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FUNCTIONAL POLYMERS 65. SYNTHESIS AND BRIEF CHARACTERIZATION OF SURFACE ACTIVE 2(2-HYDROXYPHENYL)2H-BENZO-TRIAZOLE ULTRAVIOLET STABILIZERS

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FUNCTIONAL POLYMERS 65. SYNTHESIS AND BRIEF CHARACTERIZATION OF SURFACE ACTIVE 2(2-HYDROXYPHENYL)2H-BENZOTRIAZOLE ULTRAVIOLET STABILIZERS

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Key Words: 2(2-Hydroxyphenyl)2H-benzotriazoles, Surface Active UV Stabilizers, Morphology Engineering, 2(2-Hydroxy-5-Substituted-phenyl)2H-benzotriazoles, Polymerizable and Polymer Bound 2(2-Hydroxyphenyl)2H-benzotriazoles, Contact Angle Measurements

ABSTRACT

A number of 2(2-hydroxyphenyl)2H-benzotriazoles substituted in the 5-position with reactive hydroxyl and carboxyl groups have been synthesized. They include compounds with a *tert* butyl substitution in the 3-position or without substitution. The latter compounds were subjected to a reaction with N-hydroxy-

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methyl-(meth)acrylamide to form acrylic polymerizable 3(meth) acrylamidomethyl-2(2-hydroxyphenyl)2H-benzotriaz-oles. Hydroxyl reactive compounds were allowed to react with long chain acids, compounds with carboxyl groups with long chain hydrocarbon, fluorocarbon or silicon oligomer alcohols. The polymerizable 2(2-hydroxyphenyl)2H-benzotriazoles were then copolymerized with methyl methacrylate. Films made from such polymers showed by contact angle measurements, substantial migration of the fluorocarbon or silicon component to the surface of the film.

INTRODUCTION

Ultraviolet stabilizers (UV) are needed to protect most polymers from the detrimental effect of the exposure to sunlight, particularly the radiation between 290 and 400 nm. For each category of polymeric materials there is a favored UV stabilizer. The most common stabilizers are UV screeners. A number of categories of this kind of UV stabilizers were developed and are used. They include aminobenzoates, salicylates, and 4-hydroxybenzophenones [1].

Since the 1960's, 2(2-hydroxyphenyl)2H-benzotriazoles, first synthesized by Elbs [2, 3], and recognized as UV stabilizers in the mid 50's [4, 5], have been investigated. Cost and consequently limited demand, have kept them from wide use until quite recently [6].

For 20 years, we have been interested in 2(2-hydroxyphenyl)2H-benzotriazoles, because of our inherent interest in polymerizable functional monomers. During this period we developed:

(I) a) 2(2-hydroxyphenyl)2H-benzotriazole derivatives with various substituents to control the maximum absorptivity [7-10]; b) 2(2-hydroxyphenyl)2H-benzotriazoles with more than one benzotriazole group in the molecule [11, 12]; c) 2(2-hydroxyphenyl)2H-benzotriazole derivatives with functional groups for further reactions [13-15]; d) 2(2-hydroxyphenyl)2H-benzotriazole derivatives with other chromophores in the molecule [16].

(II) a) Polymerizable 2(2-hydroxyphenyl)2H-benzotriazole derivatives: a.) Styryl type 2(2-hydroxyphenyl)2H-benzotriazole derivatives [17-20]; b) (Meth)acrylate type 2(2-hydroxyphenyl)2H-benzotriazole derivatives [21-24];. c) (Meth)acrylamidomethyl and maleimidomethyl substituted 2(2-hydroxyphenyl)2H-benzotriazole derivatives; d) Dihydroxy and dicarboxy substituted bisbenzotriazole derivatives as (co)monomers for polyesters, polycarbonates and polyamides [25-28]; e) 2(2-hydroxyphenyl)2H-benzotriazole derivatives suitable for incorporation into “drying oil” type polymers including Japanese lacquers [29].

(III) Reactions on polymers with reactive groups; a) Reactions of poly(glycidyl methacrylate) with the appropriate 2(2-hydroxyphenyl)2H-benzotriazole derivatives [30]; b) Reactions of hydroxyl containing 2(2-hydroxyphenyl)2H-benzotriazole derivatives with epoxylated polymers [30]; c) Grafting of polymerizable 2(2-hydroxyphenyl)2H-benzotriazole derivatives onto polymers [31-33].

(IV) Polymerizable 2(2-hydroxyphenyl)2H-benzotriazole derivatives with the right functionalities that allow the use of copolymers for the manufacture of contact lense applications (32-34% water absorption and more than 80% of light absorption at 400 nm).

It was the objective of the work in this paper to develop 2(2-hydroxyphenyl)2H-benzotriazoles for specific tasks, in our case to effect the assembly of specifically designed 2(2-hydroxyphenyl)2H-benzotriazole derivatives where they are most needed. Our work was divided into two parts. First, to blend the specific 2(2-hydroxyphenyl)-2H-benzotriazole derivatives with the designated polymer. Second to design polymerizable 2(2-hydroxyphenyl)2H-benzotriazole derivatives that could be homopolymerized or copolymerized with the desired monomer. With the proper design, we expected the stabilizer to stratify, concentrate, or bloom to the surface and provide stabilization where it is most needed. For polymer bound stabilizers where the entire (co)polymer chain containing the stabilizer migrates toward the surface, we coined the expression “morphology engineering”. In any case, the polymer surface would be covered by long “functional” side groups of the UV stabilizing molecules.

EXPERIMENTAL

Materials

The following chemicals were obtained from the sources indicated.

N,N'-carbonyl diimidazole (CDI) (A), hexadecanol-1(A), N-(hydroxymethyl)acrylamide (A), 2(2-hydroxy-5-methylphenyl)2H-benzotriazole (C), 3(4-hydroxyphenyl)propionic acid (A), 2-nitroaniline (A), 2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctanol-l (A), 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctanol-1 (A), mixtures of perfluoroalcohols, (× = 8-18)(AG), polydimethylsiloxane, carbinol terminated (MW = 2,400) (P), p-toluene sulfonic acid (A), Tinuvin 1130 (C).

Sources: A=Aldrich Chemical Co.; AG=Asahi Glass Co.; C=Ciba-Geigy Co.; P=Petrarch Systems.

Purification of Solvents and Chemicals

The solvents for the absorption and fluorescence measurements were all used as received from Aldrich Chemical Co. (HPLC, Sure Seal bottles). Chlorinated solvents were not used for fluorescence measurements. For all chemical reactions, anhydrous grade solvents as obtained from Aldrich Chemical Co. were found to be satisfactory. All other chemicals were used as received.

Measurements

^{1}H NMR and ^{13}C NMR measurements were carried out on a Varian EM-390 90-MHz or on a General Electric GN 300 MHz spectrometer. The 2(2-hydroxyphenyl)2H-benzotriazole derivatives were measured in deuterated acetone, dimethylsulfoxide or chloroform, depending on their solubility. Chemical shifts are reported in parts per million (ppm) downfield from TMS.

Melting points were determined on a Mel-Temp melting point apparatus. Open capillary tubes were used in the measurements. The melting points were measured at a heating rate of 2°C/min.; they are uncorrected.

The nominal molecular weights of the synthesized 2(2-hydroxyphenyl)2H-benzotriazole compounds were determined by potassium ionization of desorbed species (K^+IDS) mass spectrometry. The measurements were performed on a modified Finnigan 4615B quadrupole GC/MS system. An elactron impact, El, source configuration was used in all experiments. The molecular weights are reported in daltons (Da) where one Da =1/12 of the mass of a single atom of the isotope carbon-12. See Reference [34] for a more detailed description of the K^+IDS technique.

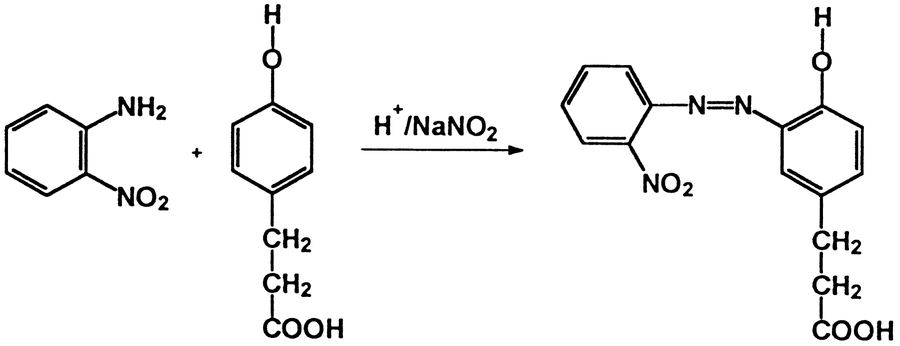
Infrared spectra were recorded on a Perkin Elmer model 727 or on a Shimadzu IR435 spectrometer. Solid samples of low molecular weight compounds were measured as potassium bromide pellets.

Ultraviolet-visible absorption spectra were recorded on a Varian-Cary 2300 or a 210 spectrophotometer in a double-beam servo mode. The spectra of the 2-(2-hydroxyphenyl)2H-benzotriazole derivatives were determined in chloroform at concentrations in the range 10^{-4} to 10^{-5} M. The sample solutions were measured in quartz cells which had either a 0.01 cm or a 1.0 cm optical path length. The spectra were recorded and digitized. After digitization, the spectra were compared with the original spectra to ascertain accuracy.

