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Silsesquioxanes as Synthetic Platforms. III. Photocurable, Liquid Epoxides as Inorganic/Organic Hybrid Precursors

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Supporting Information

Experimental

All reactions were performed under N_2 atmosphere. Toluene was distilled from sodium benzophenone ketyl. $(HMe_2SiOSiO_{1.5})_8$, $(Q_8M_8^H)$ and $(HSiO_{1.5})_8$, (T_8^H) were synthesized from known procedures (see below).[1,2,3] Platinumdivinyltetramethyldisiloxane [Pt(dvs)] (Karstedt's catalysts) was purchased from United Chemical Technologies and used as a 2.0 mmol solution in xylene. The triarylsulfonium hexafluorophosphate cationic photoinitiator (Cyracure 313) was purchased from Union Carbide as a 50% solution in propylene carbonate. All other chemicals were used as received.

Octa(dimethylsiloxy)silsesquioxane $(Q_8M_8^H)$ from $Si(OCH_2CH_2O)_2$, $Si(eg)_2$

$Si(eg)_2$ (1.0 g and ≈ 80% pure)[3] is added to a solution containing 2.0 M tetramethylammonium hydroxide (2.7 mL) (TMAH) in methanol (prepared from TMAH• 5 H_2O), water (0.5 mL), and methanol (1.7 mL). The final solution should be 1.0 M in "Si", 1:1 molar ratio "Si": "N", and 10:1 molar ratio of water:"Si". The mixture is stirred overnight until clear. ^{29}Si-NMR of this solution reveals one peak at -99.4 ppm indicating formation of the 'octaanion cube'. This solution (3 mL) is added to an addition funnel and is slowly added to an ice cooled stirring solution of hexane (11 mL) and HMe_2SiCl (4 mL). After the addition is complete, the mixture is allowed to come to room temperature with a total stirring time of one hour. The layers are separated, and the aqueous layer is washed with hexane (3 X 10 mL) and the total hexane portion volume is reduced to yield a white solid. The solid is washed with cold methanol (≈ 10 mL) and dried under vacuum to yield 0.55 g of octa(dimethylsiloxy)silsesquioxane (80% yield). ^{1}H NMR (360 MHz, $CDCl_3$, 25°C) δ Si-$\underline{H}$ 4.73 (septet, *J* 2.77 Hz, 8H), $(C\underline{H}_3)_2SiH$ 0.22 (d, *J* 2.72 Hz, 48.2H). ^{13}C NMR (90 MHz, $CHCl_3$, 25°C) δ $(\underline{C}H_3)_2SiH$ 0.05. ^{29}Si NMR (71.5 MHz, $CHCl_3$, 25°C) δ $(CH_3)_2\underline{Si}H$ -1.4, $\underline{Si}OSi(CH_3)_2H$ -107.1. Mass spectra (chemical ionization, NH_3): m/z = 1034 ($Q_8M_8^H$+ NH_3), 100% intensity.

Preparation of tetra(dimethylsiloxypropylglycidylether) silsesquioxane, $Q_8M_4^HM_4^E$

$Q_8M_8^H$ (0.50 g, 0.49 mmol) was added to a 25 mL schlenk flask equipped with a magnetic stir bar and condenser. The flask was evacuated and refilled with N_2 gas 3 times at 50°C. Toluene (5 mL) was added and the solution was stirred for ≈ 5 min. AGE (0.23 mL, 1.96 mmol) was added to the solution followed by 5 drops of 2.0 mmol Pt(dvs). The reaction was stirred for 4 hrs at 50°C, cooled and dry activated charcoal was added.. After 10 min. of stirring, the mixture was filtered through a 0.45 μm Teflon membrane into a vial and stored as ≈ 10 wt. % clear solution. Removal of solvents affords an opaque viscous liquid soluble in common solvents. Yield: 0.68 g (94%). ^{1}H NMR (360 MHz, $CDCl_3$, 25°C) δ Si-$\underline{H}$ 4.72 (septet, *J* 2.77 Hz, 4H), (epoxy) $C\underline{H}_2O(CH_2)_3$ diastereotopic 3.72, 3.66 (dd, *J* 3.17 Hz, 4.3H) (Due to peak overlap, all resonances between 3.5 and 3.3 are integrated as one peak, 13.6H) 3.45, 3.41 (dd, *J* 2.74 Hz), $SiCH_2CH_2C\underline{H}_2O$ 3.43 (m), $OCH_2C\underline{H}$ (epoxy) 3.14 (m, 3.7H), $C\underline{H}_2$ (epoxy) diastereotopic 2.79 (dd, *J* 4.97 Hz, 3.9H), 2.59 (dd, *J* 2.67 Hz, 4H), $SiCH_2C\underline{H}_2CH_2O$ 1.64 (m, 8H), $SiC\underline{H}_2CH_2CH_2O$ 0.61 (m, 8.3H), $(C\underline{H}_3)_2SiH$ 0.25 (d, *J* 2.72 Hz, 24H), $(C\underline{H}_3)_2SiCH_2$ 0.15 (s, 26H); ^{13}C NMR (90 MHz, $CHCl_3$, 25°C) δ $SiCH_2CH_2\underline{C}H_2O$ 74.1, 73.9, (epoxy) $\underline{C}H_2O(CH_2)_3$ 71.4, $OCH_2\underline{C}H$ (epoxy) 50.7, $\underline{C}H_2$ (epoxy) 44.2, $SiCH_2\underline{C}H_2CH_2O$ 22.9, $Si\underline{C}H_2CH_2CH_2O$ 13.5, $(\underline{C}H_3)_2SiH$ -0.05, $(\underline{C}H_3)_2SiCH_2$ -0.60; ^{29}Si NMR (71.5 MHz, $CHCl_3$, 25°C) δ

$(CH_3)_2\underline{Si}CH_2$ 13.9, $(CH_3)_2\underline{Si}H$ -1.1, $\underline{Si}OSi(CH_3)_2H$ -107.8, $\underline{Si}OSi(CH_3)_2CH_2$ -108.1. Size exclusion chromatography (SEC) polystyrene standards, THF solvent, toluene reference; Mn = 1260, Mw = 1290, PDI = 1.02, calc. MW = 1475 g/mol. FTIR (neat film, cm^{-1}) 3035, 2962, 2934, 2874 (m, C-H str.); 2142 (m, Si-H str.); 1257 (s, C-O-C str.); 1095 (vs, Si-O str.); 902 (s, C-O-C bend).

