by silica gel chromatography, eluting with 1:4 ethyl acetate:hexane. Following vacuum filtration, 2.8 g of colorless oil were collected (75% yield). ^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ 0.94 (t, *J* = 7.3, 12H), 0.98 (t, *J* = 7.3, 12H), 1.33 (d, *J* = 6.5, 12H), 1.35 (m, 16H), 1.74 (m, 16H), 2.60 (m, 20H), 3.45 (dd, *J* = 7.3, 4H), 3.71 (m, 12H), 3.94 (t, *J* = 7.3, 8H), 4.25 (m, 8H), 5.15 (m, 4H), 5.28 (m, 2H). MALDI-TOF: *m/z* 1646.5 $[M^{\bullet}]^+$ (theory: 1646.7).

Second Generation Dithiocarbamate Dendrimers (G2-DTC): Mono acid **7** (1.88 g, 5.2 mmol), compound **4** (0.5 g, 0.52 mmol), and DMAP (0.54 g, 4.4 mmol) were dissolved in CH_2Cl_2 (30 mL). The reaction flask was flushed with nitrogen, and then DCC (1.13 g, 5.5 mmol) was added. The reaction mixture was stirred at room temperature for 14 h under a nitrogen atmosphere. Upon reaction completion, DHU was filtered and washed with a small amount of CH_2Cl_2 (10 mL). The organic phase was washed with 1 N $NaHCO_3$ and then dried over $MgSO_4$. After filtration, the crude product was purified by silica gel chromatography, eluting with 1:4 ethyl acetate:hexane. Following vacuum filtration, 1.4 g of colorless oil were collected (72% yield). ^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ 0.94 (t, *J* = 7.3, 24H), 0.98 (t, *J* = 7.3, 24H), 1.33 (d, *J* = 6.8, 24H), 1.35 (m, 32H), 1.74 (m, 32H), 2.6 (broad, m, 52H), 3.45 (q, *J* = 7.5, 8H), 3.7 (m, 24H), 3.94 (t, *J* = 7.8, 16H), 4.25 (m, 24H), 5.15 (m, 8H), 5.28 (m, 6H). MALDI TOF: *m/z* 3697.5 $[M-30]^+$.

Third Generation of Dithiocarbamate Dendrimers (G3-DTC): Mono acid **7** (1.5 g, 5 mmol), compound **5** (0.5 g, 0.21 mmol), and DMAP (0.44 g, 3.6 mmol) were dissolved in CH_2Cl_2 (30 mL). The reaction flask was flushed with nitrogen, and then DCC (0.74 g, 3.6 mmol) was added. The reaction mixture was stirred at room temperature for 14 h under nitrogen atmosphere. Upon reaction completion, DHU was filtered and washed with a small amount of CH_2Cl_2 (10 mL). The organic phase was washed with 1 N $NaHCO_3$ and then dried over $MgSO_4$. After filtration, the crude product was purified by silica gel chromatography, eluting with ethyl acetate:hexane (1:4 to 1:2). Following vacuum filtration, 2.21 g of colorless oil were collected (60% yield). ^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ 0.94 (t, *J* = 7.3, 48H), 0.98 (t, *J* = 7.3, 48H), 1.33 (d, *J* = 6.5, 48H), 1.35 (m, 64H), 1.74 (m, 64H), 2.60 (m, 116H), 3.45 (q, *J* = 7.2, 16H), 3.7 (m, 48H), 3.94 (t, *J* = 7.5, 32H), 4.25 (m, 56H), 5.15 (m, 16H), 5.28 (m, 14H).