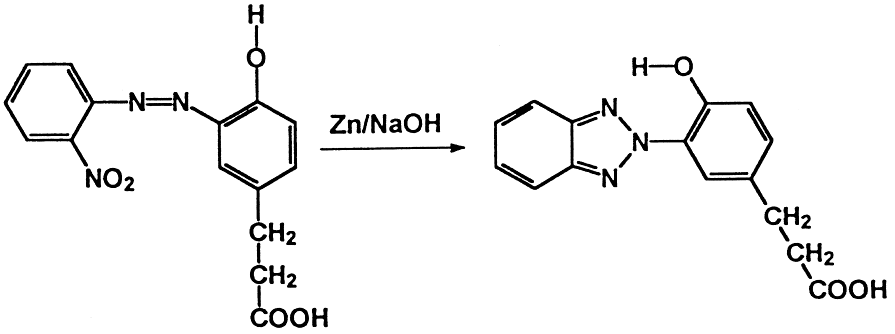
Procedures

Synthesis of 2(2-Hydroxyphenyl)2H-benzotriazoles

2[2-Hydroxy-5(2-carboxyethyl)phenyl]2H-benzotriazole or (3'[5(2H-Benzotriazol-2-yl) 4-hydroxyphenyl]propionic acid (BHPA)

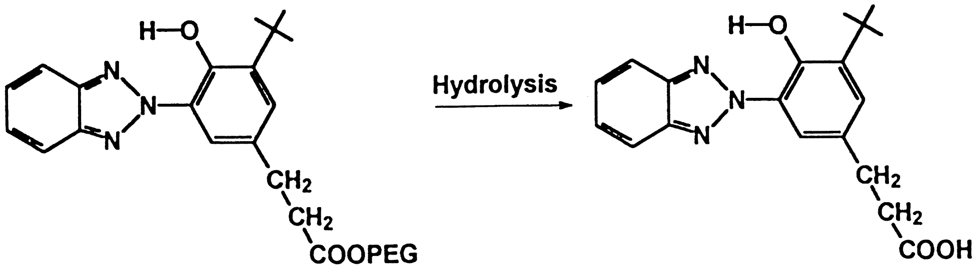


A 1.0 L beaker in a salt ice-water bath at -5°C was charged with 2-nitroaniline (41 g, 0.3 mol), 150 mL conc. hydrochloric acid and 300 mL water. The resulting 2-nitroaniline hydrochloride was kept at -5°C and a solution of sodium nitrite (21 g, 0.3 mol) in 70 mL water, also chilled to -5°C, was added over a period of one hour; the diazonium salt was obtained. At the final stage of the addition of the sodium nitrite solution the mixture became homogeneous, except for a small amount of insoluble material that was filtered off while the solution was kept at -5°C. A 5.0 L three-neck round bottom flask was charged with sodium carbonate (192 g), sodium hydroxide (60 g) in 1.5 L water and 3(4-hydroxyphenyl)propionic acid (51 g, 0.3 mol). The solution was cooled to 20°C and the cold orange colored diazonium chloride salt solution was added through a dropping funnel under mechanical stirring over a period of two hours. The reaction mixture was stirred at room temperature for an additional 3 hours. The dark red brown solution was then slowly acidified with conc. hydrochloric acid to pH =1. A red precipitate formed; it was collected by filtration and washed with water (2.5 L). After drying, a dark red powder weighing 82 g (87% yield) was obtained.



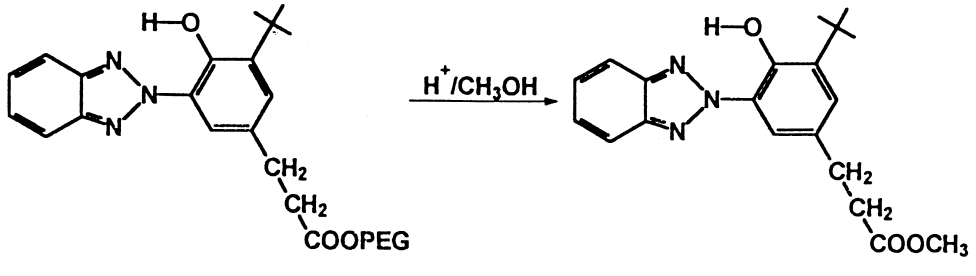
A 3.0 L three-neck round bottom flask was charged with the reddish-brown azo-compound (82 g) and a solution of sodium hydroxide (40 g) in 1.0 L of water. Under mechanical stirring, zinc powder (88 g, 1.35 mol) was added over a period of one hour to the suspension, followed by sodium hydroxide (300 g) in 750 mL water over a period of two hours. The suspension was stirred at room temperature for an additional 3 days, filtered, and the filter cake was washed several times with an aqueous 5% sodium hydroxide solution. The dark orange filtrate turned brown on standing and conc. hydrochloric acid was carefully added. At pH =12 a brown precipitate formed which was separated by filtration. The filter cake (53 g) was dissolved in 2N hydrochloric acid; a dark brown residue (5 g) remained. The solution was adjusted to pH = 7-8; a greenish precipitate formed which was isolated by filtration. It was washed with hydrochloric acid and had a brownish-gray color. The residue was extracted with ethanol and recrystallized from ethanol several times, yielding 41 g (48%) of 3'[5(2H-benzotriazol-2-yl)4-hydroxyphenyl]propionic acid (BHPA); m.p.: 169-172°C. The K^+IDS mass spectrum showed a cluster of ions at 322 Da including K^+, which gives a nominal mass of [M] = 283 Da and isotopes supporting a $[C_{15}H_{13}N_3O_3]K^+$ formula. The ^{1}H-NMR spectrum (in deuterated acetone) showed chemical shift peaks at δ (ppm): 2.6-2.8 (Ar-C$\underline{H}_2$-CH$_2$-COOH, 2H, t), 2.9-3.1 (Ar-C$\underline{H}_2$-CH$_2$-COOH, 2H, t), 7.1-8.3 (protons of the phenoxy and benzotriazole groups, 7H). The ^{13}C NMR spectrum showed chemical shift peaks at δ (ppm): 29-32 (Ar-C$\underline{H}_2$-CH$_2$-COOH, 1 C), 35-36 (Ar-CH$_2$C$\underline{H}_2$-COOH, 1C), 118-129 (carbons of the phenoxy and benzotriazole groups, 12 C). The ul-traviolet-visible spectrum in chloroform showed maxima at λ = 3 00 nm, ε_1 = 12,750 and at λ = 339 nm, ε_2 = 16,000 L/mol.cm.

2[2-Hydroxy-3-*tert* butyl-5-(2-carboxyethylphenyl]2H-benzotriazole or 3'[5(2H-Benzotriazol-2-yl)-4-hydroxy-3-*tert* butyl-phenylpropionic acid (BHTPA)]



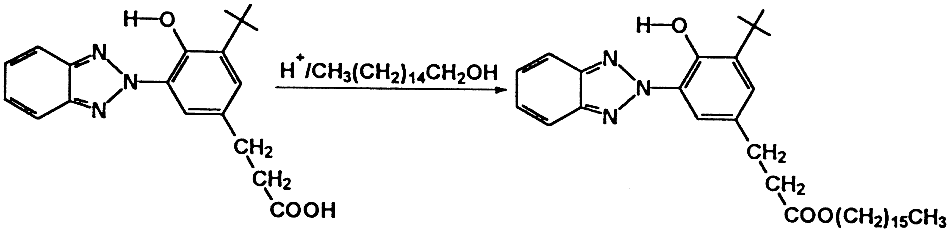
A mixture of polyethyleneglycol-3'[5(2H-benzotriazol-2-yl)4-hydroxy-3-*tert* butylphenyl]propionate (107 g, 0.15 mol) was placed in a 1.0 L round bottom flask. Sodium hydroxide (30 g, 0.75 mol), a five times excess, in 300 mL water were added. The 1.0 L three-neck round bottom flask was equipped with a reflux condenser and the solution was heated under reflux for four hours. The solution was added to 1.0 L of water and conc. hydrochloric acid was added until the precipitation caused by the acid addition was completed. The precipitate was separated by filtration, washed several times with water and the solid was recrystallized from ethanol. Fine white needles were obtained which were dried and 3'[5(2H-benzotriazol-2-yl) 4-hydroxy-3-*tert* butylphenyl]-propionic acid (BHTPA) 50.5 g (yield about 99%) was obtained; m.p.: 199-200°C. The K^+IDS mass spectrum showed: a nominal molecular ion of 378 Da including K^+ and an isotope envelope supporting a $[C_{19}H_{21}N_3O_3]K^+$ molecular formula. The ^{1}H NMR spectrum (in deuterated acetone) showed chemical shift peaks at δ (ppm): 1.5-1.6 (*tert* butyl group, 9H, s), 2.6-2.8 (Ar-C$\underline{H}_2$-CH,-COOH, 2H, t), 2.9-3.1 (Ar-C$\underline{H}_2$-CH$_2$-COOH, 2H, t), 7.1-8.3 (protons of phenoxy and benzotriazole groups, 7H), 11.8-11.9 (intramolecular hydrogen bond). The ^{13}C NMR spectrum showed chemical shift peaks at δ (ppm): 29-32 (carbons of *tert* butyl group and Ar-C$\underline{H}_2$-CH$_2$-COOH, 5C), 35-36 (Ar-C$\underline{H}_2$-CH$_2$-COOH, 1C), 118-129 (carbons of the phenoxy and benzotriazole groups, 12 C). The ultraviolet-visible spectrum in chloroform showed maxima at λ=303 nm, ε_1=14,300 and at λ=344, ε_2=14,600 L.mol.cm.

2[2-Hydroxy-3-*tert* butyl-5(2-carbomethoxyethyl)phenyl]2H-benzotriazole or Methyl 3'[5(2H-benzotriazol-2-yl)4-hydroxy-3-*tert* butylphenyl]-propionate] (MBHTPA)



A 500 mL three-neck round bottom flask equipped with a reflux condenser and a Dean-Stark trap,was charged with a mixture of poly-ethyleneglycol-3'-[5(2H-benzotriazol-2-yl)4-hydroxy-3-*tert* butylphenyl]propi- onate (21 g, 0.03 mol) and 200 mL methanol. Under mechanical stirring 30 mL conc. sulfuric acid were added and the reaction mixture was heated to reflux for 4 hours. After 30 minutes, a white precipitate started to form. After 4 hours the reaction mixture was cooled to room temperature and the precipitate was isolated by filtration. The filter cake was washed several times with water and the product was recrystallized from ethanol. After drying the yield of methyl 3'-[5(2H-benzotriazol-2-yl)-4-hydroxy-3-*tert* butylphenyl]propionate (MBHTP) was 10.5 g (99%); m.p.: 127-128°C. The K^+IDS mass spectrum showed a nominal molecular ion of 392 Da including K^+ and an isotope distribution supporting a $[C_20H_{23}N_3O_3]K^+$ molecular formula. The ^1H NMR spectrum (in deuterated acetone) showed chemical shift peaks at δ (ppm): 1.5-1.6 (*tert* butyl group, 9H, s), 2.6-2.8 ($Ar-CH_2-CH_2COOCH_3$, 2H, t), 2.9-3.1 ($Ar-CH_2-CH_2$- $COOCH_3$, 2H, t), 3.6-3.7 ($Ar-CH_2-CH_2COOCH_3$, s), 7.1-8.3 (protons of phenoxy and benzotriazole groups, 7H), 11.8-11.9 (intramolecular hydrogen bond). The ^{13}C NMR spectrum (in deuterated acetone) showed chemical shift peaks at δ (ppm): 29-32 (*tert* butyl group and $Ar-CH_2-CH_2-COOCH_3$, 5C), 36-37 ($Ar-CH_2-CH_2-COOCH_3$, 1C), 51-52 ($Ar-CH_2-CH_2-COOCH_3$, 1C), 118-129 (carbons of the phenoxy and benzotriazole groups, 12C), 173-174 ($Ar-CH_2-CH_2-COOCH_3$, 1C,). The ultraviolet-visible spectrum showed maxima at λ=303 nm, ε_1=14,800 and λ=344 nm, ε_2=14,900 L.mol.cm.