Preparation of octa(dimethylsiloxypropylglycidylether)silsesquioxane, $Q_8M_8^E$

$Q_8M_8^H$ (0.40 g, 0.39 mmol) was added to a 25 mL schlenk flask equipped with a magnetic stir bar and condenser. The flask was evacuated and refilled with N_2 gas 3 times at 50°C. Toluene (5 mL) was added and the solution was stirred for ≈ 5 min. AGE (0.46 mL, 3.89 mmol) was added to the solution followed by 5 drops of 2.0 mmol Pt(dvs). The reaction was stirred for 12 hrs at 50°C, cooled and dry activated charcoal was added.. After 10 min. of stirring, the mixture was filtered through a 0.45 μm Teflon membrane into a vial and stored as ≈ 10 wt. % clear solution. Removal of the solvents affords an opaque viscous liquid soluble in common solvents. Yield: 0.78 g (92%). ^1H NMR (360 MHz, $CDCl_3$, 25°C) δ $C\underline{H}_2O(CH_2)_3$ diastereotopic 3.72, 3.66 (dd, *J* 3.17 Hz, 8H) (Due to peak overlap, all resonances between 3.5 and 3.3 are integrated as one peak, 24.7H) 3.45, 3.41 (dd, *J* 2.74 Hz), $SiCH_2CH_2C\underline{H}_2O$ 3.43 (m), $OCH_2C\underline{H}$ (epoxy) 3.14 (m, 8.1H), $C\underline{H}_2$ (epoxy) diastereotopic 2.79 (dd, *J* 4.97 Hz, 7.9H) 2.59 (dd, *J* 2.67 Hz, 7.9H), $SiCH_2C\underline{H}_2CH_2O$ 1.64 (m, 16.4H), $SiC\underline{H}_2CH_2CH_2O$ 0.61 (m, 15H), $(C\underline{H}_3)_2SiCH_2$ 0.15 (s, 48H); ^{13}C NMR (90 MHz, $CHCl_3$, 25°C) δ $SiCH_2CH_2\underline{C}H_2O$ 74.0, (epoxy) $\underline{C}H_2O(CH_2)_3$ 71.4, $OCH_2\underline{C}H$ (epoxy) 50.8, $\underline{C}H_2$ (epoxy) 44.2, $SiCH_2\underline{C}H_2CH_2O$ 23.1, $Si\underline{C}H_2CH_2CH_2O$ 13.6, $(\underline{C}H_3)_2SiCH_2$ -0.45; ^{29}Si NMR (71.5 MHz, $CHCl_3$, 25°C) δ $(CH_3)_2\underline{Si}CH_2$ 13.8, $\underline{Si}OSi(CH_3)_2CH_2$ -108.1. Size exclusion chromatography (SEC) polystyrene standards, THF solvent, toluene reference; Mn = 1480, Mw = 1500, PDI = 1.02, calc. MW = 1931 g/mol. FTIR (neat film, cm^{-1}) 3040, 2958, 2939, 2870 (m, C-H str.); 1262 (s, C-O-C str.); 1085 (vs, Si-O str.); 908 (s, C-O-C bend).

Preparation of tetra(propylglycidylether) silsesquioxane, $T_4^HT_4^E$

T_8^H (0.48 g, 1.13 mmol) was added to a 25 mL schlenk flask equipped with a magnetic stir bar and condenser. The flask was evacuated and refilled with N_2 gas 3 times at 80°C. Experiments to study the α-addition product were conducted using toluene, toluene containing triphenylphosphine (4/1 PPh_3/Pt) and 1/1 toluene/n-butylether solvent systems. Toluene (2 mL) and n-butylether (2 mL) were added and the solution was stirred for ≈ 5 min. AGE (0.23 mL, 1.94 mmol) was added to the solution followed by 5 drops of 2.0 mmol Pt(dvs). The reaction was stirred for 12 hrs at 80°C, cooled and dry activated charcoal was added. After 10 min. of stirring, the mixture was filtered through a 0.45 μm Teflon membrane into a vial and stored as ≈ 10 wt. % clear solution. Removal of the solvents affords an opaque viscous liquid soluble in common solvents. Yield: 0.67 g (95%). ^{1}H NMR (360 MHz, $CDCl_3$, 25°C) δ (data reported here for α-isomer content of 35%) Si-$\underline{H}$ 4.18 (m, 4H), (Due to peak overlap, all resonances between 3.75 and 3.30 are integrated as one peak, 14.4H) (epoxy) $C\underline{H_2}O(CH_2)_3$ diastereotopic 3.71, 3.67 (dd, *J* 2.72 Hz) 3.45, 3.41 (m), $SiCH_2CH_2C\underline{H_2}O$ and $SiCH(CH_3)C\underline{H_2}O$ 3.5-3.3 (m), $OCH_2C\underline{H}$ (epoxy) 3.12 (m, 3.4H), $C\underline{H_2}$ (epoxy) diastereotopic 2.80 (m, 3.5H), 2.61 (m, 3.6H), $SiCH_2C\underline{H_2}CH_2O$ 1.72 (m, 4.7H), $SiC\underline{H}(CH_3)CH_2O$ 1.32 (m, 1.6H), $SiCH(C\underline{H_3})CH_2O$ (dd, *J* 7.72 Hz, 3.8H), note that this should be a dt but the presence of several oligomers broadens the resultant peaks, $SiC\underline{H_2}CH_2CH_2O$ 0.72 (m, 4.9H); ^{13}C NMR (90 MHz, $CHCl_3$, 25°C) δ $SiCH_2CH_2\underline{C}H_2O$ 73.1, $SiCH(CH_3)\underline{C}H_2O$ 72.7, (epoxy) $\underline{C}H_2O(CH_2)_3Si$ 71.3, (epoxy) $\underline{C}H_2O(CH_2)CHCH_3Si$ 71.0, $OCH_2\underline{C}H$ (epoxy) 50.8, $\underline{C}H_2$ (epoxy) 44.3, $SiCH_2\underline{C}H_2CH_2O$ 22.7, $Si\underline{C}H(CH_3)CH_2O$ 19.2, $SiCH(\underline{C}H_3)CH_2O$ 11.3, $Si\underline{C}H_2CH_2CH_2O$ 8.2, 7.7; ^{29}Si NMR (71.5 MHz, $CHCl_3$, 25°C) δ $\underline{Si}CH_2CH_2CH_2O$ -65.2, $\underline{Si}CH(CH_3)CH_2O$ -67.5, $\underline{Si}H$ -83.7, $\underline{Si}H$ -85.8 ($T_{10-n}^HT_n^E$). Size exclusion chromatography (SEC) polystyrene standards, THF solvent, toluene reference; Mn = 780, Mw = 890, PDI = 1.14, calc. MW =

