

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C07D 251/24, C08J 3/24, C08K 5/3492		A1	(11) International Publication Number: WO 97/05122
			(43) International Publication Date: 13 February 1997 (13.02.97)
(21) International Application Number: PCT/US96/12384			(81) Designated States: JP, US, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>
(22) International Filing Date: 26 July 1996 (26.07.96)			
(30) Priority Data: 60/001,449 26 July 1995 (26.07.95) US			
(60) Parent Application or Grant (63) Related by Continuation US 60/001,449 (CON) Filed on 26 July 1995 (26.07.95)			
(71) Applicant (for all designated States except US): E.I. DU PONT DE NEMOURS AND COMPANY [US/US]; 1007 Market Street, Wilmington, DE 19898 (US).			
(72) Inventors; and (75) Inventors/Applicants (for US only): HUNG, Ming-Hong [US/US]; 601 Andover Road, Wilmington, DE 19803-2202 (US). LOGOTHETIS, Anestis, Leonidas [US/US]; 2816 Kennedy Road, Wilmington, DE 19810-3430 (US).			
(74) Agent: SIEGELL, Barbara, C.; E.I. Du Pont de Nemours and Company, Legal/Patent Records Center, 1007 Market Street, Wilmington, DE 19898 (US).			
(54) Title: FLUORINATED ALKENYLTRIAZINES AND THEIR USE AS CROSSLINKING AGENTS			
(57) Abstract Disclosed herein are novel fluorinated vinyl and allyl substituted fluoroalkyl containing triazines and a process in which they are used as curing agents for the crosslinking of suitable fluoroelastomers. These polymers are useful in elastomeric seals and for other uses in which high temperature and/or chemical resistance is needed.			

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AM	Armenia	GB	United Kingdom	MW	Malawi
AT	Austria	GE	Georgia	MX	Mexico
AU	Australia	GN	Guinea	NE	Niger
BB	Barbados	GR	Greece	NL	Netherlands
BE	Belgium	HU	Hungary	NO	Norway
BF	Burkina Faso	IE	Ireland	NZ	New Zealand
BG	Bulgaria	IT	Italy	PL	Poland
BJ	Benin	JP	Japan	PT	Portugal
BR	Brazil	KE	Kenya	RO	Romania
BY	Belarus	KG	Kyrgyzstan	RU	Russian Federation
CA	Canada	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic	KR	Republic of Korea	SE	Sweden
CG	Congo	KZ	Kazakhstan	SG	Singapore
CH	Switzerland	LI	Liechtenstein	SI	Slovenia
CI	Côte d'Ivoire	LK	Sri Lanka	SK	Slovakia
CM	Cameroon	LR	Liberia	SN	Senegal
CN	China	LT	Lithuania	SZ	Swaziland
CS	Czechoslovakia	LU	Luxembourg	TD	Chad
CZ	Czech Republic	LV	Latvia	TG	Togo
DE	Germany	MC	Monaco	TJ	Tajikistan
DK	Denmark	MD	Republic of Moldova	TT	Trinidad and Tobago
EE	Estonia	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	UG	Uganda
FI	Finland	MN	Mongolia	US	United States of America
FR	France	MR	Mauritania	UZ	Uzbekistan
GA	Gabon			VN	Viet Nam

TITLE
 FLUORINATED ALKENYLTIAZINES AND THEIR
 USE AS CROSSLINKING AGENTS

FIELD OF THE INVENTION

5 This invention concerns selected novel fluorinated alkenyltriazines, and
 their use as crosslinking agents for fluorinated elastomers.

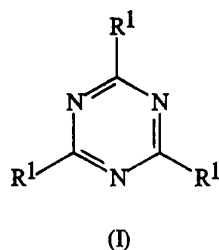
TECHNICAL BACKGROUND

Fluorinated elastomers are items of commerce, being used for a variety of
 applications where chemical and/or thermal resistance is important. They are
 10 especially useful for a variety of seals, such as O-rings and chevron rings. These
 elastomers are normally crosslinked when formed into their final part shapes, and it
 is desirable that the crosslinks formed have at least as much chemical and thermal
 stability as the elastomeric polymer itself.

One method of forming crosslinks with polymers which have certain
 15 functional groups attached is the free radical "grafting" of certain polyolefins, see
 for instance U.S. Patents 4,320,216, 4,303,761, 4,299,958 and 4,035,565, which
 are all hereby included by reference. The alkenyl triazines described herein give
 vulcanizates with good properties and have good curing characteristics, such as
 fast curing but good scorch resistance.

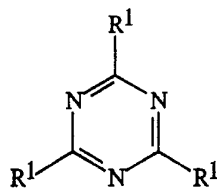
SUMMARY OF THE INVENTION

20 This invention concerns a compound of the formula



25 wherein R^1 is $CH_2=CH(CF_2)_n-$, $CH_2=CHCH_2(CF_2)_n-$,
 $CH_2=CHCF_2CF(CF_3)OCF_2CF_2-$ or
 $CH_2=CHCF_2CF_2CF(CH=CH_2)OCF_2CF(CF_3)OCF_2CF_2-$, and n is an integer of 1
 to about 10.

30 This invention also concerns a process for the crosslinking of a fluoro-
 elastomer, comprising, contacting a free radical generator, a fluoroelastomer which
 is capable of crosslinking with a polyolefin under free radical conditions, and a
 compound of the formula



(I)

- wherein R^1 is $CH_2=CH(CF_2)_n-$, $CH_2=CHCH_2(CF_2)_n-$,
 $CH_2=CHCF_2CF(CF_3)OCF_2CF_2-$ or
 5 $CH_2=CHCF_2CF_2CF(CH=CH_2)OCF_2CF(CF_3)OCF_2CF_2-$, and n is an integer of 1
 to about 10, and provided said contacting is done at a temperature at which said
 free radical generator generates free radicals.