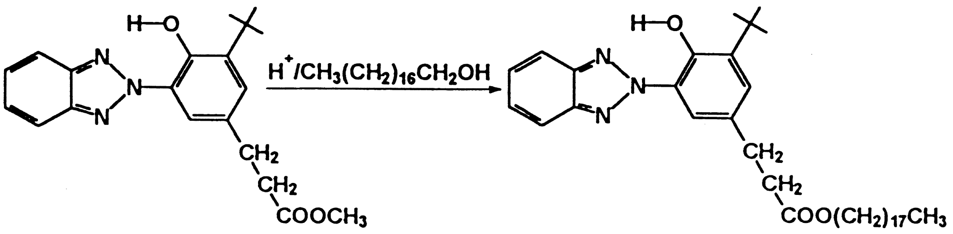
2(2-Hydroxy-3-*tert* butyl-5(2-carbohexadecyloxyethyl)phenyl]-2H-benzotriazole or [1-Hexa-decyl 3'[5(2H-benzotriazol-2-yl)- 4-hydroxy-3-*tert* butylphenyl]propionate] (HBHTPA)



A 250 mL three-neck round bottom flask equipped with a reflux condenser and a Dean-Stark trap, was charged with 3'[5(2H-benzotriazol- 2-yl)-4-hydroxy-3-*tert* butylphenyl]propionic acid (BHTPA) (2.0 g, 6 mmol), hexadecanol-1 (3.45 g, 6 mmol) and p-toluenesulfonic acid (1.2 g, 6 mmol). The mixture was heated to reflux in 100 mL chloroform for 4 hours, cooled and washed in a separation funnel with water, sodium hydrogen carbonate and sodium carbonate. With the addition of sodium carbonate, a precipitate formed throughout both layers. The addition of 20 mL chloroform separated both layers. It was again washed with sodium hydrogen carbonate. The solvent was removed *in vacuo* and the remaining white solid was recrystallized from ethanol. After drying the yield of 1-hexadecyl-3'-[5(2H-benzotriazol-2-yl)-4-hydroxy-3-*tert* butylphenyl]propionate (HBHTP) was 1.7 g (50%, 3 mmol); m.p.: 69-70°C. The K^+IDS mass spectrum showed a nominal molecular ion of 602 Da including K^+ plus an isotope distribution supporting a $[C_{35}H_{53}N_3O_3]K^+$ molecular formula. The ^{1}H NMR spectrum (in deuterated chloroform) showed chemical shift peaks at δ (ppm): 0.8-0.9 (Ar-$C\underline{H}_2$-CH_2-COO$(CH_2)_{15}CH_3$,3H, t), 1.2-1.6 (*tert* butyl-methyl groups and -methylene groups, 35H), 2.1-2.2 (Ar-$C\underline{H}_2$-CH_2-$COOCH_2$-CH_2-R, 2H, s), 2.6-2.8 (Ar-$C\underline{H}_2$-CH_2-$COOCH_2$-CH_2-R, 2H, t), 2.9-3.1 (Ar-$C\underline{H}_2$-CH_2-$COOCH_2$-CH_2-R, 2H, t), 4.0-4.2 (Ar-$C\underline{H}_2$-CH_2-$COOCH_2$-CH_2-R, 2H, t), 7.1-8.3 (protons of phenoxy and benzotriazole groups, 7H), 11.8-11.9 (intramolecular hydrogen bond). The ^{13}CNMR spectrum (in deuterated chloroform) showed chemical shift peaks at δ (ppm): 14-15 (Ar-$\underline{C}H_2$-CH_2-$COOCH_2$-CH_2-R-$(CH_2)_{13}$-CH_3, 1C), 22-23 (Ar-$\underline{C}H_2$-CH_2-$COOCH_2$-CH_2-R-$(CH_2)_{12}$-CH_2-CH_3, 1C), 25-26 (Ar-$\underline{C}H_2$-CH_2-$COOCH_2$-CH_2-R-CH_2-$(CH_2)_{12}$-CH_3, 1C), 28-31 (carbons in *tert* butyl group and Ar-$\underline{C}H_2$-CH_2-$COOCH_2$-$\underline{C}H_2$-CH_2-

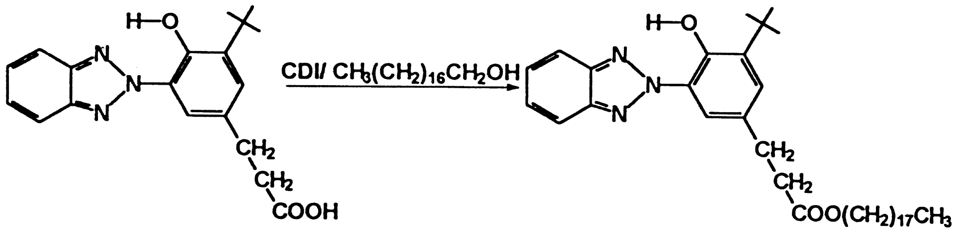
$(\underline{C}H_2)_{10}$-CH_2-CH_2-CH_3, 16C), 31-32 (Ar-CH_2-CH_2-COO-$(CH_2)_{13}$-$\underline{C}H_2$-CH_2-CH_3, 1C), 35-37 (Ar-CH_2-$\underline{C}H_2$-COOR, 1C), 64-65 (ArCH_2-CH_2-COO$\underline{C}H_2$-R, 1C, s), 117-148 (carbons of the phenoxy and benzotriazole groups, 12C), 173-174 (Ar-CH_2-CH_2-$\underline{C}$OOR, 1C). The ultraviolet-visible spectrum showed maxima at λ=303 nm, $^{\varepsilon}{}_1$=14,700 and at λ=344 nm, $^{\varepsilon}{}_2$=14,800 L.mol.cm.

2[2-Hydroxy-3-*tert* butyl-5-(2-carbooctadecyloxyethyl)phenyl]2H-benzotriazole or 1-Octadecyl-3'[5(2H-benzotriazol-2-yl)-4-hy-droxy-3-*tert* butylphenyl]propionate (OBHTPA)



A 250 mL three-neck round bottom flask equipped with a reflux condenser and a Dean-Stark trap, was charged with methyl 3'[5(2H-benzo-triazol-2-yl)4-hydroxy-3-*tert* butylphenylpropionate (MBHTP) (1.0 g, 3 mmol), octadecanol-1 (0.8 g, 3 mmol) and p-toluenesulfonic acid (0.6 g, 3 mmol). The mixture was heated to reflux in 50 mL benzene for 4 hours; it lost its cloudiness at about 60°C. The reaction mixture was cooled down and the solvent was removed under reduced pressure. The remaining white solid was recrystallized from ethanol. The yield of 1-octadecyl-3'-[5(2H-benzotri-azol-2-yl)-4-hydroxy-3-*tert* butylphenyl]propionate (OBHTP) was 1.2 g (65%).

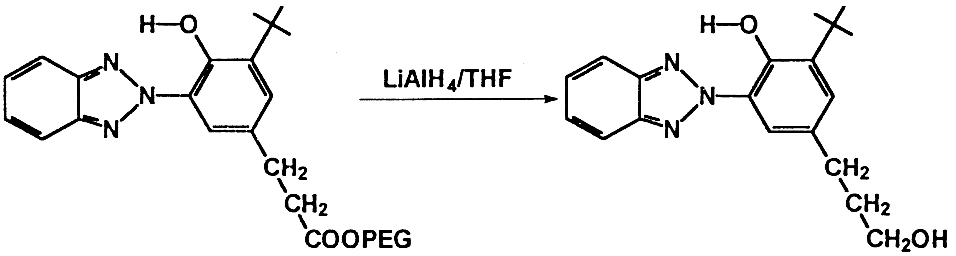
A 250 mL three-neck round bottom flask was equipped with a reflux condenser and a Dean-Stark trap was charged with 3'[5(2H-benzotriazol-2-yl)-4-hydroxy-3-*tert* butylphenyl]propionic acid (BHTPA) (1.4 g, 4 mmol), octadecanol-1 (0.8 g, 3 mmol) and p-toluenesulfonic acid (0.6 g, 3 mmol). The mixture was heated to reflux in 50 mL benzene for 4 hours; it lost its cloudiness at about 65°C. The reaction mixture was cooled and the solvent was removed under reduced pressure. The remaining white solid was recrystallized from ethanol. The yield of 1-octadecyl-3'-[5(2H-benzo-triazol-2-yl)-4-hydroxy-3-*tert* butylphenyl]propionate (OBHTP) was 1.6 g (88%).