881 g/mol. FTIR (neat film, cm^{-1}) 3030, 2966, 2932, 2875 (m, C-H str.); 2259 (m, Si-H str.); 1200 (s, C-O-C str.); 1108 (vs, Si-O str.); 887 (s, C-O-C bend).

Preparation of septa(propylglycidylether) silsesquioxane, $T_1^HT_7^E$

T_8^H (0.48 g, 1.13 mmol) was added to a 25 mL schlenk flask equipped with a magnetic stir bar and condenser. The flask was evacuated and refilled with N_2 gas 3 times at 80°C. Experiments to study the α-addition product were conducted using toluene, toluene containing triphenylphosphine [4 equiv. with respect to Pt(dvs)] and toluene/n-butylether solvent systems. Toluene (6 mL) were added and the solution was stirred for ≈ 5 min. AGE (1.6 mL, 13.5 mmol, 12 equiv.) was added to the solution followed by 5 drops of 2.0 mmol Pt(dvs). The reaction was stirred for 24 hrs at 100°C, cooled and dry activated charcoal was added. After 10 min. of stirring, the mixture was filtered through a 0.45 μm Teflon membrane into a vial and stored as ≈ 10 wt. % clear solution. Removal of the solvents affords an opaque viscous liquid soluble in common solvents. Yield: 1.45 g (96%). ^1H NMR (360 MHz, $CDCl_3$, 25°C) δ (data reported here for α-isomer content of 10%) $Si\text{-}\underline{H}$ 4.14 (m, 1.2H), (Due to peak overlap, all resonances between 3.71 and 3.37 are integrated as one peak, 29.6H) (epoxy) $C\underline{H_2}O(CH_2)_3$ diastereotopic 3.72, 3.68 (dd, J 2.81 Hz) 3.46, 3.42 (m), $SiCH_2CH_2C\underline{H_2}O$ and $SiCH(CH_3)C\underline{H_2}O$ 3.5-3.3 (m), $OCH_2C\underline{H}$ (epoxy) 3.14 (m, 7.2H), $C\underline{H_2}$ (epoxy) diastereotopic 2.79 (m, 7.2H), 2.61 (m, 7.1H), $SiCH_2C\underline{H_2}CH_2O$ 1.67 (m, 15.5H), $SiC\underline{H}(CH_3)CH_2O$ 1.30 (m, 0.8H), $SiCH(C\underline{H_3})CH_2O$ 1.07 (m, 2.7H), $SiC\underline{H_2}CH_2CH_2O$ 0.66 (m, 14H); ^{13}C NMR (90 MHz, $CHCl_3$, 25°C) δ $SiCH_2CH_2\underline{C}H_2O$ 73.4, $SiCH(CH_3)\underline{C}H_2O$ 72.8, (epoxy) $\underline{C}H_2O(CH_2)_3Si$ 71.4, $OCH_2\underline{C}H$ (epoxy) 50.8, $\underline{C}H_2$ (epoxy) 44.3, $SiCH_2\underline{C}H_2CH_2O$ 22.9, $Si\underline{C}H(CH_3)CH_2O$ 19.3, $SiCH(\underline{C}H_3)CH_2O$ 11.3, $Si\underline{C}H_2CH_2CH_2O$ 8.1, 7.9; ^{29}Si NMR (71.5 MHz, $CHCl_3$, 25°C) δ $\underline{Si}CH_2CH_2CH_2O$ -66.2, $\underline{Si}CH(CH_3)CH_2O$ -68.2, $\underline{Si}H$ -83.7, $\underline{Si}H$ -85.6 ($T_{10-n}^{H}T_n^{E}$). FTIR (neat film, cm^{-1}) 3044, 2962, 2934, 2874 (m, C-H str.); 2260 (w, Si-H str.); 1210 (s, C-O-C str.); 1102 (vs, Si-O str.); 885 (s, C-O-C bend).