DETAILS OF THE INVENTION

- By a fluoroelastomer herein is meant a polymer containing fluorine whose
 10 glass transition temperature and melting point (if any) is at or below about $40^\circ C$.
 It is preferred that the fluoroelastomer contain about 45% or more by weight of
 fluorine, and more preferred that it is a perfluoroelastomer.

- Compound (I) can generally be made by the trimerization of a nitrile of the
 formula R^1CN (see Examples 9, 12, 15, 20 and 25). These nitriles, and precursors
 15 thereto, can be made by methods illustrated in the Examples or found in the
 following references: G. A. Grindahl, et al., J. Org. Chem., vol. 32, pp. 603-607
 (1967); and P. B. Sargent, et al., J. Am. Chem. Soc., vol. 91, p. 415ff (1969).

In compound (I), when R^1 is $CH_2=CH(CF_2)_n-$, it is preferred that n is 1 or
 2, when R^1 is $CH_2=CHCH_2(CF_2)_n-$, it is preferred that n is 1.

- 20 When (I) is used as a crosslinking agent, it may be used to crosslink
 fluoroelastomers made from the following monomer combinations: hexafluoro-
 propylene/vinylidene fluoride; tetrafluoroethylene/vinylidene fluoride/hexafluoro-
 propylene; tetrafluoroethylene/perfluoro(alkyl vinyl ether) wherein the alkyl group
 contains 1 to 5 carbon atoms, preferably wherein the alkyl group is methyl or
 25 propyl; and tetrafluoroethylene/perfluoro(alkyl vinyl ether) wherein the alkyl group
 contains one or more ether oxygen atoms and 2 to 20 carbon atoms. In all of the
 these polymers, 0.1 to 5 mole percent (based on total repeat units) of a repeat unit
 derived from a curesite monomer may optionally be present. A curesite monomer
 is a monomer which provides a repeat unit which aids in the crosslinking process.
 30 A crosslinked polymer wherein (I) is used as a crosslinking agent is also novel,
 since the crosslink itself has not been included in such polymers.

The crosslinked polymers of this invention are useful wherever chemical
 and/or high temperature resistance is required. They are especially useful in sealing

applications requiring such properties, such as in O-rings, chevron rings, gaskets, etc.

In the Examples, the following abbreviations are used:

- Krytox® 16350 - poly(hexafluoropropylene oxide) available from
- 5 E. I. du Pont de Nemours and Company, Wilmington, DE, USA
- Luperc® 101XL - 2,5-dimethyl-2,5-bis(t-butylperoxy)hexane
- PCN42 - a postcure cycle under nitrogen of 6 h at 90°C, 10 h ramp from
- 90 to 304°C, and 26 h at 304°C
- PCN260 - a postcure cycle under nitrogen of 8 h ramp to 260°C, and
- 10 then 40 h at 260°C
- TAIC - triallyl isocyanurate

In Examples 25-27, numbers such as DXXXX refer to ASTM test methods for the tests performed. Abbreviations used herein to give the test results are given in the ASTM test methods.

15

EXAMPLE 1

Preparation of c-C₃F₅OCF₂CF(CF₃)OCF₂CF₂CO₂CH₃

- A 1 L autoclave was charged with 425 g of CF₂=CFOCF₂CF(CF₃)OCF₂CF₂CO₂CH₃ and 335 g of hexafluoropropylene oxide and heated at 185°C for 10 hrs. The crude product (476.6 g) was distilled to give
- 20 391.6 g of pure product, bp 83-84°C/4.7 kPa. ¹⁹F NMR: -80.4 (s, 3F), -83.5 (m, 2F), -85.2 to -86.4 (m, 2F), -121.6 (s, 2F), -145.7 (t, J = 22 Hz, 1F), -152.9 9d, J = 193.4 Hz, 2F), -155.7 (dm, J = 194 Hz, 2F), -162.4 (t, J = 8.7 Hz, 1F). ¹H NMR: 3.97 (s). IR(neat): 1791 (s), 1308 (s), 1276 (s), 1239 (s), 1152 (s). Anal: calcd for C₁₀H₃F₁₅O₄: C, 25.44; H, 0.64. Found: C, 26.19; H, 0.73.

25

EXAMPLE 2

Reaction of c-C₃F₇OCF₂CF(CF₃)OCF₂CF₂CO₂CH₃ with Iodine

- A 1 L autoclave was charged with 200 g of c-C₃F₇OCF₂CF(CF₃)OCF₂CF₂CO₂CH₃ (c = cyclo) and 108 g of I₂ and heated at 150°C for 5 hr. The product was washed with aqueous Na₂SO₃ solution, checked
- 30 by GC, indicating 90% of product with 10% of starting material, and distilled to give 236.5 g of pure ICF₂CF₂CFIOCF₂CF(CF₃)OCF₂CF₂CO₂CH₃, bp 107-110°C/399 Pa, and 21.6 g of bp 60-106°C/399 Pa material containing starting material. ¹⁹F NMR: -55.2 (d, J = 205.1 Hz, 1F), -58.8 (dm, J = 204.4 Hz, 1F), -69.0 (m, 1F), -80.0 (s, 3F), -79.6 to -80.7 (m, 1F), -82.5 to -84.0 (m, 2F),
- 35 -89.9 (m, 0.5 F), -90.3 (m, 0.5F), -102.1 (d, J = 277.1 Hz, 1F), -104.6 (dt, J = 277 Hz, J = 8.4 Hz, 1F), -121.5 (s, 2F), -145.7 (t, J = 11.3 Hz, 0.5F), -146.0 (t, J = 11.7 Hz, 0.5F). ¹H NMR: IR(neat): 2990 (w), 1786 (s), 1306 (s), 1243 (s), 1194

(s), 1152 (s), 1134 (s), 1128 (s). Anal: Calcd for $C_{10}H_3F_{15}I_2O_4$: C, 16.55; H, 0.42; I, 34.96. Found: C, 17.03; H, 0.51; I, 35.21.