A 250 mL round bottom flask was charged with 3'-[5-(2H-benzo-triazol-2-yl)-4-hydroxy-3-*tert* butylphenyl]propionic acid (BHTPA) (1.0 g, 3 mmol) in 50 mL benzene. Under nitrogen atmosphere N,N'-carbonyl diimidazole (0.6 g, 3.7 mmol) were added. The mixture was stirred for an additional 30 minutes and octadecanol-1 (0.8 g, 3 mmol) were added. The color of the solution remained yellowish. The solution was heated to reflux for 4 hours and stirred at room temperature for an additional 4 days. The solvent was removed *in vacuo* and the remaining white solid was recrystallized from ethanol. The yield of 1-octadecyl-3'[5(2H-benzotriazol-2-yl) 4-hydroxy-3-*tert* butylphenyl]-propionate (OBHTP) was 1.1 g (62%). m.p.: 68-69°C. The K^+IDS mass spectrum showed a [M] of 591 Da (630 Da including K^+) plus an isotope distribution supporting a $[C_{37}H_{57}N_3O_3]K^+$ molecular formula, calc. [M] = 591 Da.

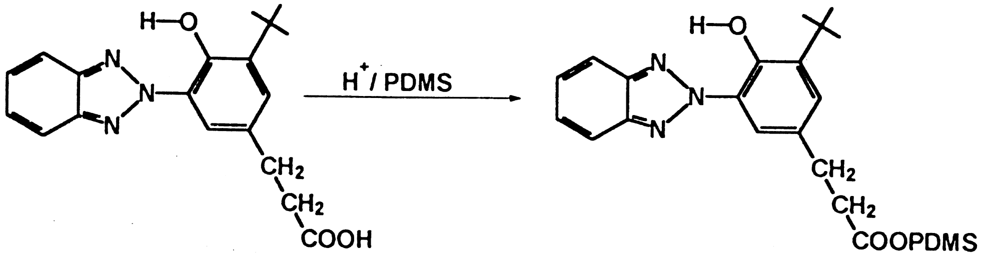
The ^{1}H NMR spectrum (in deuterated chloroform) showed chemical shift peaks at δ ppm): 0.8-0.9 ($Ar\text{-}CH_2CH_2\text{-}COO(CH_2)_{12}\text{-}CH_3$, 3H, t), 1.2-1.6 (*tert* butylmethyl groups and methylene groups, 39H), 2.1-2.2 ($Ar\text{-}CH_2CH_2\text{-}COOCH_2\text{-}CH_2\text{-}R$, 2H, s), 2.6-2.8 ($Ar\text{-}CH_2CH$,$\text{-}COOCH_2\text{-}CH_2\text{-}R$, 2H, t), 2.9-3.1 ($Ar\text{-}CH_2CH_2\text{-}COOCH_2CH_2\text{-}R$, 2H, t), 4.04.2 ($Ar\text{-}CH_2CH_2\text{-}COOCH_2\text{-}CH_2\text{-}R$, 2H, t), 7.1-8.3 (protons of phenoxy and benzotriazole groups, 7H), 11.8-11.9 (intramolecular hydrogen bond). The ^{13}C NMR spectrum (in deuterated chloroform) showed chemical shift peaks at δ (ppm): 14-15 ($Ar\text{-}CH_2CH_2COOCH_2CH_2\text{-}(CH_2)_{15}\text{-}CH_3$, ^{1}C), 22-23 ($Ar\text{-}CH_2CH_2\text{-}COOCH_2CH_2\text{-}(CH_2)_{14}\text{-}CH_2\text{-}CH_3$, 1C), 25-26 ($Ar\text{-}CH_2CH_2COOCH_2CH_2CH_2\text{-}(CH_2)_{12}\text{-}CH_3$, 1C), 28-31 (carbons in *tert* butyl group and Ar $CH_2CH_2\text{-}COOCH_2\text{-}CH_2CH_2\text{-}(CH_2)_{12}\text{-}CH_2CH_2\text{-}CH_3$, 16C), 31-32 ($Ar\text{-}CH_2CH_2COO\text{-}(CH_2)$,s-$CH_2CH_2\text{-}CH_3$, 1C), 35-37 ($Ar\text{-}CH_2CH_2\text{-}COOR$, 1C), 64-65 ($Ar\text{-}CH_2CH_2\text{-}COOCH_2\text{-}R$, 1C, s), 117-148 (carbons of the phenoxy and benzotriazole groups, 12C), 173-174 ($Ar\text{-}CH_2\text{-}CH_2\text{-}COOR$, 1C). The ultraviolet-visible spectrum showed maxima at λ = 303 nm, ε_1 = 14,700 and at λ = 344 nm, ε_2=14,800 L.mol.cm.

2[2-Hydroxy-3-*tert* butyl-5-(2-hydroxypropyl)phenyl]2H- benzotriazole or 3'[5(2H-Benzo-triazol-2-yl)-4-hydroxy-3-*tert* butylphenyl]propanol (BHTP)]



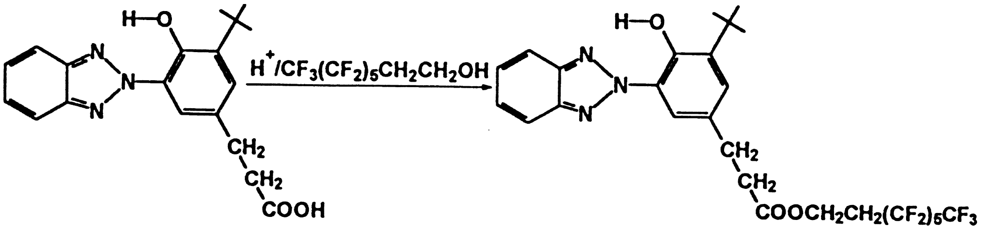
A 500 mL round bottom flask was charged under nitrogen atmosphere with lithium aluminum hydride (1.6 g, 0.042 mol). 100 mL of THF were added slowly from a dropping funnel. A solution of polyethyleneglycol-3'-[5(2H-benzotriazol-2-yl)-4-hydroxy-3-*tert* butylphenyl]propionate (15 g, 0.02 mols) in 80 mL THF was slowly added through a dropping funnel over a two hour period. After the addition of about 90%, lumps had formed and the addition was stopped, stirred for an additional 30 minutes and 50 mL n-butanol were added slowly through the dropping funnel. In addition, 40 mL water was added and the reaction mixture was acidified with 1:1 aqueous hydrochloric acid. The mixture was extracted several times with dichloromethane and the organic phase was isolated. The solvent was removed under reduced pressure and an off-white solid was obtained. 3'[5(2H-benzotriazol-2-yl)-4-hydroxy-3-*tert* butylphenyl]-propanol (BHTP) was recrystallized from isopropanol and yielded 5.4 g (79%) of the product; m.p.: 127-128°C. The K$^+$IDS mass spectrum showed a [M] of 325 Da (364 Da including K$^+$ plus isotopes). The ^{1}H NMR spectrum (in deuterated acetone) showed chemical shift peaks at δ (ppm): 1.5-1.6 (*tert* butyl-methyl groups, 9H), 1.8-1.9 (Ar-$CH_2CH_2CH_2OH$, 2H, p), 2.6-2.8 (Ar- $CH_{2.}CH_{2.}CH_2OH$, 2H, t), 3.6-3.8 (Ar-$CH_2CH_2CH_2OH$, 2H, t), 7.3-8.2 (protons of phenoxy and benzotriazole groups, 7H), 11.8-11.9 (intramolecular hydrogen bond). The ^{13}C-NMR spectrum (in deuterated acetone) showed chemical shift peaks at δ (ppm): 28-30 (carbons in *tert* butyl group, 4C), 32-33 (Ar-CH_2CH_2- CH_2OH, 1C), 35-36 (Ar-$CH_2CH_2CH_2OH$, 1C), 61-62 (Ar-$CH_2CH_2CH_2OH$, 1C), 118-129 (carbons of the phenoxy and benzotriazole groups, 12C). The ultraviolet-visible spectrum showed maxima at $\lambda = 303$ nm, $\varepsilon_1 = 14{,}750$ and at $\lambda = 344$ nm, $\varepsilon_2 = 14{,}350$ L.mol.cm.

2[2-Hydroxy-3-*tert* butyl-5-(2-carbopoly(dimethylsiloxane) oxyethyl)) phenyl]-2H-benzo-triazole or (Polydimethylsiloxane 3'[5(2H-benzotriazol-2-yl)-4-hydroxy-3-*tert* butylphenyl]propionate) (PMS-BHTP)



A 250 mL three-neck round bottom flask equipped with a reflux condenser and a Dean-Stark trap was charged with 3'[5(2H-benzotriazol- 2-yl)-4-hydroxy-3-*tert* butylphenyl]propionic acid (BHTPA) (3.0 g, 9 mmol), poly(dimethylsiloxane) (7.2 g, 3 mmol, MW 2400 g/mol) and p-toluenesulfonic acid (0.6 g). The solution was heated to reflux in 150 mL benzene for 4 hours, cooled, and the solvent was removed under reduced pressure and 50 mL of dichloromethane was added. The organic phase was washed with sodium hydroxide and water, dried with magnesium sulfate, filtered, and the filtrate was brought to dryness. The yield of the viscous yellow polydimethylsiloxane-3'-[5(2H-benzotriazol-2-yl)-4-hydroxy-3-*tert* butylphenyl]propionate (PDMS-BHTP) was 2.2 g (30%). Unfortunately, the molecular weight of this compound was beyond the molecular weight regime amenable to K^+IDS.

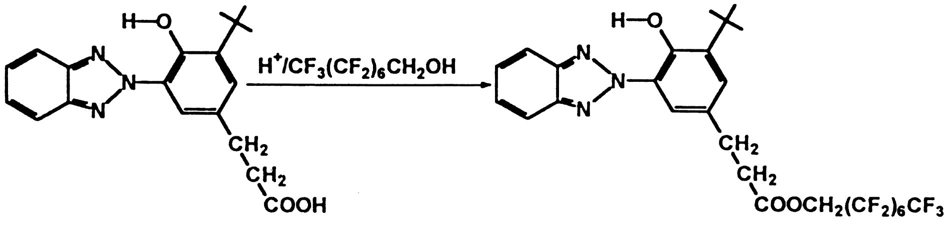
2[2-Hydroxy-3-*tert* butyl-5(2-carbo-3,3,4,4,5,5,6,6,7,7,8,8,8,-tridecafluoro-1-octyloxy-ethyl)phenyl]2H-benzotriazole or 3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluoro-1-octyl-3'-[5(2H-benzotriazol-2-yl)-4-hydroxy-3-*tert* butylphenyl]propionate (TDF-BHTP)



A 500 mL three-neck round bottom flask equipped with a reflux condenser and a Dean-Stark trap was charged with BHTPA (9.3 g, 27 mmol), 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctanol-1 (10 g, 27 mmol) and p-toluenesulfonic acid (2.6 g). The benzene solution (200 mL) was heated under reflux for 5 hours, cooled, and the solvent was removed under reduced pressure. The remaining white solid was recrystallized from ethanol. The yield of 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-1-octyl-3'[5(2H-benzotriazol-2-yl)4-hydroxy-3-*tert* butylphenyl]propionate (TDF-BHTP) was 8.5 g (45%); m.p.: 69-71°C. The K^+IDS mass spectrum showed a [M] of 685 Da (724 Da including K^+ plus isotopes).