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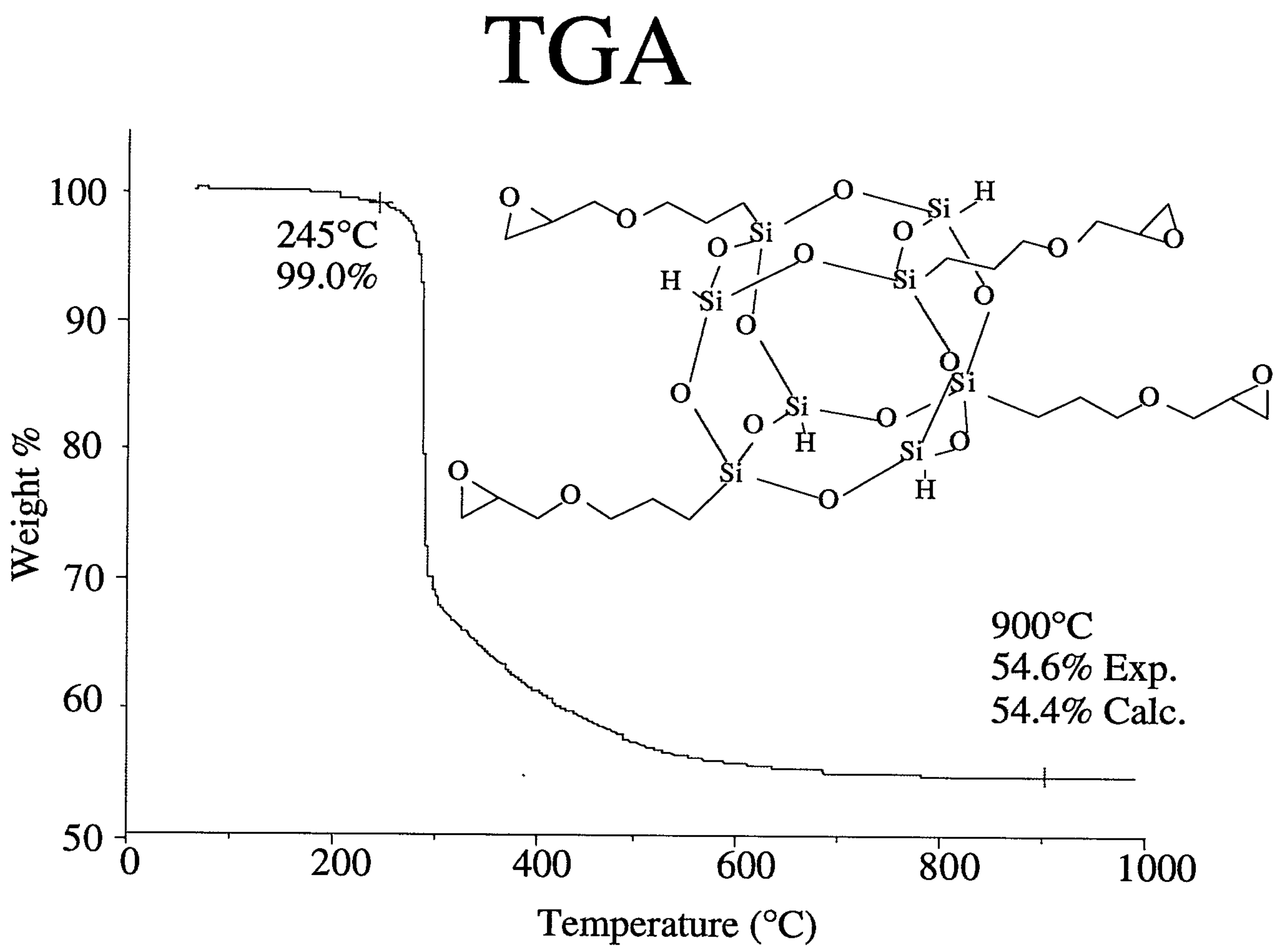