Bis(2-(5-(decylthio)-1,3,4-thiadiazol-2-ylthio)ethyl) succinate (G0-TDA): Succinic acid (0.53 g, 4.5 mmol), 2-(5-(decylthio)-1,3,4-thiadiazol-2-ylthio)ethanol (3.35 g, 10 mmol), and DMAP (0.61 g, 5 mmol) were dissolved in THF (40 mL). The reaction flask was flushed with nitrogen, and then DCC (4.12 g, 20 mmol) was added. The reaction mixture was stirred at room temperature for 24 h under a nitrogen atmosphere. Upon reaction completion, DHU was filtered and washed with a small amount of THF (10 mL). The product mixture was purified using silica gel chromatography, eluting with 1:4 ethyl acetate:hexane to remove excess DMAP and DCC. The organic solution was evaporated and purified again, eluting with 1:5 ethyl acetate:hexane. Following evaporation, 2.4 g of a white solid were collected (73% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 0.88 (t, *J* = 7.3, 6H), 1.26 (broad, s, 24H), 1.42 (m, 4H), 1.78 (m, 4H), 2.64 (s, 4H), 3.28 (t, *J* = 7.1, 4H), 3.55 (t, *J* = 7.1, 4H), 4.45 (t, *J* = 7.0, 4H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 14.09, 22.65, 28.70, 28.88, 29.04, 29.17, 29.26, 29.54, 29.49, 31.85, 32.28, 34.37, 62.58, 163.47, 166.04, 171.79. MALDI-TOF: *m/z* 773.7 $[M+Na]^+$ (theory: 773.3).

First Generation 1,3,4-Thiadiazole Dendrimers (G1-TDA): Compound **3** (0.27 g, 1 mmol), compound **8** (2.6 g, 6 mmol), and DMAP (0.37 g, 3 mmol) were dissolved in THF (20 mL). The reaction flask was flushed with nitrogen, and then DCC (1.85 g, 9 mmol) was added. The reaction mixture was stirred at room temperature for 24 h under a nitrogen atmosphere. Upon reaction completion, DHU was filtered and washed with a small amount of CH_2Cl_2 (10 mL). The product mixture was purified by silica gel chromatography, eluting with 1:2 ethyl acetate:hexane to 1:1 ethyl acetate: hexane. Following evaporation, 1.28 g of colorless oil were collected (66.2% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 0.88 (t, *J* = 7.3, 12H), 1.26 (broad, s, 48H), 1.42 (m, 8H), 1.78 (m, 8H), 2.65 (broad, s, 20H), 3.27 (t, *J* = 7.1, 8H), 3.55 (t, *J* = 7.1, 8H), 4.19 (m, 4H), 4.32 (m, 4H), 4.45 (t, *J* = 7.1, 8H), 5.28 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 14.07, 22.62, 28.67, 28.71, 28.74, 28.86, 29.01, 29.12, 29.23, 29.42, 29.46, 31.82, 32.21, 34.33, 62.33, 62.54, 69.24, 163.45, 166.97, 171.68, 171.70, 171.73. MALDI-TOF: *m/z* 1955.1 $[M+Na]^+$ (theory: 1954.6).