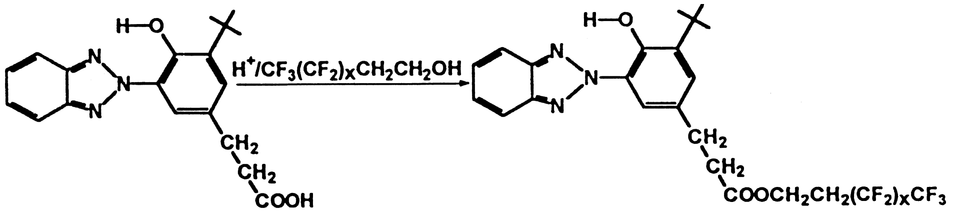
The ^1H NMR spectrum (in deuterated chloroform) showed chemical shift peaks at δ (ppm): 1.5-1.6 (*tert* butylmethyl groups, 9H, s), 2.6-2.8 ($Ar\text{-}CH_2CH_{2}.COOCH_2CH_2\text{-}R$, 2H, t), 2.9-3.1 ($Ar\text{-}CH_2CH_2\text{-}COOCH_2CH_2\text{-}R$,2H, t), 4.3-4.4 ($Ar\text{-}CH_2CH_2\text{-}COOCH_2CH_2\text{-}R$, 4H), 7.1-8.3 (protons of phenoxy and benzotriazole groups, 7H), 11.8-11.9 (intramolecular hydrogen bond). The ^{13}C NMR spectrum (in deuterated chloroform) showed chemical shift peaks at δ (ppm): 28-31 (carbons in *tert* butyl group and $Ar\text{-}CH_2CH_2COOCH_2CH_2\text{-}(CF_2)_nCF_3$, 10C), 30-31 ($Ar\text{-}CH_2CH_2COOR$, 1C), 35-37 ($Ar\text{-}CH_2CH_2COOCH_2CH_2\text{-}R$, 1C), 56-57 ($Ar\text{-}CH_2CH_2COOCH_2\text{-}R$, 1C), 117-148 (carbons of the phenoxy and benzotriazole groups, 12 C), 172-173 ($Ar\text{-}CH_2CH_2\text{-}COOR$, 1C). The ultraviolet-visible spectrum showed: ε_1 = 14,400 L.mol.cm (λ = 303 nm), ε_2=14,300 L.mol.cm (λ = 344 nm).

2(2-Hydroxy-3-*tert* butyl-5-(2-carbo-2,2,3,3,4,4,5,5,6,6,7,7,8,8,8.-pentadecafluoro-1-octyl oxy ethyl)phenylethyl)2H-benzotriazole or 2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-Pentadecafluoro-1-octyl-3'[5(2H-benzotriazol-2-yl)-4-hydroxy-3-*tert* butylphenyl]propionate) (PDF-BHTPA)



A 500 mL three-neck round bottom flask was equipped with a reflux condenser and a Dean-Stark was charged with BHTPA (3.4 g, 0.01 mol), 2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctanol-1 (4.1 g, 0.01 mol) and p-toluenesulfonic acid (5.8 g). The mixture was heated under reflux in 200 mL benzene for 5 hours, cooled, and the solvent was removed under reduced pressure. The remaining white solid was recrystallized from ethanol. The yield of 2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluoro-1-octyl-3'[5(2H-benzotriazol-2-yl)-4-hydroxy-3-*tert* butylphenyl]propionate (PDF-BHTP) was 3.3 g (45%); m.p.: 69-71°C. The K^+IDS mass spectrum showed a normal mass of 724 Da including K^+, plus isotopes,: calcd. [M] =685 Da. The ^{1}H NMR spectrum (in deuterated chloroform) showed chemical shift peaks at δ (ppm): 1.5-1.6 (*tert* butylmethyl groups, 9H, s), 2.6-2.8 (Ar-CH_2CH_2-$COOCH_2CH_2$-R, 2H, t), 2.9-3.1 (Ar-CH_2CH_2-$COOCH_2CH_2$-R, 2H, t), 4.3-4.4 (Ar-CH_2CH_2-$COOCH_2$-CH_2-R, 4H), 7.1~.3 (protons of phenoxy and benzotriazole groups, 7H), 11.8-11.9 (intramolecular hydrogen bond). The ^{13}C NMR spectrum (in deuterated chloroform) showed chemical shift peaks at δ (ppm): 28-31 (carbons in *tert* butyl group and Ar-CH_2CH_2COO-CH_2CH_2-$(CF_2)_5CF_3$, 10C), 30-31 (Ar-CH_2CH_2-COOR, 1C), 35-37 (Ar-CH_2CH_2-$COOCH_2CH_2$-R, 1C), 56-57 (Ar-CH_2CH_2-$COOCH_2$-R, 1C), 117-148 (carbons of the phenoxy and benzotriazole groups, 12C), 172-173 (Ar-CH_2CH_2-COOR, 1C). The ultraviolet- visible spectrum showed: ε_1 = 14,400 L.mol.cm (λ = 303 nm), ε_2 = 14,300 L.mol.cm (λ = 344 nm).

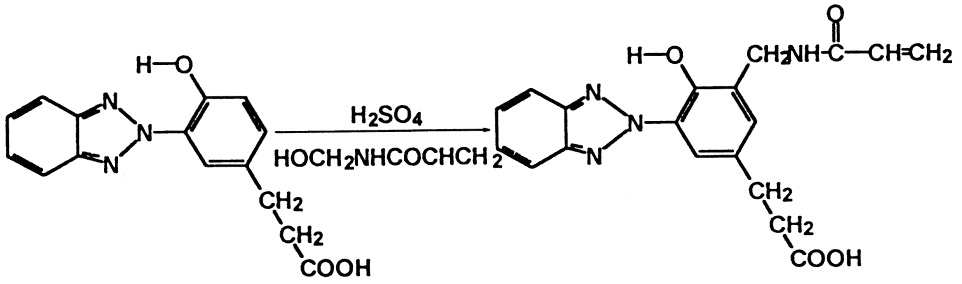
2[2-Hydroxy-3-*tert* butyl-5-(2-carbo)1H,1H,2H,2H-perfluoro-1-alkyloxyethylphenyl]-2H-benzatriazole or 1H,1H,2H,2H-Perfluoro-1-alkyl 3'-[5(2H-benzotriazol-2-yl)-4-hydroxy-3-*tert* butylphenyl]propionate (PFA-BHTP)



A 500 mL three-neck round bottom flask was equipped with a reflux condenser and a Dean-Stark trap was charged with BHTPA (5.7 g, 16 mmol), a mixture of 1H,1H,2H,2H-perfluoro-1-alcohols (perfluorohexanol-1 0.4%; perfluorooctanol-1 16%; perfluorodecanol-1 39%; perfluoro-dodecanol-1 31%; perfluorotetradecanol-1 10%; perfluorohexadecanol-1 2.9%; perfluoro-octadecanol-1 0.2%) (10 g, 16.4 mmol) and p-toluenesulfonic acid (6.3 g). The benzene solution (200 mL) was heated under reflux for 5 hours, the mixture cooled and the solvent removed under reduced pressure. The remaining white solid was recrystallized from ethanol. The yield of 1H,1H,2H,2H-perfluoro-1-alkyl-3'-[5-(2H-benzotriazol-2-yl)-4-hydroxy-3-*tert* butyl-phenyl]-propionate (PFA-BHTP) was 8.5 g (45%); m.p.: 69-71°C. The K^+IDS mass spectrum showed the nominal mass at 724 Da including K^+. This corresponds to a calculated molecular weight of 685 Da for x = 6. The ^{1}H NMR spectrum (in deuterated chloroform) showed chemical shift peaks at δ (ppm): 1.5-1.6 (*tert* butylmethyl groups, 9H, s), 2.6-2.8 (Ar-CH_2CH_2-$COOCH_2CH_2$-R, 2H, t) 2.9-3.1 (Ar-CH_2CH_2-$COOCH_2CH_2$-R, 2H, t), 4.3-4.4 (Ar-CH_2CH_2-$COOCH_2CH_2$-R, 4H), 7.1-8.3 (protons of phenoxy and benzotriazole groups, 7H), 11.8-11.9 (intramolecular hydrogen bond). The ^{13}C NMR spectrum (in deuterated chloroform) showed chemical shift peaks at δ (ppm): 28-31 (carbon in *tert* butyl group and Ar-CH_2-CH_2COO-CH_2-CH_2-$(CF_2)_5CF_3$, 10C), 30-31 (Ar-CH_2CH_2-COOR, 1C), 35-37 (Ar-CH_2CH_2-$COOCH_2CH_2$-R, 1C), 56-57 (Ar-CH_2CH_2-$COOCH_2$-R, 1C), 117-148 (carbons of the phenoxy and benzotriazole groups, 12C), 172-173 (Ar-CH_2CH_2-COOR, 1C). The ultraviolet-visible spectrum showed: ε_{11}= 14,200 L.mol.cm (λ = 303 nm), ε_2 = 14,100 L.mol.cm (λ = 344 nm).