EXAMPLE 3

Reaction of $c\text{-C}_3\text{F}_5\text{OCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{CO}_2\text{CH}_3$

5 with Iodine at Higher Temperature

A 0.4 L shaker tube was charged with 189 g of $c\text{-C}_3\text{F}_5\text{OCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{CO}_2\text{CH}_3$ and 100 g of I_2 and heated at 150°C for 3 hrs and 240°C for 8 hrs. Distillation of the reaction mixture gave 78.3 g of $\text{ICF}_2\text{CF}_2\text{COF}$, bp $57\text{--}58^\circ\text{C}$ and 129.3 g of $\text{ICF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{CO}_2\text{Me}$, bp $98\text{--}100^\circ\text{C}/8.0\text{ kPa}$. ^{19}F NMR for $\text{ICF}_2\text{CF}_2\text{COF}$: +28.0 (m, 1F), -62.1 (m, 2F), -111.4 (m, 2F); for $\text{ICF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{CO}_2\text{Me}$: -58.8 (dm, $J = 210\text{ Hz}$, 1F), -59.9 (dm, $J = 210\text{ Hz}$, 1F), -76.8 (m, 3F), -82.7 (dm, $J = 158.7\text{ Hz}$, 1F), -83.7 (dm, $J = 158\text{ Hz}$, 1F), -121.6 (t, $J = 3.3\text{ Hz}$, 2F), -134.3 (m, 1F). IR for $\text{ICF}_2\text{CF}_2\text{COF}$: 1768 (s), 1187 (s), 1150 (s); IR for $\text{ICF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{CO}_2\text{Me}$: 1768 (s), 1342 (s), 1304 (s), 1232 to 1110 (s). Anal: Calcd. for $C_7H_3F_{10}IO_3$: C, 18.60; H, 0.67; F, 42.38; I, 28.08. Found: C, 18.24; H, 0.52; F, 42.38; I, 29.46.

EXAMPLE 4

Preparation of Ethyl 2-Iodotetrafluoropropanoate

A 300 mL shaker tube was charged with 50.8 g iodine and 50 g of trifluoromethoxypentafluorocyclopropane and heated at 150°C for 4 hrs and 240°C for 8 hrs. After the tube was cooled to room temperature, 57.6 g of crude product was obtained, which was treated with 75 mL of EtOH and 11 g of KF at 10°C for 4 hours. The reaction mixture was poured into water. The lower layer was separated, washed with Na_2SO_3 solution and dried over molecular sieves to give 51.2 g of crude ester. Distillation gave 45.3 g of pure product, bp $72\text{--}73^\circ\text{C}/4.0\text{ kPa}$. ^1H NMR: 4.43 (q, $J = 7.0\text{ Hz}$, 2H), 1.39 (t, $J = 7.2\text{ Hz}$, 3H). ^{19}F NMR: -60.6 (t, $J = 7.0\text{ Hz}$, 2F), -111.9 (t, $J = 7.0\text{ Hz}$, 2F). IR (neat): 2995 (w), 1778 (s), 1374 (m), 1709 (s), 1185 (s), 1141 (s), 1076 (s). Anal: Calcd for $C_3H_5F_4IO_2$: C, 20.02; H, 1.68; F, 25.33; I, 42.30. Found: C, 19.83; H, 1.52; F, 27.74; I, 43.46.

EXAMPLE 5

Reaction of $\text{ICF}_2\text{CF}_2\text{CO}_2\text{Et}$ with Ethylene

A 0.4 L shaker tube was charged with 100 g of $\text{ICF}_2\text{CF}_2\text{CO}_2\text{Et}$, 0.5 g of limonene and 20 g of ethylene and heated at 210°C for 6 hours. Distillation of the reaction mixture gave 85 g of pure product, bp $83\text{--}84^\circ\text{C}/665\text{ Pa}$ and 11 g of 84% pure product, bp $35\text{--}84^\circ\text{C}/665\text{ Pa}$. ^{19}F NMR: -115.9 (t, $J = 17.2\text{ Hz}$, 2F), -120.4 (s, 2F). ^1H NMR: 4.41 (q, $J = 7.1\text{ Hz}$, 2H), 3.23 (m, 2H), 2.75 (m, 2H), 1.38 (t, $J = 7.1\text{ Hz}$, 3H). IR (neat): 2995 (w), 1774 (s), 1320 (s), 1167 (s), 1134 (s), 1113

(s). Anal: Calcd for $C_7H_9F_4IO_2$: C, 25.63; H, 2.77; F, 23.17; I, 38.68. Found: C, 26.50; H, 2.86; F, 25.38; I, 39.38.

EXAMPLE 6

Preparation of $CH_2=CHCF_2CF_2CO_2Et$

- 5 To a stirred solution of 705.2 g of $ICH_2CH_2CF_2CF_2CO_2Et$ and 1 L of CH_2Cl_2 was slowly added 353 g of DBU over 3 hrs at 23 to 30°C. After the addition was complete, the reaction mixture was stirred at room temperature for 20 min. and then neutralized with 5% HCl solution. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 . The combined
10 organic layers were washed with water and NaCl solution and dried over $MgSO_4$. After removal of CH_2Cl_2 , the residue was distilled to give 331.5 g of $CH_2=CHCF_2CF_2CO_2Et$, bp 75°C/16 kPa.