Figure 1- TGA trace for tetra(propylglycidylether)silsesquioxane, $T_4^HT_4^E$

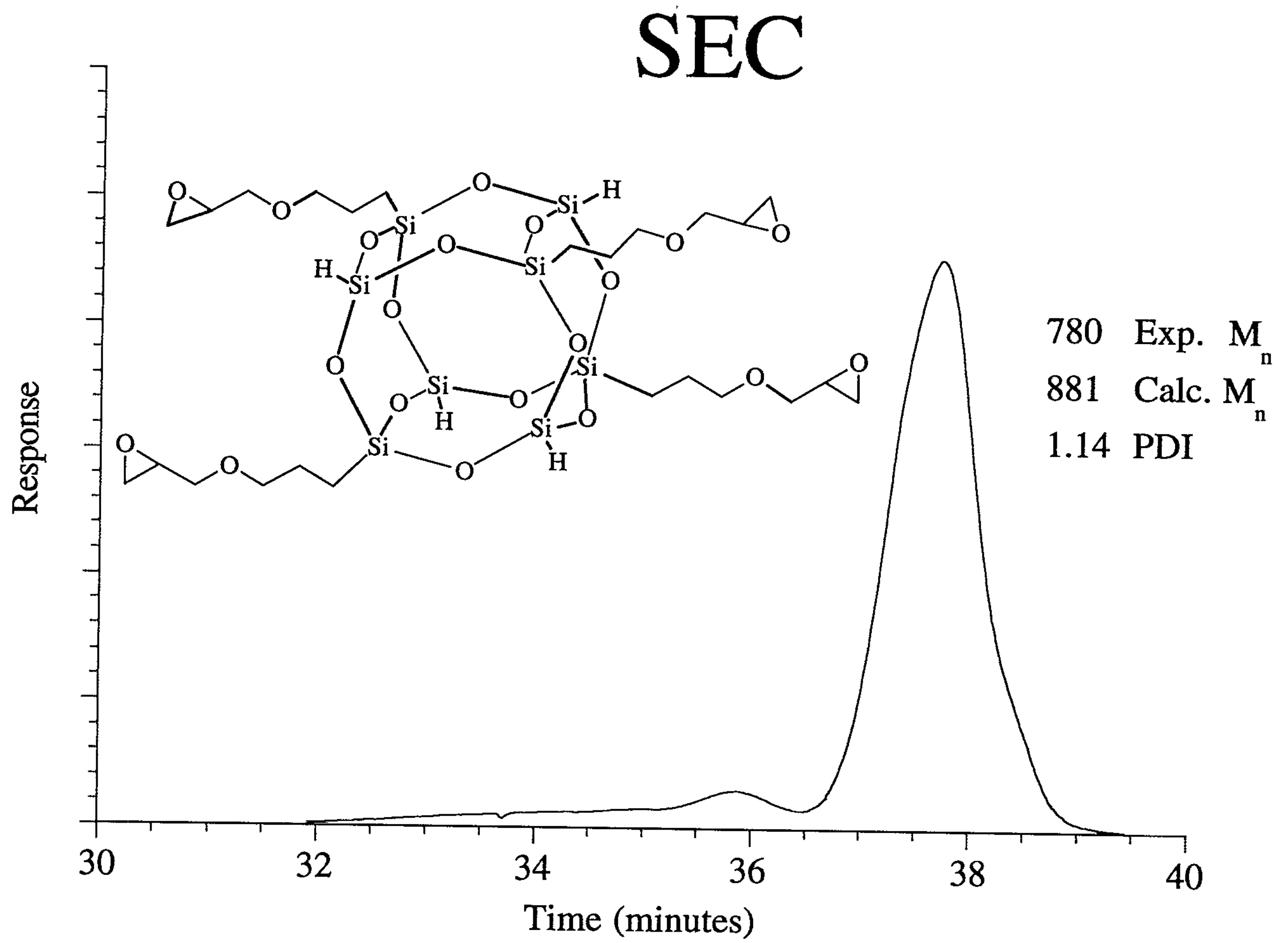

Figure 2- SEC trace for tetra(propylglycidylether)silsesquioxane, $T_4^HT_4^E$

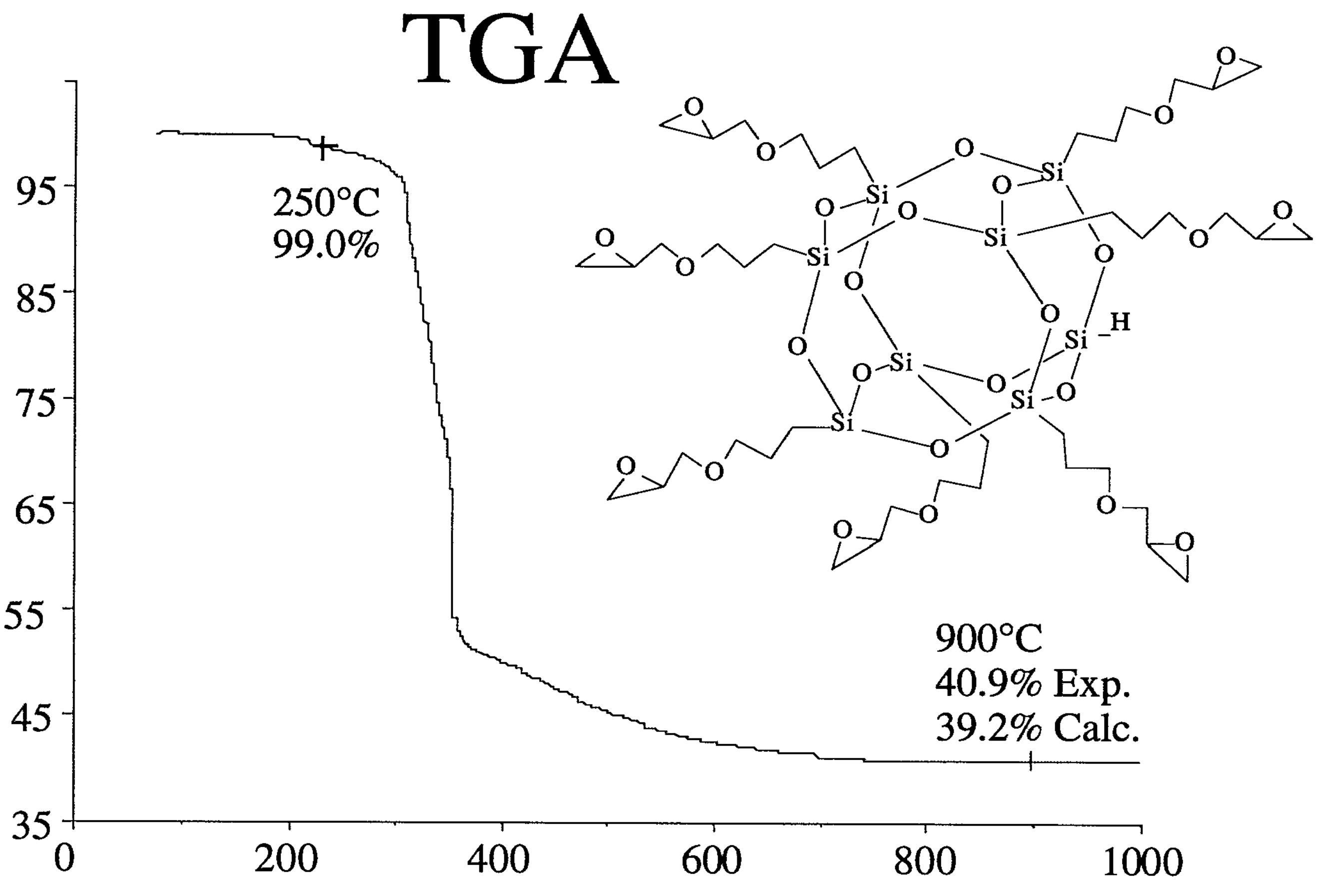

Figure 3- TGA trace for octa(propylglycidylether)silsesquioxane, $T_1^HT_7^E$