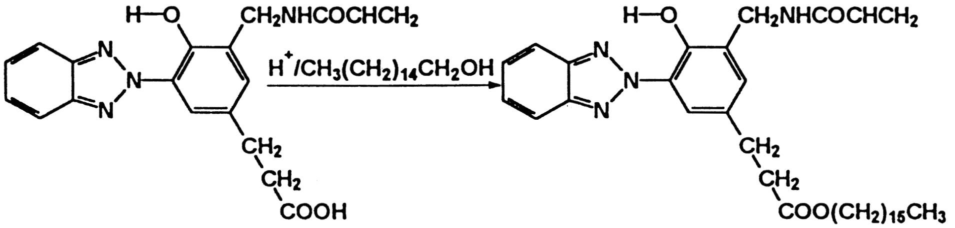
Polymerizable UV Stabilizers

2[2-Hydroxy-3(N-methyleneacrylamido)-5(-2-carboxyethyl)-phenyl]2H-benzotriazole or 3'[5(2H-Benzotriazol-2-yl)-4-hydroxy-3-acrylamidomethylphenyl]propionic acid (BHAPA))



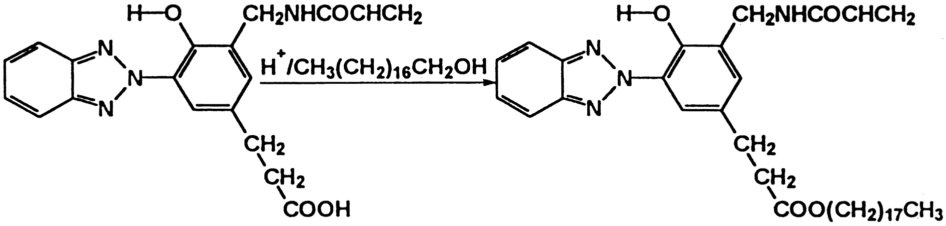
A 250 mL round bottom flask was charged with 3'[5-(2H-benzotriazol-2-yl)-4-hydroxyphenyl]propionic acid (BHPA) (5.0 g, 0.0177 mol) and 40 mL conc. sulfuric acid, while keeping the flask in an ice-water bath. Under nitrogen atmosphere an aqueous N(hydroxymethyl)acryl amide (48% w/v) (4.0 g, 0.0177 mol) solution was added dropwise . It was stirred for one day and the reaction mixture was poured into ice water and produced a white precipitate. The suspension was filtered, the filter cake washed twice with ice-water and once with ethanol. The yield of dried off-white 3'[5(2H-benzotriazol-2-yl)4-hydroxy-3-acrylamidomethylphenyl]propionic acid (BHAPA) was 5.1 g (79%). The K^+IDS mass spectrum showed a nominal mass of 405 Da including K^+, calcd. for [M], 366 Da. The ^1H NMR spectrum (in deuterated acetone) showed chemical shift peaks at δ (ppm): 2.6-2.8 (Ar-CH_2CH_2-COOH, 2H, t), 2.9-3.1 (Ar-CH_2CH_2-COOH, 2H, t), 4.5-4.6 (Ar-CH_2-NHCO-, 2H d), 7.1-8.3 (protons of phenoxy and benzotriazole groups, 7H), 11.8-11.9 (intramolecular hydrogen bond). The ^{13}C NMR spectrum (in deuterated acetone) showed chemical shift peaks at δ (ppm): 35-36 (Ar-CH_2CH_2-COOR, 1C), 38-39 (Ar-CH_2CH_2-COOR, 1C), 117-148 (carbons of the phenoxy and benzotriazole groups, 12C). The ultraviolet-visible spectrum showed maxima at λ = 303 nm, $^{\varepsilon}{}_1$ = 14,100 L.mol.cm and at λ = 344 nm, $^{\varepsilon}{}_2$= 15,000 L.mol.cm.

2[2-Hydroxy-3-(N-methyleneacrylamido)-5-(2-carbohexadecyloxy-ethyl)phenyl]2H-benzotriazole of 1-Hexadecyl-3'[5(2H-benzotriazol-2-yl-)-4-hydroxy-3-acryl-amidomethyl]phenyl-propionate (HBHAPA)



A 500 mL three-neck round bottom flask was equipped with a reflux condenser and a Dean-Stark trap, was charged with 3'[5(2H-benzotriazol-2-yl)4hydroxy-3-acrylamidomethyl-phenyl]propionic acid (BHAPA) (5.0 g, 0.0137 mol), hexadecanol-1 (5.1 g, 0.021 mol) and p-toluenesulfonic acid (1.3 g, 6.9 mmol). Benzene (250 mL) was added and the reaction mixture was stirred for half an hour at room temperature and then heated to reflux temperature for an additional 4 hours. After cooling, the solvent was removed and the product recrystallized from isopropanol. The yield of the off-white1-hexadecyl-3'-[5-(2H-benzotriazol-2-yl)4-hydroxy-3-acryl-amidomethylphenyl]propionate (HBHAPA) was 2.5 g (31%). The K^+IDS mass spectrum showed a nominal molecular weight of 629 Da including K^+), calcd. [M]=590 Da. The ^1H NMR spectrum (in deuterated chloroform) showed chemical shift peaks at δ (ppm): 0.8-0.9 (Ar-CH_2CH_2-COO$(CH_2)_{15}CH_3$, 3H, t), 1.2-1.6 (methylene groups, 28H), 2.6-2.8 (Ar-CH_2CH_2-COOR, 2H, t), 2.9-3.1 (Ar-CH_2CH_2-COOR, 2H, t), 4.04.2 (Ar-CH_2CH_2-COOCH_2-R, 2H, t), 4.5-4.7 (Ar-CH_2-NHCO-R, 2H, d), 7.1-8.3 (protons of phenoxy and benzotriazole groups, 7H), 11.8-11.9 (intramolecular hydrogen bond). The ^{13}C NMR spectrum (in deuterated chloroform) showed chemical shift peaks at δ (ppm): 14-15 (Ar-CH_2CH_2-COOCH_2CH_2-$(CH_2)_{13}$-CH_3, 1C), 22-23 (Ar-CH_2CH_2-$COOCH_2CH_2$.$(CH_2)_{12}CH_2$-CH_3, 1C), 25-26 (Ar-CH_2CH_2-$COOCH_2CH_2CH_2$-$(CH_2)_{12}$-CH_3, 1C), 28-31 (Ar-CH_2CH_2-$COOCH_2$ CH_2CH_2-$(CH_2)_{10}$-CH_2CH_2-CH_3, 12C), 31-32 Ar-CH_2CH_2-COO-$(CH_2)_{13}$-CH_2 CH_2-CH_3, 1C), 35-37 (Ar-CH_2CH_2- COOR, 1C), 39-41 (Ar-CH_2-NHCO-R, 1C), 64-65 (Ar-CH_2CH_2-$COOCH_2$-R, 1C), 117-148 (carbons of the phenoxy and benzotriazole groups, 12C), 173-174 (Ar-CH_2.CH_2-COOR, 1 C). The ultraviolet-visible spectrum showed maxima at λ = 303 nm, ε_1=14,100 L.mol.cm and at λ = 344 nm, ε_2 = 14,900 L.mol.cm.

2[2-Hydroxy-3-(N-methyleneacrylamido)-5-(2-carbooctadecyloxyethyl)phenyl]-2H-benzotriazole or 1-Octadecyl-3'-[5-(2H-benzotriazol-2-yl)-4-hydroxy-3-acrylamidomethyl-phenyl] propionate (OBHAPA)



A 250 mL round bottom flask was charged with a solution of 3'-[5(2H-benzotriazol-2-yl)-4-hydroxy-3-acrylamidomethylphenyl]propionic acid (BHAPA) (0.55 g, 1.5 mmol) and in THF (50 mL). Under a nitrogen atmosphere, a solution of N,N'-carbonyl diimidazole (0.3 g) in 25 mL of THF was added. This mixture was stirred for 2 hours, octadecanol-1 (0.4 g, 1.5 mmol) in 50 mL of THF was added through a dropping funnel and the reaction mixture was stirred for 3 days at room temperature. The reaction was stopped and the solvent removed. The residue was recrystallized from isopropanol. The yield of off-white 1-octadecyl-3'-[5-(2H-benzotriazol-2-yl)-4-hydroxy-3-acrylamidomethylphenyl] propionate (OBHAPA) was 0.2 g (21%). The ^{1}H-NMR spectrum (in deuterated chloroform) showed chemical shift peaks at δ (ppm): 0.8-0.9 (Ar-CH_2CH_2-$COO(CH_2)_{17}CH_3$, 3H, t), 1.2-1.6 (methylene groups, 32H), 2.6-2.8 (Ar-CH_2CH_2-COOR, 2H, t), 2.9-3.1 (Ar-CH_2CH_2-COOR, 2H, t), 4.0-4.2 (Ar-CH_2CH_2-$COOCH_2$-R, 2H, t), 4.5-4.7 (Ar-CH_2-NHCO-R, 2H, d), 7.1-8.3 (protons of phenoxy and benzotriazole groups, 7H), 11.8-11.9 (intramolecular hydrogen bond). The ^{13}C NMR spectrum (in deuterated chloroform) showed chemical shift peaks at δ (ppm): 14-15 (Ar-CH_2CH_2-$COOCH_2CH_2$-$(CH_2)_{13}$-CH 1C), 22-23 (Ar-$CH_2CH_2COOCH_2CH_2$-$(CH_2)_{14}$-CH_2-CH_3, 1C), 25-26 (Ar-

CH_2CH_2-$COOCH_2CH_2CH_2$-$(CH_2)_{14}$-CH_3, 1C), 28-31 (Ar-CH_2CH_2-$COOCH_2CH_2CH_2$-$(CH_2)_{12}$-CH_2CH_2-CH_3, 14C), 31-32 (Ar-CH_2CH_2-COO$(CH_2)_{15}$-CH_2CH_2-CH_3, 1C), 35-37 (Ar-CH_2CH_2COOR, 1C), 39-41 (Ar-CH_2-NHCO-R, 1C), 64-65 (Ar-CH_2CH_2-$COOCH_2$-R, 1C), 117-148 (carbons of the phenoxy and benzotriazole groups, 12C), 173-174 (Ar-CH_2CH_2-COOR, 1C). The ultraviolet-visible spectrum showed maxima at λ= 303 nm, ε_1 =14,100 L.mol.cm and at λ = 344 nm, ε_2 = 14,900 L.mol.cm.