EXAMPLE 7

Preparation of $CH_2=CHCF_2CF_2CONH_2$

- 15 To a stirred solution of 305 g (1.525 mol) of $CH_2=CHCF_2CF_2CO_2Et$ and 700 mL of CH_2Cl_2 was added 34 g (2.0 mol) of NH_3 at 0°C over 1.5 hrs. After the addition was complete, the resulting mixture was stirred at room temperature overnight. Removal of all volatiles gave 221.3 g of white solid product. ^{19}F NMR: -115.5 (2F), -122.0 (2F). 1H NMR: 6.91 (br, 1H), 6.43 (br, 1H),
20 6.10-5.75 (m, 3H). IR(KBr): 3376 (m), 3268 (m), 3192 (m), 1706 (s), 1629 (m), 1245 (s), 1147 (s), 1014 (s), 956 (s).

EXAMPLE 8

Preparation of $CH_2=CHCF_2CF_2CN$

- A mixture of 100 g of fine powder $CH_2=CHCF_2CF_2CONH_2$ and 261 g of
25 P_2O_5 was heated at 130 to 170°C, during which volatiles were distilled out and collected in an ice-water cooled receiver. After 5 hours, 84.1 g of volatiles were obtained and GC analysis indicated the product was 97% pure. Two runs were combined, a drop of Hg added (to remove pink color), and distilled to give 160.7 g of colorless product, yield 90%, bp 53°C. ^{19}F NMR: -107.5 (t, J = 4.3 Hz, 2F),
30 -11.4 (t, J = 4.3 Hz, 2F). 1H NMR: 6.10 to 5.90 (m).

EXAMPLE 9

Trimerization of $CH_2=CHCF_2CF_2CN$

- A 100 mL tube was charged with 40.0 g of $CH_2=CHCF_2CF_2CN$, 0.85 g of Ag_2O and cooled in liquid nitrogen. After being evacuated and pressured with
35 nitrogen for six times, the tube was sealed and the contents in the tube were stirred at 120°C for 40 hours. The solids were dissolved in CH_2Cl_2 and transferred to a column with silica gel (CH_2Cl_2 as solvent) to give 35.0 g of pure $(CH_2=CHCF_2CF_2)_3C_3N_3$. ^{19}F NMR: -113.7 (d, J = 11.1 Hz, 6F), -118.1 (s, 6F).

IR: 1651 (w), 1552 (s), 1186-1014 (s). Anal: Calcd. for $C_{15}H_9F_{12}N_3$: C, 39.23; H, 1.98; N, 9.15. Found: C, 39.05; H, 1.94; N, 8.91.

EXAMPLE 10

Preparation of $CH_2=CHCF_2CF(CF_3)OCF_2CF_2CO_2Me$

- 5 A mixture of 68.0 g of $ICF_2CF(CF_3)OCF_2CF_2CO_2Me$ and 8.0 g of $CH_2=CH_2$ was heated in a 0.1 L shaker tube at 210°C for 6 hours, and 63 g of crude product was obtained. The crude product was diluted with 100 mL of CH_2Cl_2 and treated with 25 g of DBU at room temperature overnight. The reaction mixture was poured to water and neutralized with a 5% HCl solution.
- 10 The lower layer was separated and washed with water. After removal of the CH_2Cl_2 , the residue was distilled to give 40.1 g (76%) of $CH_2=CHCF_2CF(CF_3)OCF_2CF_2CO_2Me$, bp 71-72°C/2.7 kPa. ^{19}F NMR: -79.1 (m, 3F), -82.6 to -84.3 (m, 2F), -113.7 (dm J = 264.8 Hz, 1F), -115.0 (dm, J = 264.3 Hz, 1F), -121.9 (t, J = 3.0 Hz, 2F), -145.3 (t, J = 21.8 Hz, 1F). 1H NMR: 3.96 (s, 3H), 5.99-5.78 (m, 3H).

EXAMPLE 11

Preparation of $CH_2=CHCF_2CF(CF_3)OCF_2CF_2CN$

- 20 A mixture of 21.1 g of $CH_2=CHCF_2CF(CF_3)OCF_2CF_2CO_2Me$ and 12.0 g of NH_4OH (30% in H_2O) in 25 mL of acetone was stirred at room temperature overnight. After removal of all volatiles, 17.3 g of crude $CH_2=CHCF_2CF(CF_3)OCF_2CF_2CONH_2$ was obtained. ^{19}F NMR: -79.1 (m, 3F), -82.5 (dd, J = 138.2 Hz, J = 24.0 Hz, 1F), -83.9 (dm, J = 138 Hz, 1F), -113.7 (dm, J = 264 Hz, 1F), -114.8 (dm, J = 264 Hz, 1F), -123.2 (m, 2F), -145.3 (m, 1F). 1H NMR: 7.08 (br, 1H), 6.53 (br, 1H), 5.76-5.98 (m, 3H).
- 25 A flask fitted with a distillation head was charged with 13.0 g of the above amide and 18.0 g of P_2O_5 and was heated at 150 to 200°C for 2 hours, during which 9.3 g of $CH_2=CHCF_2CF(CF_3)OCF_2CF_2CN$ was collected in a receiver, bp 103 to 104°C, 97.5% purity. ^{19}F NMR: -79.1 (m, 3F), -83.6 (dm, J = 136 Hz, 1F), -85.3 (dm J = 136.8 Hz, 1F), -108.9 (m, 2F), -113.4 (dm, J = 264.8 Hz, 1F), -115.0 (dm, J = 265 Hz, 1F), -144.8 (m, 1F). 1H NMR: 5.84 to 6.06 (m, 3H). Anal: Calcd for $C_8H_3F_{10}NO$: C, 30.11; H, 0.95; F, 59.54; N, 4.39. Found: C, 30.61; H, 1.17.