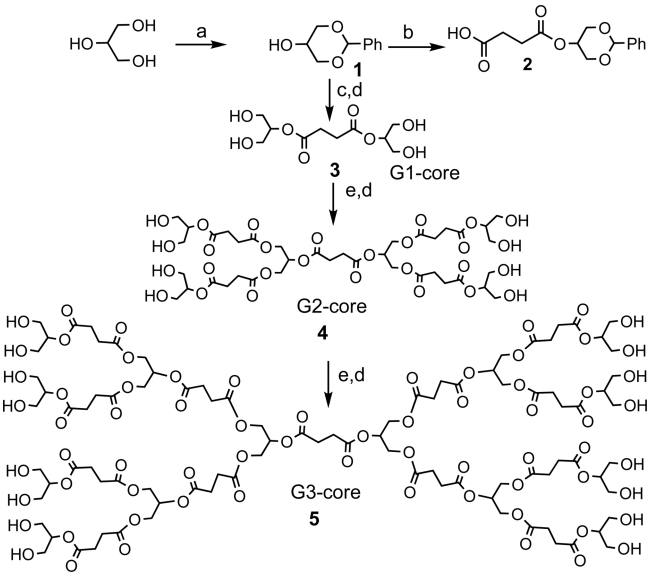
Second Generation of 1,3,4-Thiadiazole Dendrimers (G2-TDA): Compound **4** (0.49 g, 0.5 mmol), compound **8** (2.6 g, 6 mmol), and DMAP (0.37 g, 3 mmol) were dissolved in THF (20 mL). The reaction flask was flushed with nitrogen, and then DCC (12.47 g, 12 mmol) was added. The reaction mixture was stirred at room temperature for 24 h under a nitrogen atmosphere. Upon reaction completion, DHU was filtered and washed with a small amount of CH_2Cl_2 (10 mL). The product mixture was purified by silica gel chromatography, eluting with 1:1 ethyl acetate:hexane to 3:2 ethyl acetate:hexane. Following evaporation, 1.33 g of colorless oil were collected (62% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 0.88 (t, *J* = 7.3, 24H), 1.27 (broad, s, 96H), 1.43 (m, 16H), 1.78 (m, 16H), 2.65-2.70 (broad, m, 52H), 3.27 (t, *J* = 7.1, 16H), 3.55 (t, *J* = 7.1, 16H), 4.22 (m, 12H), 4.33 (m, 12H), 4.45 (t, *J* = 7.0, 16H), 5.27 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 14.09, 22.65, 28.66, 28.69, 28.72, 28.77, 28.80, 28.87, 29.04, 29.14, 29.25, 29.44, 29.48, 31.84, 32.23, 34.36, 62.37, 62.56, 66.30, 68.94, 69.26, 163.49, 166.00, 171.71, 171.77, 172.07.

Results and Discussion

Synthesis of Cores. G1-core, G2-core, and G3-core were prepared using known procedures,[31,34] as shown in Scheme 1. First, the 1,3-diol of glycerol was protected as 1,3-benzylideneglycerol **1** by treatment with p-TsOH and benzaldehyde.[32,35] Succinic acid was coupled to **1** in the presence of *N,N*-dicyclohexyl carbodiimide (DCC) and 4-(dimethylamino) pyridinium 4-toluenesulfonate (DPTS); the product was then purified by column chromatography. The benzylidene acetal group of the core was subsequently removed by hydrogenolysis (20% (w/w) with $Pd(OH)_2$/C at 50 psi H_2 in THF) to yield the tetrahydroxy G1-core **3** (76% yield). The branching ligand **2** was prepared by treating 1,3-*O*-benzylideneglycerol with succinic anhydride in pyridine and was isolated after recrystallization from ethyl ether (85% yield).

Compounds **2** and **3** were coupled in the presence of DCC and DPTS to afford the protected G2-core, which was easily separated from the branching ligand by column chromatography. The product was deprotected by hydrogenolysis in THF to yield the G2-core **4** (86% yield). Compound **4** was coupled to **2** in the presence of DCC and DPTS, and then column chromatography was used to isolate the product after residual DCC was removed by precipitating the dendrimer in ethyl ether. Finally, G3-core **5** was obtained after removing the benzyl group by hydrogenolysis (85% yield).



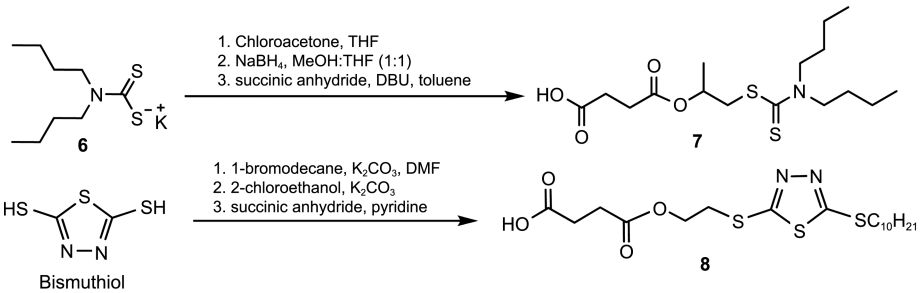
(a) benzaldehyde, p-TsOH, 50 °C, 10 mmHg; (b) succinic anhydride, pyridine, 25 °C, 18 h; (c) succinic acid, DPTS, DCC, CH_2Cl_2, 25 °C, 18 h; (d) 50 psi H_2, $Pd(OH)_2$/C 20% w/w, THF, 25 °C, 3 h; (e) 2, DPTS, DCC, THF, 25 °C, 24 h

Scheme 1. Synthesis of G1-core, G2-core, and G3-core.