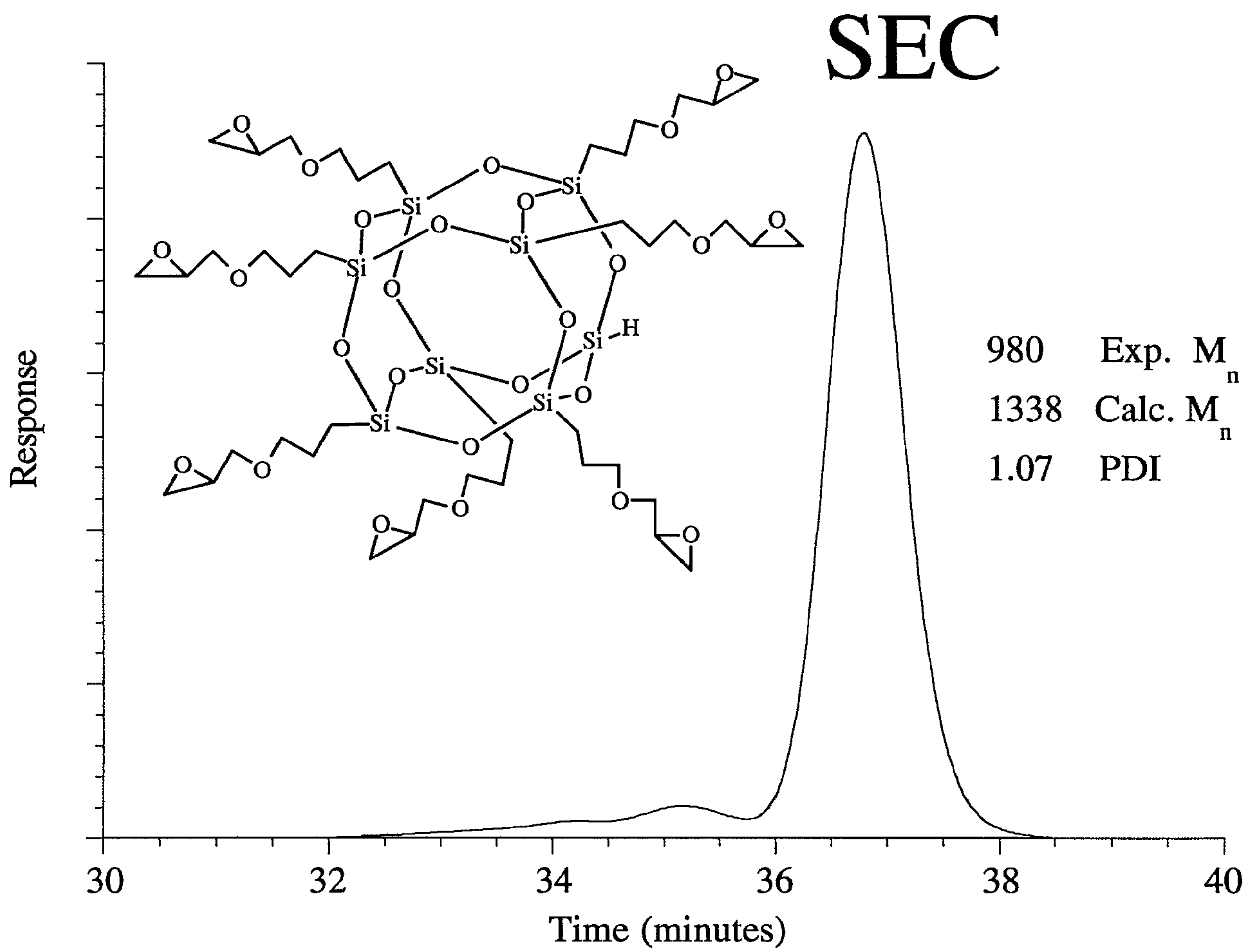

Figure 4- SEC trace for octa(propylglycidylether)silsesquioxane, $T_1^HT_7^E$

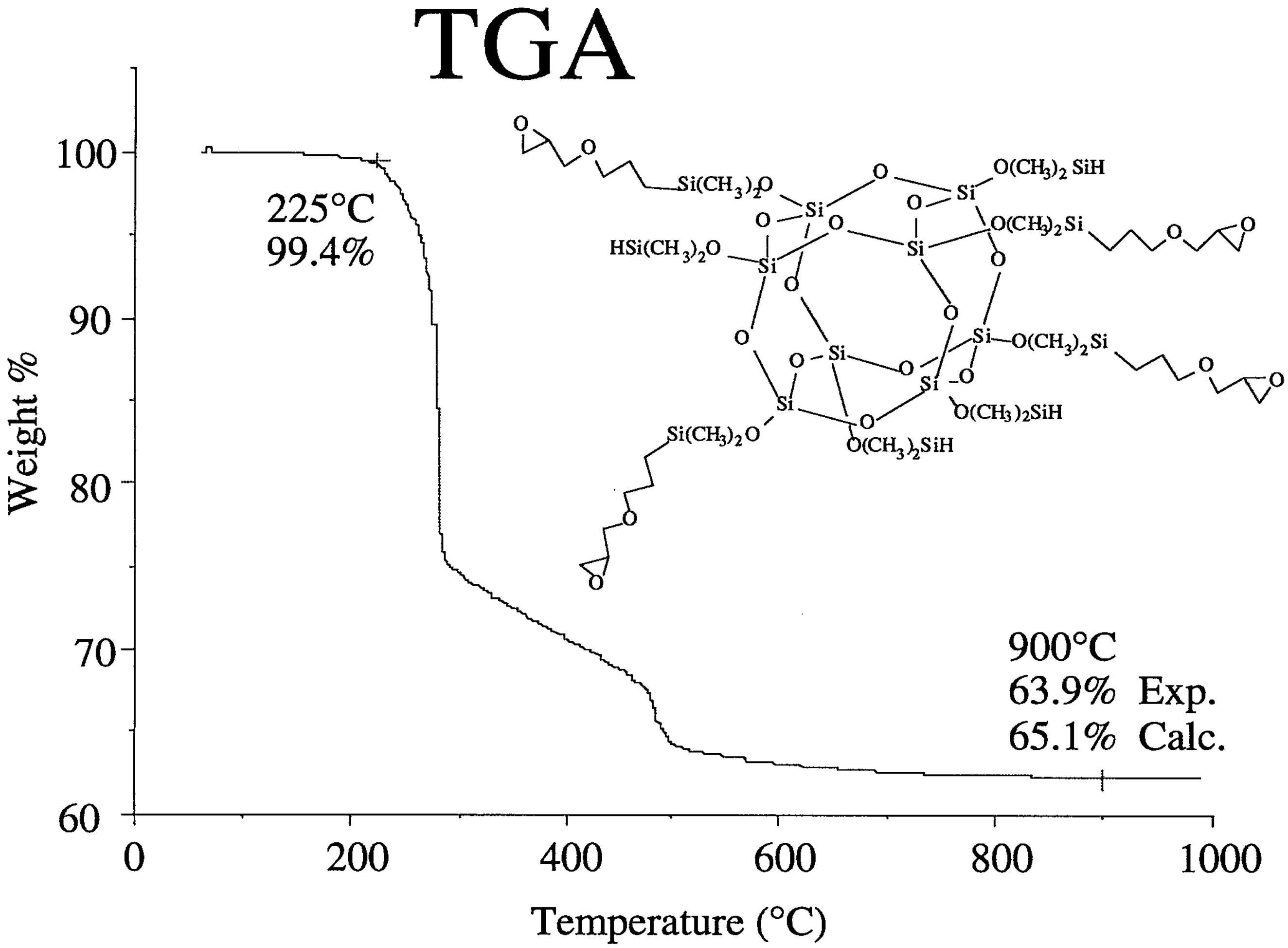

Figure 5- TGA trace for tetra(dimethylsiloxypropylglycidylether)silsesquioxane, $Q_8M_4{}^HM_4{}^E$