EXAMPLE 12

Trimerization of $CH_2=CHCF_2CF(CF_3)OCF_2CF_2CN$

- 35 A mixture was 4.0 g of $CH_2=CHCF_2CF(CF_3)OCF_2CF_2CN$ and 0.12 g of Ag_2O was stirred at 140 to 150°C for 15 hours and then purified by chromatography on silica gel using a mixture of hexane and ethyl acetate in a 90 to 10 ratio as eluent to give 3.5 g of pure $[CH_2=CHCF_2CF(CF_3)OCF_2CF_2]_3C_3N_3$.

^{19}F NMR: -79.4 (m, 9F), -82.30 (m, 6F), -113.8 (dm, $J = 265$ Hz, 3F), -114.6 (dm, $J = 265$ Hz, 3F), -119.4 (m, 6F), -144.8 (m, 3F). ^1H NMR: 5.98-5.75 (m, 9H). IR: 1651 (m), 1554 (s), 1423 (s), 1316 (s), 1219 to 1027 (s), 980 (s). Anal: Calcd for $\text{C}_{24}\text{H}_9\text{F}_{30}\text{N}_3\text{O}_3$: C, 30.11; H, 0.95; F, 59.54; N, 4.39. Found: C, 29.86; H, 1.02; F, 60.53; N, 4.45.

EXAMPLE 13

Preparation of $\text{CH}_2=\text{CHCF}_2\text{CF}_2\text{CF}(\text{CH}=\text{CH}_2)\text{OCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{CO}_2\text{Me}$

A mixture of 70.0 g of $\text{ICF}_2\text{CF}_2\text{CFIOCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{CO}_2\text{Me}$ and 12.0 g of $\text{CH}_2=\text{CH}_2$ was heated in a 0.1 L shaker tube at 160°C for 3 hours and 190°C for 2 hours, and 65 g of crude product was obtained. The crude product was diluted with 60 mL of CH_2Cl_2 and treated with 33.4 g of DBU at room temperature for 3 hours. The reaction mixture was poured to water and neutralized with a 5% HCl solution. The lower layer was separated and washed water. After removal of the CH_2Cl_2 , the residue was distilled to give 28.3 g (58%) of $\text{CH}_2=\text{CHCF}_2\text{CF}_2\text{CF}(\text{CH}=\text{CH}_2)\text{OCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{CO}_2\text{Me}$, bp $108-110^\circ\text{C}/665$ Pa. ^{19}F NMR: -78.5 to -79.4 (m, 1F), -80.2 (m, 3F), -82.5 (m, 1F), -83.1 (dm, $J = 138.5$ Hz, 1F), -84.2 (dm, $J = 138.5$ Hz, 1F), -112.8 (s, 2F), -121.8 (m, 2F), -124.6 (dd, $J = 282.7$ Hz, $J = 24.8$ Hz, 1F), -125.3 (dm, $J = 282.7$ Hz, 1F), -127.8 (m, 1F), -145.8 (m, 1F). ^1H NMR: 3.95 (s, 3H), 5.10-5.69 (m, 6H). Anal: Calcd. for $\text{C}_{14}\text{H}_9\text{F}_{15}\text{O}_4$: C, 31.96; H, 1.72. Found: C, 31.98; H, 1.72.

EXAMPLE 14

Preparation of $\text{CH}_2=\text{CHCF}_2\text{CF}_2\text{CF}(\text{CH}=\text{CH}_2)\text{OCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{CN}$

A mixture of 20.0 g of $\text{CH}_2=\text{CHCF}_2\text{CF}_2\text{CF}(\text{CH}=\text{CH}_2)\text{OCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{CO}_2\text{Me}$ and 3.0 g of NH_3 in 40 mL of CH_2Cl_2 was stirred at room temperature for 20 hours. After removal of all volatiles, 19.0 g of crude $\text{CH}_2=\text{CHCF}_2\text{CF}_2\text{CF}(\text{CH}=\text{CH}_2)\text{OCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{CONH}_2$ was obtained. ^1H NMR: 8.11 (br, 1H), 7.80 (br, 1H), 6.34-5.84 (m, 6H).

A flask fitted with a distillation head was charged with 17.0 g of above amide and 18.0 g of P_2O_5 and was heated at 160 to 200°C for 2.5 hours, during which 14.7 g of $\text{CH}_2=\text{CHCF}_2\text{CF}_2\text{CF}(\text{CH}=\text{CH}_2)\text{OCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{CN}$ was collected in a receiver, bp 103 to 104°C . ^{19}F NMR: -78.1 to -79.0 (m, 1F), -80.3 (m, 3F), -81.6 to -82.4 (m, 1F), -84.3 (dm $J = 134.8$ Hz, 1F), -85.2 (dm $J = 134.8$ Hz, 1F), -108.8 (m, 2F), -112.8 (dm, 2F), -124.4 (ddd, $J = 283.8$ Hz, $J = 28$ Hz, $J = 4$ Hz, 1F), -125.6 (dd, $J = 282.6$ Hz, $J = 10.0$ Hz, 1F), -127.8.8 (m, 1F), -145.2 (m, 1F). ^1H NMR: 5.70-6.20 (m). Anal: Calcd. for $\text{C}_{13}\text{H}_6\text{F}_{15}\text{NO}_2$: C, 31.66; H, 1.23; N, 2.84. Found: C, 31.73; H, 1.40; N, 3.10.