Polydimethylsiloxane-3'[5(2H-benzotriazol-2-yl)-4-hydroxy-3-methacrylamidomethylphenyl)propionate (PDMS-BHMPA)

A 100 mL three-neck round bottom flask was charged with 3'[5-(2H-benzotriazol-2-yl)-4-hydroxy-3-methacrylamidomethylphenyl] propionic acid (BHMPA, 1.27 g, 3.3 mmol) and THF (25 mL). To this solution was added,over a 30 minute period, solid carbonyl diimidazole (CDI, 0.59 g, 3.7 mmol) in small portions. A separate 100 mL three-neck round bottom flask, equipped with an addition funnel and a magnetic stirring bar was charged, under a nitrogen atmosphere, with THF (25 mL) and carbinol terminated polydimethylsiloxane (2.1 g, 1.6 mmol, MW = 1250). To this solution was then added dropwise, over a one hour period, the imidazolide solution.

Upon completion of the addition, the addition funnel was substituted for a reflux condenser and the solution was heated to reflux for 8 hours. After an additional 16 hours at ambient temperature, the light orange solution was transferred to a Kjeldahl flask and concentrated to a volume of 15 mL, diluted with benzene (60 mL), washed twice with brine, and 3 times with water. Evaporation of the solvent under reduced pressure gave a dark orange oil weighing 0.52 g which was dissolved in THF; the solution was then passed through a chromatography column containing 5.0 g of silica-gel. Solvent evaporation and drying in a desiccator at ambient temperature for one day gave 0.35 g of a tacky solid. TLC in THF:Hex. = 1:3 gave a spot with R_f = 0.75. The infrared spectrum showed peaks at 3350 cm^{-1} (NH stretch), 1740 cm^{-1} (ester C=O stretch) and 1650 cm^{-1} (amide C=O stretch). The ^{1}H NMR spectrum (DMSO-d_6) showed δ (ppm): 1.3-1.8 (aliphatic protons), 2.0 ($C\underline{H}_3$-C=CH_2, 3H, s), 2.6-2.7 (Ar-CH_2-$C\underline{H}_2$-COO-, 2H, t), 2.7-2.9 (Ar-CH_2-$C\underline{H}_2$-, 2H, t), 3.4 (O-$C\underline{H}_2$-CH_2-O, s), 4.4-4.5 (Ar-$C\underline{H}_2$-NHCO-, 2H, d), 5.4 ($\underline{H}_{cis}$-C=C, s), 5.8 ($\underline{H}_{trans}$-C=C, s) and 7.3-8.5 (protons of phenoxy and benzotriazole groups, 6H). K^+IDS mass spectrum; found, 447 Da. This product was used directly in a copolymerization reaction with MMA.

2-Perfluoroalkylethyl-3'-5(2H-benzotriazol-2-yl)-4-hydroxy-3-methacrylamidomethylphenyl)propionate (PFAE-BHMPA)

The following recipe describes a modification of the synthesis described above. A 100 mL three-neck round bottom flask was charged with 3'[5-(2H-benzotriazol-2-yl)-4-hydroxy-3-methacrylamidomethylphenyl]propionic acid (BHMPA, 2.0 g, 5.3 mmol) THF (30 mL) and carbonyl diimidazole (CDI) (1.8 g, 11 mmol). A 250 mL three-neck round bottom flask was charged, under a nitrogen atmosphere, with THF (30 mL) and 2-perfluoroalkylethyl alcohol (2.7 g, 5.3 mmol) of average MW 511 g/mol. The reaction was carried out at ambient temperature for 17 hours, and at reflux for 8 hours. After work up and evaporation of the excess solvent, a soft dark orange solid was obtained (5.4 g) which was dissolved in the minimum amount of chloroform and passed through a silica gel filled chromatography column. After solvent evaporation, a sticky brown solid (3.2 g) was obtained, m.p., 85-102°C. The infrared spectrum showed peaks at 3300 cm^{-1} (N-H stretch), 1740 cm^{-1} (ester C=O stretch), 1655 cm^{-1} (amide C=O stretch), 1205 cm^{-1} and 1150 cm^{-1} (C-F stretch). The ultraviolet spectrum showed two absorption bands at 340 nm and at 302 nm with ε = 12,500 L.mol.cm and 12,700 L/mol × cm, respectively. K^+IDS mass spectrum: found 825 Da.

Elemental Analysis for $C_{30}H_{23}N_40_4F_{17}$: Calcd: C, 43.60%; H, 2.82%; N, 6.78%; F, 39.08%. Found: C, 42.47%; H, 2.89%; N, 6.15%; F, 39.5%. The elemental analysis indicates an average molecular weight of about 830 Da.

Polymerizations

Copolymerization of polydimethylsiloxane 3'[5 (2H-benzotriazol-2-yl)-4-hydroxy-3-methacrylamidomethylphenyl)propionate (PDMS-BHMPA) with Methyl Methacrylate

A 40 ml thick wall pressure reaction tube was charged with PDMS-BHMPA (0.35 g), MMA (1.75 g, 17.5 mmol), DMAc (15 mL) and AIBN (16 mg, 0. 5 mol%). After deoxygenation with argon gas for 0.75 hours, the tube was capped with a silicone septum and placed in an oil bath at 60°C for 18 hours. Work up by pouring the solution into methanol gave 1.1 g (52%) of polymer, which was Soxhlet extracted with ethanol for 6 hours, dissolved in chloroform and reprecipitated by pouring the solution into methanol. The polymer was collected by vacuum filtration and dried at ambient temperature under reduced pressure. The inherent viscosity (0.5 w/v%, toluene, 30°C) was 0.34 dL/g.

Elemental Analysis for $-(C_5H_8O_2)_{\overline{0.86}}-(C_{11.58}H_{142}N_8O_{24}Si_{14})_{\overline{0.14}}-$: Calcd: Si, 2.80%; N, 0.80%. Found: Si, 2.78%; N, 0.77%.

Copolymerization of 2-perfluoroalkylethyl-3'[5(2H-benzotriazol-2-yl)-4-hydroxy-3-methacrylamidomethylphenyl]propionate (PFAE-BHMPA) with Methyl Methacrylate

A 40 mL thick wall pressure reaction bottle was charged with PFAE-BHMPA (1.0 g, 1.2 mmol), MMA (5.0 g, 0.05 mol), DMAc (15 mL) and AIBN (42 mg). After deoxygenation with helium gas for 0.5 hours, the tube was capped with a silicone septum and placed into an oil bath at 50°C for 1.5 days. Work up by pouring the solution into methanol gave a suspension from which 4.7 g (78%) of a light pink colored polymer was collected by filtration. A portion of the copolymer (3.7 g) was Soxhlet extracted with ethanol for 6 hours, dissolved in chloroform and the solution poured into methanol (400 mL); 2.0 g of the copolymer precipitated and were recovered by filtration and gave an inherent viscosity of 1.06 dL/g (0-5 w/v%, toluene, 30°C). The crude polymer had an inherent viscosity of 0.88 dL/g (0.5 w/v%, toluene, 30°C).

Elemental Analysis for $-(C_5H_8O_2)_{\overline{0..917}}-$ $(C_{30}H_{23}N_4O_3F_{17})_{\overline{0.07}}-$ $(C_{20}H_{2O}N_40_4)_{\overline{0.02}}-$: Calcd: N, 0.67% F, 2.7%. Found: N, 0.68%; F, 2.7%.

Copolymerization of 3'[5(2H-benzotriazol-2-yl)-4-hydroxy-3-methacrylamidomethyl-phenyl)propionic acid (BHMPA) with Methyl-Methacrylate

<u>On a 9 mol% basis</u>: A 40 mL thick wall pressure reaction tube was charged with BHMPA (1.14 g, 3 mmol), MMA (3.0 g, 30 mmol), DMAc (10 mL) and AIBN (27 mg) . After deoxygenation with argon gas for 0.5 hours, the tube was capped with a silicone septum and placed in an oil bath at 50°C for one day. Work up by diluting the very viscous solution with 15 mL of chloroform and pouring the solution into methanol gave a suspension from which 3.0 g (72%) of a light pink polymer was obtained after filtration. The copolymer was extracted twice by suspending it in 75 mL of methanol at 45°C. The air-dried polymer was dissolved in chloroform and precipitated into methanol (150 mL); 2.0 g (48%) of polymer with an inherent viscosity of 0.28 dL/g (0.5 w/v%, toluene, 30°C) were obtained. From the ultraviolet spectrum, the composition of BHMPA in the copolymer is 16 wt%.

Elemental Analysis for $-(C_5H_8O_2)_{\overline{0.85}}-$ $(C_2H_{2O}N_4O_4)_{\overline{0.15}}-$: Caulked: C, 60.45%; H, 7.64%; N, 2.20%. Found: C, 60.14%; H, 7.55%; N, 2.27%.

<u>On a 2 mol % basis</u>. A 40 mL thick wall pressure reaction bottle was charged with BHMPA (0.38 g, 1 mmol), MMA (5.0 g, 50 mmol), THF (15 mL) and AIBN (42 mg). After deoxygenation with argon gas for 0.5 hours, the tube

was capped with a silicone septum and placed in an oil bath at 50°C for 3 days. Work up by pouring the solution into methanol gave a suspension from which 3.8 g (71%) of a light pink polymer was isolated after filtration. The copolymer was Soxhlet extracted with ethanol for 6 hours, dissolved in chloroform and precipitated by pouring the solution into methanol; 3.5 g (65%) of polymer with an inherent viscosity of 0.30 dL/g (0.5 w/v%, toluene, 30°C) was obtained. The U.V. spectrum showed a major absorption band at 336 nm and a minor band at 300 nm.

Elemental Analysis for $-(C_5H_8O_2)_{\overline{0.95}}-$ $(C_{20}H_{20}N_4O_4)_{\overline{0.05}}-$: Calcd.: N, 0.68%. Found: N, 0.68%.