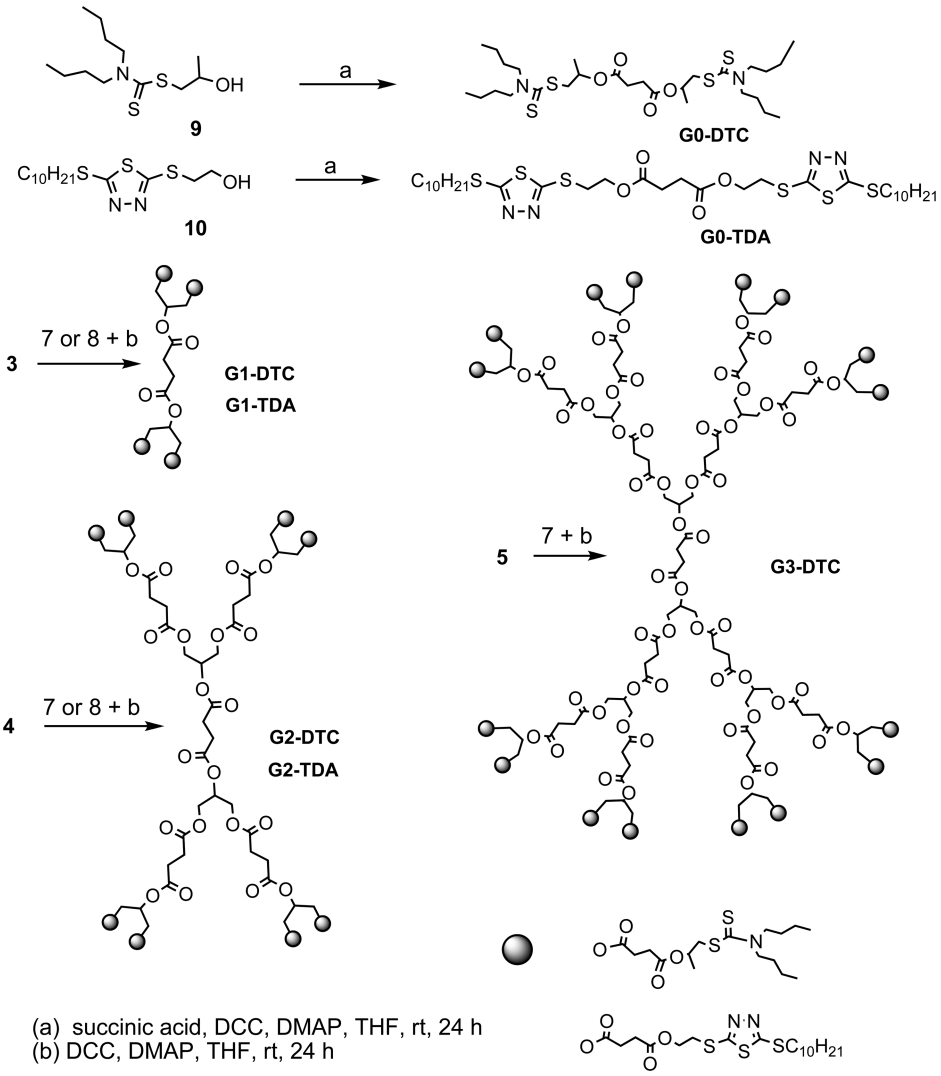
Synthesis of Dithiocarbamate and 1,3,4-Thiadiazole Terminal Moieties. Synthesis of the dithiocarbamate terminal moiety **7** was carried out in three steps, as shown in Scheme 2. S-Alkylation of **6** with chloroacetone produced a ketone. This ketone was then reduced to an alcohol using sodium borohydride in THF (97.7% yield) to yield **9**.[33,36] This alcohol was coupled to succinic anhydride in the presence of DBU as a base catalyst to produce **7** (42% yield). Compound **8**, containing 1,3,4-thiadiazole terminal group, was prepared in three steps, as shown in Scheme 2. In the first step, 5-(decylthio)-1,3,4-thiadiazole-2-thiol was prepared by treating 1-bromodecane with bismuthiol in the presence of 1 equivalent of anhydrous potassium carbonate as a base catalyst (89% yield).[37] Di-S-alkyl substitution was obtained as the byproduct when more than 1 equivalent of potassium carbonate was used. Attempts to make the monothioester of 5-(decylthio)-1,3,4-thiadiazole-2-thiol directly from the reaction with succinic anhydride in various conditions were unsuccessful. Therefore, 5-decylthio-2-(2-hydroxyl)ethylthio-1,3,4-thiadiazole **10**, which contains more reactive hydroxyl groups for esterification, was synthesized by coupling 5-(decylthio)-1,3,4-thiadiazole-2-thiol and 2-chloroethanol in the presence of potassium carbonate (76% yield). Finally, monoester **8** was obtained from the reaction of 5-decylthio-2-(2-hydroxyl)ethylthio-1,3,4-thiadiazole with succinic anhydride in moderate yield (72% yield).