EXAMPLE 15Trimerization of $\text{CH}_2=\text{CHCF}_2\text{CF}_2\text{CF}(\text{CH}=\text{CH}_2)\text{OCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{CN}$

A mixture of 2.0 g

- 5 $\text{CH}_2=\text{CHCF}_2\text{CF}_2\text{CF}(\text{CH}=\text{CH}_2)\text{OCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{CN}$ and 0.1 g of NH_3 was heated at 140°C in a sealed tube for 36 hours. The viscous oil was diluted with CH_2Cl_2 and transferred to a flask. After removal of solvent, the residue was purified by chromatography using ethyl acetate and hexane (9:1) as solvent to give 1.6 g of product. ^{19}F NMR: -78.3 to -78.9 (m, 3F), -80.5 (m, 9F), -81.9 to -83.3 (m, 3F), -113.1 (d, $J = 7.3$ Hz, 6F), -119.5 (m, 6F), -124.6 (dd, $J = 283.6$ Hz, $J =$
- 10 18.3 Hz, 3F), -126.0 (dd, $J = 282.5$ Hz, $J = 18.2$ Hz, 3F), -127.9 (m, 3F), -145.6 (m, 3F). IR: 3101 (w), 1735 (w), -1651 (w), 1555 (s), 1238-1008 (s). Anal: Calcd. for $\text{C}_{39}\text{H}_{18}\text{F}_{45}\text{N}_3\text{O}_6$: C, 31.66; H, 1.23; F, 57.78; N, 2.84. Found: C, 31.03; H, 1.45; N, 2.67.

EXAMPLE 16Preparation of Ethyl 4-Iodo-2,2-difluorobutyrate

- 15 In a one-liter pressure reactor was charged ethyl iododifluoroacetate (200 g, 0.8 mol, from accompanied patent proposal), CH_3CN (80 mL) and water (300 mL). The mixture was cooled to -10°C and then a mixture of $\text{Na}_2\text{S}_2\text{O}_4$ (40 g) and NaHCO_3 (20 g) was added. The reactor was closed, cooled evacuated
- 20 and charged with ethylene (60 g, 2.14 mol). The reaction mixture was then warmed to room temperature in a 4 hr period and kept at 40°C for 2 hr. After the reaction was over the lower layer was separated from the reaction mixture and the aqueous layer was extracted with ether. The combined organic layer was washed with brine and dried over MgSO_4 . Distillation gave the title compound (200 g,
- 25 90% yield), bp. $70^\circ\text{C}/266$ Pa. ^1H NMR (300 MHz, CDCl_3): δ 1.38 (t, 3H), 2.70 (m, 2H), 3.20 (m, 2H), 4.37 (q, 2H). ^{19}F NMR (188.24 MHz, CDCl_3): -107.3 (t, $J = 16$ Hz, 2F). Anal. Calcd. for $\text{C}_6\text{H}_9\text{F}_2\text{IO}_2$: C, 25.92; H, 3.26; F, 13.67. Found: C, 26.69; H, 3.28; F, 13.39. IR (neat): 1780 cm^{-1} ($\text{C}=\text{O}$). Mass: Calcd. for $[(\text{M}+\text{H})^+]$: 278.9691; Found: 278.9659.

EXAMPLE 17Preparation of Ethyl 2,2-Difluoro-3-butenolate

- 30 To a stirred solution of $\text{ICH}_2\text{CH}_2\text{CF}_2\text{CO}_2\text{Et}$ (450 g, 1.62 mol) in ether (1000 mL) was added dropwise 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 260 g, 1.71 mol) in a 2 hr period. The temperature was maintained at between 10 - 20°C
- 35 with external cooling. After the addition was complete, the reaction mixture was stirred at room temperature for 4 hrs. Water (600 mL) was added and the ethereal layer was separated and washed with brine, dried over MgSO_4 . Distillation gave the desired product (200 g, 82% yield), bp. $60^\circ\text{C}/9.3$ kPa. ^1H NMR (300 MHz,

- CDCl₃): δ 1.32 (t, 3H), 4.30 (q, 2H), 5.60 (d, 1H), 5.80 (dt, 1H), 6.00 (m, 1H).
¹⁹F NMR (188.24 MHz, CDCl₃): -106.2 (2F). Anal. Calcd. for C₆H₈F₂O₂: C, 48.00; H, 5.37; F, 25.31. Found: C, 47.82; H, 5.72; F, 27.32. IR (neat): 1770 cm⁻¹ (C=O), 1650 cm⁻¹ (C=C). Mass: Calcd. for [(M-CH₂=CH₂)⁺]:
 5 122.0179; Found: 122.0191.

EXAMPLE 18

Preparation of 2,2-Difluoro-3-butenamide

- Ethyl 2,2-difluoro-3-butenonate (51 g, 0.34 mol) was added dropwise into a solution of ammonium hydroxide (28-30 wt%, 24 g, 0.4 mol) and THF (25 mL)
 10 with stirring. The temperature was maintained at 10-20°C with external cooling during the addition. After addition was completed, the reaction mixture was stirred at ambient temperature for 3 hr. The disappearance of the starting material was monitored by GC. Extraction with ether followed by evaporation of solvent gave pure amide as a white crystal (30.5 g, 74%), mp. 85-86°C. ¹H NMR
 15 (300 MHz, acetone-d₆): δ 5.65 (m, 1H), 5.80 (m, 1H), 6.18 (m, 1H), 7.33 (br., 1H), 7.62 (br., 1H). ¹⁹F NMR (188.24 MHz, acetone-d₆): -104.9 (2F). Anal. Calcd. for C₄H₅F₂NO: C, 39.68; H, 4.16; N, 11.57. Found: C, 39.83; H, 4.01; N, 11.23. IR (KBr): 3200, 3380 cm⁻¹ (br, CONH₂), 1690 cm⁻¹ (C=O), 1650 cm⁻¹ (C=C). Mass: Calcd. for [(M-F)⁺]: 102.0355; Found: 102.0372.

20

EXAMPLE 19

Preparation of 2,2-Difluoro-3-butenenitrile

- 2,2-Difluoro-3-butenamide (14.0 g, 0.118 mol) was well mixed with P₂O₅ (10 g) and heated slowly to 200°C. The product was distilled at 42-43°C to give the nitrile product (10.8 g, 91% yield). ¹H NMR (300 MHz, CDCl₃): δ 5.80 (m,
 25 1H), 6.05 (m, 2H). ¹⁹F NMR (188.24 MHz, CDCl₃): -86.5 (m, 2F). Mass: Calcd. for [M⁺]: 103.0233; Found: 103.0227.