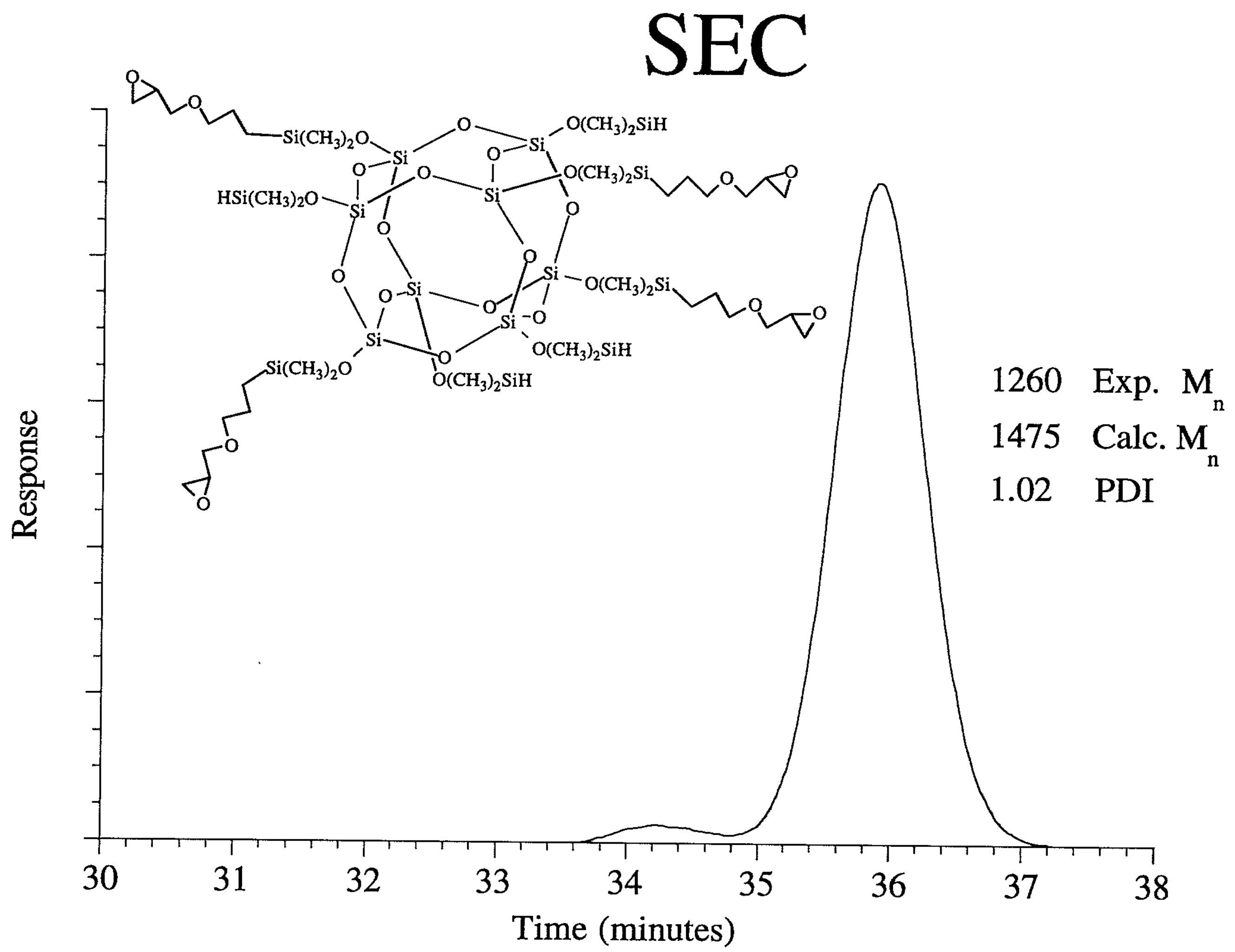

Figure 6- SEC trace for tetra(dimethylsiloxypropylglycidylether)silsesquioxane, $Q_8M_4^HM_4^E$