Synthesis and Characterization of Dithiocarbamate and 1,3,4-Thiadiazole Dendrimers: A series of dithiocarbamate dendrimers (**G0-DTC**, **G1-DTC**, **G2-DTC**, and **G3-DTC**) were synthesized using Steglich esterification,[38] as shown in Scheme 3.

Compound **9** was coupled to succinic acid in the presence of DCC and DMAP, and column chromatography was used to isolate product **G0-DTC** (84% yield). Next, compound **7** was coupled to **3**, **4**, and **5**, and the products were purified by column chromatography to afford **G1-DTC** (75% yield),



Scheme 2. Synthesis of dithiocarbamate and 1,3,4-thiadiazole terminal moieties.



Scheme 3. Synthetic schemes of dithiocarbamate and thiadiazole dendrimers.

G2-DTC (72% yield), and **G3-DTC** (60% yield), respectively. The major signals in the ^{1}H and ^{13}C-NMR spectra indicated successful formation of the desired products; potential byproducts with incompletely introduced terminal dithiocarbamate groups would have resulted in much more complex NMR spectra. On the other hand, MALDI-TOF mass spectra exhibited base peaks for **G1-DTC** and **G2-DTC** attributable to $[M-30]^{+}$ instead of the typical $[M+Na]^{+}$. The monoisotropic peak for $M^{\bullet+}$ at *m/z* 1946.5 was identified in the spectrum for **G1-DTC**, which had greater peak resolution than the spectrum of **G2-DTC**.

Three 1,3,4-thiadiazole dendrimers were also synthesized using a similar method. Succinic acid was coupled to 5-decylthio-2-(2-hydroxyl)ethylthio-1,3,4-thiadiazole **10** in the presence of DCC and DMA, and the reaction product was purified using column chromatography to yield **G0-TDA** (73% yield). Carboxylic acid **8** was coupled to alcohols **3** and **4**, and then the reaction products were purified using column chromatography to afford **G1-TDA** (66.2% yield) and **G2-TDA** (22% yield), respectively. The structures of the thiadiazole dendrimers were confirmed by ^{1}H-NMR, ^{13}C-NMR, and MALDI-TOF spectra. The MALDI-TOF base peaks were observed at *m/z* 773.7 and *m/z* 1955.1 for **G0-TDA** and **G1-TDA**, respectively, and were assigned as $[M+Na]^{+}$.