EXAMPLE 20

Preparation of 2,4,6-Tris(1',1'-difluoroallyl)-1,3,5-triazine

- A mixture of 2,2-difluoro-3-butenenitrile (18.5 g, 0.18 mol) and ammonia (ca. 0.1 g) was heated at 120-130°C for 3 hr and then distilled to give the desired triazine product (17.8 g, 96% yield), bp. 70°C/80 Pa. ¹H NMR (300 MHz, CDCl₃): δ 5.73 (d, 3H), 5.98 (d, 3H), 6.32 (m, 3H). ¹⁹F NMR (188.24 MHz, CDCl₃): -103.6. IR (neat): 1554 cm⁻¹ (triazine), 1650 cm⁻¹ (C=C). Anal. Calcd. for C₁₂H₉F₆N₃: C, 46.61; H, 2.93; N, 13.59; F, 36.86. Found: C, 44.98; H, 3.13; N, 13.30; F, 38.08. Mass: Calcd. for [M⁺]: 309.0700; Found: 309.0695.

35

EXAMPLE 21Preparation of Ethyl 2,2-Difluoro-4-pentenoate

Ethyl iododifluoroacetate (100 g, 0.4 mol) was added dropwise into a well stirred suspension of copper powder (51 g, 0.803 mol) in anhydrous DMSO (250 mL) at room temperature. The temperature was maintained at below 25°C during the addition with external cooling. After that, the reaction mixture was stirred at room temperature for 45 min. Allyl bromide (60.5 g, 0.5 mol) was then added dropwise while the temperature was still controlled at 20-25°C during the addition. The reaction mixture was stirred at room temperature for another 3 hr after the addition was completed. Distillation in vacuo gave a crude product, which was extracted with ether, washed with brine and dried over MgSO_4 . Redistillation produced pure ethyl 2,2-difluoro-4-pentenoate (52.8 g, 80% yield) as a clear, colorless liquid, bp. 55°C/2.7 kPa. ^1H NMR (300 MHz, CDCl_3): δ 1.25 (t, 3H), 2.76 (dt, 2H), 4.24 (q, 2H), 5.20 (1H), 5.22 (1H), 5.63 (m, 1H). ^{19}F NMR (188.24 MHz, CDCl_3): -105.7 (t, $J = 18.9$ Hz). IR (neat): 1780 cm^{-1} (C=O), 1650 cm^{-1} (C=C). Anal. Calcd. for $\text{C}_7\text{H}_{10}\text{F}_2\text{O}_2$: C, 51.22; H, 6.14; F, 23.15. Found: C, 49.73; H, 6.06; F, 21.42. Mass: Calcd. for $[\text{M}^+]$: 164.0648; Found: 164.0645.

EXAMPLE 22Preparation of 2,2-Difluoro-4-pentenamide

To a stirred solution of ammonium hydroxide (28-30 wt%, 50 mL) and THF (200 mL) was added dropwise $\text{CH}_2=\text{CHCH}_2\text{CF}_2\text{CO}_2\text{Et}$ (51 g, 0.31 mol). The temperature was maintained at 20-25°C (external cooling if necessary) during the addition. The reaction was complete within 3 hr as monitored by GC. The product was worked up to give the corresponding amide compound (36 g, 86% yield), bp. 75°C/93 Pa.

^1H NMR (300 MHz, acetone- d_6): δ 2.85 (dt, $J = 7.2$ Hz, $J = 16$ Hz, 2H), 5.20-5.30 (m, 2H), 5.70-5.85 (m, 1H), 7.25 (br., 1H), 7.58 (br., 1H). ^{19}F NMR (188.24 MHz, acetone- d_6): -105.3 (t, $J = 16$ Hz, 2F). IR (neat): 3200-3500 cm^{-1} (N-H), 1720 cm^{-1} (C=O), 1650 cm^{-1} (C=C). Anal. Calcd. for $\text{C}_5\text{H}_7\text{F}_2\text{NO}$: C, 44.45; H, 5.22; N, 10.37; F, 28.12. Found: C, 42.31; H, 5.22; N, 10.18; F, 29.93. Mass: Calcd. for $[\text{M}^+]$: 135.0495; Found: 135.0490.

EXAMPLE 23Preparation of 2,2-Difluoro-4-pentenitrile

A mixture of $\text{CH}_2=\text{CHCH}_2\text{CF}_2\text{CONH}_2$ (33.8 g, 0.25 mol) and P_2O_5 (40 g) was heated slowly to 170-200°C to give the desired product as a colorless liquid (25.2 g, 86% yield), bp. 72-74°C. ^1H NMR (300 MHz, CDCl_3): δ 2.85 (dt, $J = 7.2$ Hz, $J = 18$ Hz, 2H), 5.30-5.50 (m, 2H), 5.62-5.78 (m, 1H). ^{19}F NMR

(188.24 MHz, CDCl_3): -89.5 (t, $J = 18$ Hz). IR (gas): 2260 cm^{-1} ($\text{C}\equiv\text{N}$), 1650 cm^{-1} ($\text{C}=\text{C}$). Mass: Calcd. for $[\text{M}^+]$: 117.0390; Found: 117.0382.