Reaction of poly(methyl methacrylate-co-3'[5(2H-benzotriazol-2-yl)-4-hydroxy-3-methacrylamidomethylphenyl]propionic acid) with 2-Perfluoroalkylethyl Ethanol

A 100 mL three-neck round bottom flask, equipped with a reflux condenser and an addition funnel, was charged with poly (methyl methacrylate)-co-3'[5(2H-benzotriazol-2-yl)-4-hydroxy-3-methacrylamidomethylphenyl] propionic acid (2.0 g, 0.18 mmol of BHMPA) and THF (50 mL). To this solution was added portionwise solid carbonyl diimidazole (CDI, 0.03 g, 0.2 mmol). In the addition funnel was placed THF (30 mL) and 2-perfluoroalkylethanol (0.092 g, 0.18 mmol). This solution was then added dropwise, over a 0.5 hour period and at ambient temperature, to the polymeric imidazolide solution. The reaction was continued at reflux temperature for one day; the reaction mixture was then cooled to ambient temperature, the solution was concentrated to 30 mL and the viscous residue added dropwise to mechanically stirred methanol (400 mL) . The precipitate was collected by vacuum filtration, washed with several small portions of fresh methanol and dried at 0.05 mm Hg; 2.2 g of polymer were obtained which were stirred in 50 mL ethanol at 50°C for several hours. Excess solvent was decanted, the polymer suspended again in 50 mL of warm ethanol, filtered and air-dried. Finally, the polymer was dissolved in chloroform and the solution poured into methanol. The precipitate was collected by filtration, washed with fresh methanol and dried under reduced pressure at ambient temperature; 1.65 g (78%) of a polymer with an inherent viscosity of 0.54 dL/g (0.5 w/v%, toluene, 30°C) were obtained.

Elemental Analysis for $-(C_5H_8O_2)_{0.95}-(C_{20}H_{20}N_4O_4)_{\overline{0.043}}-(C_{30}H_{23}N_4O_4F_{17})_{\overline{0.002}}-$ Calcd: N, 0.65%; F, 0.1%. Found: N, 0.66%; F, 0.1%.

RESULTS AND DISCUSSION

New types of polymeric UV stabilizers that are capable of migrating to the polymer surface region are reported. These UV stabilizers are designed to have a very low surface free energy, which causes the UV stabilizers to segregate to the polymer surface. It is highly desirable to synthesize UV stabilizers that migrate to the polymer surface, protecting the polymer where it is most needed. We call this principle morphology engineering or surface stratification [24]. This is important for non-polymerizable and polymerizable UV stabilizers. Non-polymerizable UV stabilizers that may be lost through leaching or evaporation from the surface will then be replaced continuously with more UV stabilizer migrating to the surface. Polymerized UV stabilizer fragments also migrate to the surface and eliminate the loss through evaporation and leaching. These surface migratable UV stabilizers are especially important for the stabilization of surfaces of fibers and films, where the surface to volume ratio is large.

Fluorocarbon and silicon compounds have been used to design surface migratable UV stabilizers [10, 24]. The hydrophobic character of fluorocarbon and silicon compounds is related to the low surface energy and the low values of the cohesive energy density of these compounds. The low surface free energy of these compounds enables them to migrate to the surface. The surface free energy of a substance can be measured by contact angle measurements. Here, the contact angle between the surface and an applied liquid droplet is measured. The measurement is sensitive to the first molecular layer in the surface. Results of contact angle measurements have shown that, for example, 2-per-fluoroalkylethyl-3'[5(2H-benzotriazol-2-yl)4-hydroxy-3-methacrylamidomethylphenyl]2H-benzotriazole (PFAE-BHMPA) cast on glass slides was highly hydrophobic, with a contact angle of 95°.

ESCA studies of copolymer film surfaces containing 2-(2-hydroxyphenyl)2H-benzotriazole derivatives have investigated the surface photo-oxidation of these copolymers [35, 36]. As expected, it was found that the surface oxygen uptake is highly dependent on the concentration of the stabilizer in the surface. Even when the surface underwent chemical changes, the polymer bulk remained protected. The differences in the chemistry of the polymer surface and the polymer bulk region during photo-oxidation are apparent.

In our efforts to develop UV stabilizers that can be useful as surface active UV materials, we have chosen PMMA copolymers with surface active stabilizing groups in the comonomers.

We have approached this problem in three ways: a) synthesis of 2(2-hydroxyphenyl)2H-benzotriazole derivatives with *tert* butyl groups in the 3-position of the phenyl ring; b) synthesis of 2(2-hydroxyphenyl)2H-benzotriazole derivatives with an open position followed by introducing in this position (meth)acrylamido groups as polymerizable groups: c) preparation of copolymers using monomers of type b) and d) surface activity measurements. We synthesized 2(2-hydroxyphenyl)2H-benzotriazole derivatives that have reactive groups in the 5-position and a *tert* butyl group in the 3-position, in part to block the reactive 3-position and in part to synthesize soluble 2(2-hydroxyphenyl)2H-benzotriazole derivatives that could be characterized and studied. We used the reactive carboxyethyl or the hydroxypropyl group as the handle for the 2(2-hydroxyphenyl)2H-benzotriazole derivatives.

BHPA was synthesized in two steps from o-nitroaniline and 4-hydroxyphenylpropionic acid (which in turn is made from phenol and acrylic acid. (Equations 1, 2). BHPA *tert* butylated in the 3-position (BHTPA) was obtained by sodium hydroxide hydrolysis from the commercially available PEG-BHTPA (Equation 3); the methyl ester (MBHPA) was obtained by transesterification from PEG-BHPA with methanol (Equation 4).

The hexadecanol ester (Equation 5) HBHTPA, the octadecanol ester (Equation 6), the esters of polydimethyl siloxane (Equation 9) (PDMS-BHTPA), of tridecafluorooctanol (Equation 10) (TDF-BHTPA), of penta-decafluorooctanol (Equation 11) (PDF-BHTPA and a technical mixture of C_6 to C_{10} fluorinated alcohols (Equation 12) (PFA-BHTPA) were synthesized in the presence of an acid catalyst (p-toluenesulfonic acid).

The octadecylester (OBHTPA) was also prepared from BHTPA via the imidazolide of BHTPA (Equation 7).

3'[5(2H-benzotriazol-2-yl)-4-hydroxy-3-*tert* butylphenyl] propanol (BHTP) was obtained by lithium aluminum hydride reduction of either the commercial PEG ester (Equation 8) or the methyl ester, (MBHTPA) of synthetic BHTPA. BHTPA was esterified by a different route via the imidazolides of the corresponding unsaturated fatty acids. They were oleic acid, linoleic acid and linolenic acid. The esters were used as UV stabilizers and as polymerizable UV stabilizers for oriental lacquers (urushiol) and drying oils.

BHPA was also treated with hydroxymethylacrylamide (Equation 13) to form BHAPA and then esterified with hexadecanol-1 (Equation 14) to HBHAP and with octadecanol-1 to OBHAP (Equation 15).

Copolymers of methyl methacrylate with PDMS-BHMPA (a tacky solid), PFAE-BHMPA (a brown solid, m.p. = 85-102°C) and BHMPA with a comonomer composition of 5-15 mol% of the comonomer were synthesized.

Determination of the Contact Angle of Perfluoroalkylethyl and Polydimethylsiloxane Functionalized 2(2-Hydroxyphenyl)2H-Benzotriazole

The measurement of the angle of contact, made between a liquid drop and a solid surface, has long been accepted as a measure of the surface free energy of a substance and thus commonly used as a method of characterization of a surface. The distinct advantage of contact angle measurements is that this method is sensitive to only the surface molecular layer. A method introduced for the determination of contact angles was developed in Professor Stanley Israel's laboratory and is known as "Laser Contact Angle Goniometry" [37]. It works by projecting a laser beam at a solid-liquid-air or solid liquid-liquid interface; two beams result which are related to the contact angle between the liquid and the solid. This method allows the measurement of contact angles on all types of surfaces utilizing very small liquid drops on samples of minimal surface area.

Table 1 column 1 lists the polymer samples that were analyzed. The second column presents the results of contact angle measurements of the polymers cast from concentrated chloroform solutions on conditioned glass slides and subsequently dried at 0.05 mm Hg at room temperature for one day. The third column shows the results of the contact angle measurements on the same polymer samples, after they were submerged in deionized water for 2 days. Both sets of measurements were taken using drops of deionized water. Sample 1 is a sample of PMMA synthesized in the laboratory synthesized sample of PMMA. Sample 2 is poly(methyl methacrylate)-co-{2-per-fluoro-alkylethyl-3' [5 (2H-benzotriazol-2-y1)-4-hydroxy-3-methacrylamidomethylphenyl] pro-pionate] before being Soxhlet extracted with ethanol. Sample 3 is the polymer of sample 2 after being extracted with ethanol. Sample 4 is a physical blend of PMMA and FHB and sample 5 is poly(methyl methacrylate)-co-polydimethyl siloxane 3'[5(2H-benzotriazol-2yl)-4-hydroxy-3-methacrylamidomethyl-phenyl] propionate).

The samples exhibited a drop in the contact angle after equilibration in distilled water. Sample #2 gave less consistent results after conditioning and it was observed that the contact angle was smaller at the edges of the cast film. Sample #4 appeared to change after conditioning. The sample became white and a white powder was visible on the surface of the film. What must have happened is that the conditioning process with water must have extracted some of the lower MW oligomeric FHB, leaving mostly PMMA behind. When the original contact

TABLE 1. Contact Angle Measurements of Perfluoroalkylalkylethyl and Polydimethylsiloxane Functionalized 2(2-Hydroxyphenyl)2H-benzotriazoles.

	Contact Angle (in degrees +/- 0.5)	
SAMPLE	As Received	After conditioning
1	90	80
2	95	92-92
3	87	74
4	5-9 (top side)	61-64 (glass side)
5	86	82

angle was measured on this sample the top side was measured. This side was somewhat rough. After conditioning, the contact angle was measured on the side of the sample that was in contact with the glass slide. A high contact angle shows a high degree of water repellency or hydrophobicity. The results do not appear to indicate that the introduction of polydimethylsiloxane functional groups drastically changes the hydrophobic properties of the polymer films. However, polymer samples #2 and #3, which contain the perfluoroalkylethyl group, do indeed show an increased hydrophobicity, as evidenced by the decrease in the contact angle of the film.

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