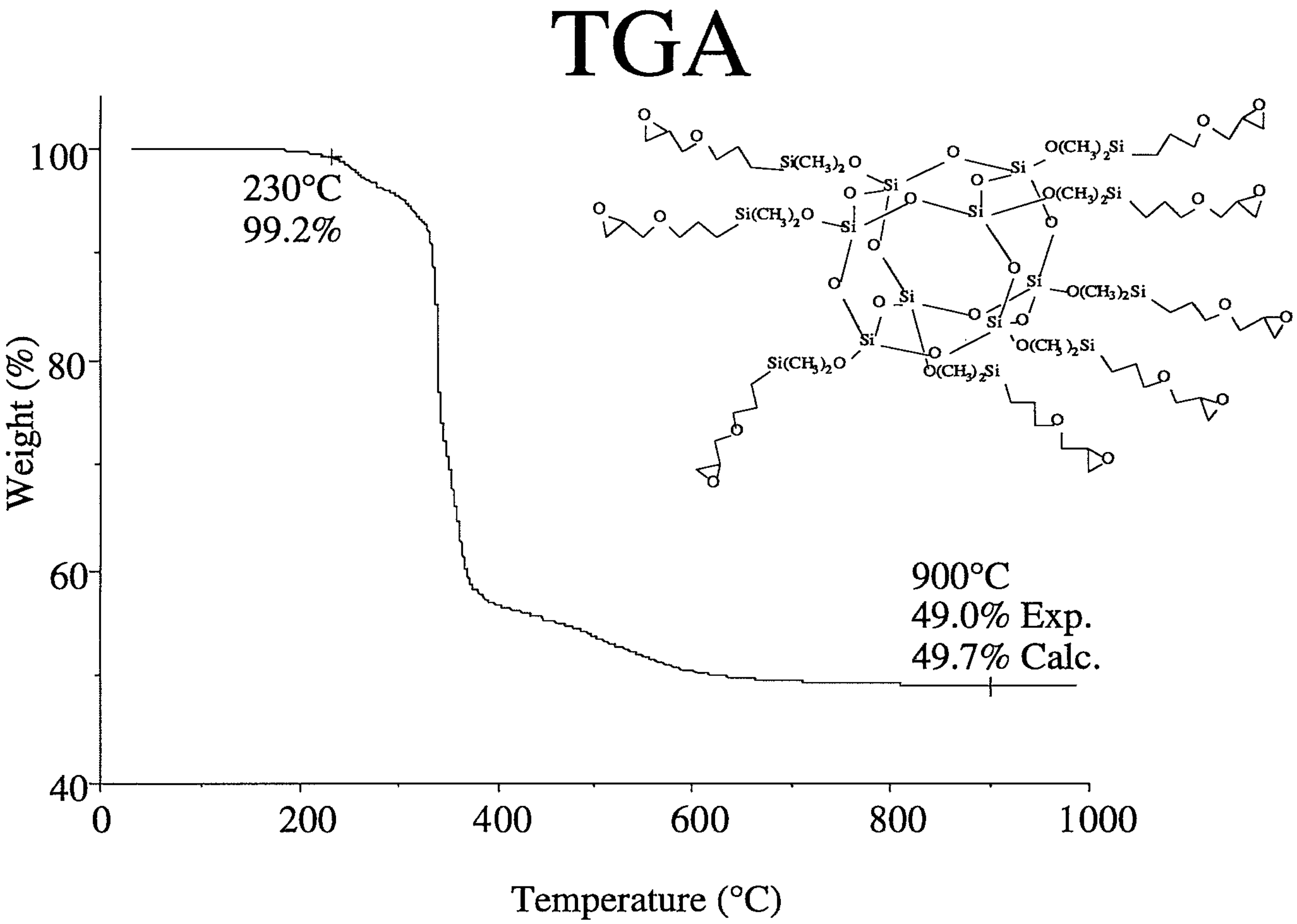

Figure 7- TGA trace for octa(dimethylsiloxypropylglycidylether)silsesquioxane, $Q_8M_8^E$

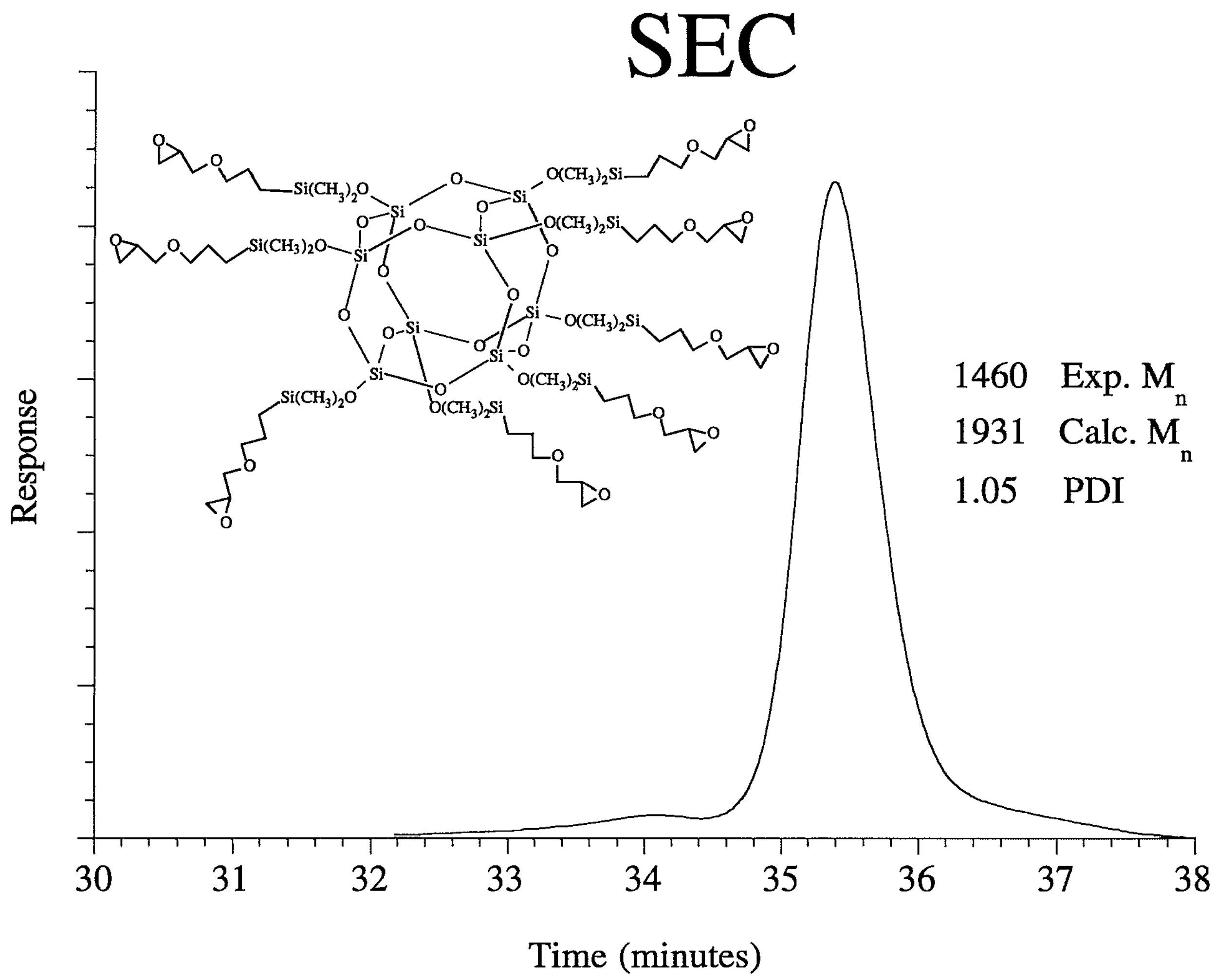

Figure 8- SEC trace for octa(dimethylsiloxypropylglycidylether)silsesquioxane, $Q_8M_8^E$