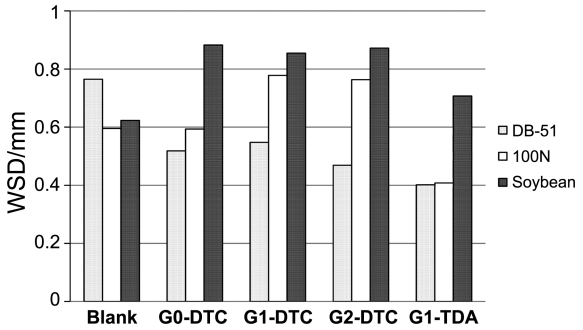


Figure 2. Comparison of four-ball wear scar diameters (WSD) in three different oils.

Anti-wear Performance. The anti-wear properties of the synthesized dendrimer additives in base oils (DB-51, 100N, and soybean oil) were evaluated using a four-ball tester

Table 1. Equivalence of functional groups in dendrimers

	G0-DTC	G1-DTC	G2-DTC	G1-TDA
Mw	609.0	1648.3	3727.0	1932.7
Number of functional groups	2	4	8	4
Equivalent per gram	1	0.74	0.65	0.63

(Seta-Shell 4-Ball Lubrication Tester 19800-4, Stanhope-Seta Co.) under the following conditions: ball (AISI52100 steel) diameter of 12.7 mm, rotating speed of 1200 rpm, test duration of 60 min, load of 20 kgf, and temperature of 25 ºC. The additive concentration was fixed at 1 wt % in oil.

The average values for wear scar diameter (WSD) of the lower steel balls in the three different oils (DB-51, 100N, and soybean oil) are shown in Figure 2. DB-51 is a mixture of diester oils, soybean oil is a mixture of triester oils of glycerol, and 100N is a mixture of hydrocarbons.[39] A lower WSD value indicates better anti-wear properties.

Moderate anti-wear performance was observed in DB-51 oil when dithiocarbamate dendrimers (**DTC**s) were used as the additives. However, although thiocarbamate groups are typically known to exhibit good anti-wear properties, either no or negative anti-wear effects were observed in 100N and soybean oil in this study. The WSD values for Mo-DTC and Zn-DPT in 100N are around 0.3 mm in our experimental condition and around 0.5 mm at a road of 40 kgf.[40] The absence of anti-wear properties in this experiment was attributed to the solubility effect. The dendrimers were not very soluble in 100N and soybean oil, especially the higher generation dendrimers. In fact, **G3-DTC** could not be evaluated as an additive because it was insoluble in all three oils.

The WSD value for **G2-DTC** in DB-51 oil was the lowest, and the WSD values for **G0-DTC** and **G1-DTC** were similar. When considered in terms of the equivalent number of dithiocarbamate groups, as shown in Table 1, the anti-wear properties were increased in the higher generation dendrimers: **G2-DTC** > **G1-DTC** > **G0-DTC**. Thiadiazole dendrimers **G0-TDA** and **G2-TDA** were insoluble in 100N oil; the WSD in 100N oil was only measured for **G1-TDA**. The WSD values of **G1-TDA** exhibited excellent anti-wear properties in DB-51 and 100N oils; the anti-wear properties of **G1-TDA** were greater than those observed for **G1-DTC**.

Although some anti-wear properties were observed for the dendrimers, no dramatic improvement in anti-wear activity was observed upon increasing the dendrimer generation. This result was attributed to the fact that only a small part of the dendrimer is in contact with the metal surface and available to form a protection layer. Overall, the contact area is relatively small in the higher generation dendrimers because of the globular shape of the higher dendrimer generations.

Conclusions

Four dithiocarbamate dendrimers (G0, G1, G2, and G3) and three 1,3,4-thiadiazole dendrimers (G0, G1, and G2) were synthesized using Steglich esterification, and their anti-wear properties were evaluated in three different oils (DB-51, 100N, and soybean oil) using four-ball WSD. The results indicated that dithiocarbamate dendrimers exhibit good anti-wear properties in DB-51 oil, while 1,3,4-thiadiazole dendrimers exhibited excellent anti-wear properties in DB-51 and 100N oil. The results also indicated that ester cores increased the solubility in DB-51 oil and improved the anti-wear properties of the additives.

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