EXAMPLE 24

Preparation of 2,4,6-Tris(1',1'-difluoro-3'-butenyl)-1,3,5-triazine

- 5 A mixture of 2,2-difluoro-4-pentenitrile (23.4 g, 0.2 mol) and ammonia gas (ca. 0.1 g) was heated at 120°C for 10 hr in a sealed tube, and then distilled to give the desired triazine (18.5 g, 79% yield), bp. $86\text{--}90^\circ\text{C}/93\text{ Pa}$. ^1H NMR (300 MHz, CDCl_3): δ 3.15 (dt, $J = 7.2$ Hz, $J = 16$ Hz, 2H), 5.18-5.30 (m, 2H), 5.70-5.90 (m, 1H). ^{19}F NMR (188.24 MHz, CDCl_3): -103.1 (t, $J = 16$ Hz, 2F).
- 10 IR (neat): 1555 cm^{-1} (triazine), 1645 cm^{-1} ($\text{C}=\text{C}$). Anal. Calcd. for $\text{C}_{15}\text{H}_{15}\text{F}_6\text{N}_3$: C, 51.29; H, 4.30; N, 11.96; F, 32.45. Found: C, 50.50; H, 4.28; N, 11.80; F, 31.22. Mass: Calcd. for $[\text{M}^+]$: 351.1170; Found: 351.1164.

EXAMPLE 25

- A perfluoroelastomer was prepared in a continuous polymerization process, similar to that described in U.S. Patent 4,983,697. The polymer was prepared in a 2 L mechanically stirred, water jacketed, stainless-steel autoclave operated continuously at 90°C and 6.2 MPa into which was pumped at a rate of 550 ml/h an aqueous polymerization medium/initiator solution comprising of 16 liters of water, 62 g of ammonium persulfate, 337 g of disodium hydrogen phosphate hepta-
- 20 hydrate, 220 g of ammonium pefluorooctanoate ("Fluorad" FC-143 from 3M Co.). At the same time a separate solution of perfluoro(-(8-cyano-5-methyl-3,6-dioxo-1-octene) (8CNVE) was added at a rate of 7.4 g/h of 8CNVE. A gaseous stream of tetrafluoroethylene (113 g/h) and perfluoro(methyl vinyl ether) (PMVE, 130 g/h) were fed in the reactor at a constant rate by means of a diaphragm compressor.
- 25 The polymer was continuously removed by means of a let-down valve and unreacted monomers were vented. The latex from 27.6 h of operation was combined and the polymer was coagulated by adding it with stirring to a hot ($90\text{--}95^\circ\text{C}$) magnesium sulfate heptahydrate solution of about 3700 g in 80 L of water. The coagulated crumb was repeatedly washed with fresh water and dried at
- 30 80°C in an air oven. Analysis of the polymer by infrared indicated that the PMVE content was 44.6 wt%, TFE 53.1 wt% and 8CNVE 2.3 wt%. The inherent viscosity was 0.44 and the Mooney viscosity (ASTM D1646) was 32 as measured at 150°C and 86 as measured at 121°C .

- The polymer was compounded on a rubber mill using the formulation shown in Table 1. The parts O-rings (size 214) and sheets were crosslinked by heating then in a hydraulic press at $175^\circ\text{C}/30\text{ min}$. under 3.45 MPa. They were then post-cured at 305°C for 42 hrs under nitrogen or at 225°C for 24 hr in air and tested using ASTM methods. Under column A we show the results of crosslinking

the above polymer using just peroxide and a coagent, using triallyl isocyanurate as the control and comparative results with the trivinyl perfluoroalkyl triazines where $n = 2$ (column B) and $n = 1$ (column C). The properties of parts molded as O-ring and as dumbbells are being compared.

5

TABLE 1

TRIS(VINYLTETRAFLUOROETHYLENE)TRIAZINE (TVTFET) AND
TRIS(VINYLDIFULOROMETHYLENE)TRIAZINE (TVDFMT) AS
COAGENTS IN THE PEROXIDE CURING OF PERFLUOROELASTOMER

	<u>A</u> (TAIC)	<u>B</u> (TVTFET)	<u>C</u> (TVDFMT)
COMPOUND			
Polymer	100	100	100
MT Black	30	30	30
Krytox [®] 16350	10	10	10
Luperco [®] 101XL	3	3	3
ZnO	2	2	2
TRIALLYL ISOCYANURATE	3	---	----
TVTFET	---	3	----
TVDFMT	---	---	3
ODR 177°/3° Arc D2084			
ML, Nm	0.60	0.23	0.68
ts ₂ , mins	1.5	3.5	7.5
MH, Nm	2.5	1.7	1.8
MH-ML, Nm	1.9	1.5	1.1

PROPERTIES	O-Rings ¹	Dumb Bells ²	O-Rings ¹	Dumb Bells ²	O-Rings ¹
Tensile D1708					
M50, MPa	5.07		4.24		4.05
M100, MPa	9.04	8.36	8.50	8.87	7.11
Tb, MPa	12.1	14.7	13.6	17.7	8.94
Eb, %	144	260	173	230	143
Comp. Set 204°C/ 70 hr D1414	56		70		60

¹Post-cured at 305°C/42 h under nitrogen (PCN42)

²Post-cured at 225°C/24 hr in air

EXAMPLE 26

- The same polymer was used as described in Example 25. The formulation shown in Table 2 is based on the dual cure system which utilizes both the peroxide/coagent and the triphenyl tin hydroxide catalyst (TPT-OH).

TABLE 2

TRIS(VINYLTETRAFLUOROETHYLENE)TRIAZINE (TVTFET) AND
TRIS(VINYLDIFULOROMETHYLENE)TRIAZINE (TVDFMT) AS
COAGENTS IN THE DUAL CURE OF PERFLUOROELASTOMER

	<u>A</u> (TAIC)	<u>B</u> (TVTFET)	<u>C</u> (TVDFMT)
COMPOUND			
Polymer	100	100	100
MT Black	30	30	30
Krytox [®] 16350	10	10	10
ZnO	2	2	2
TPT-OH	1	1	1
Luperc [®] 101XL	1	1	1
TAIC	1	----	----
TVTFETriazine	----	1	----
TVDFMTriazine	----	----	3
ODR 177°/3° Arc D2084			
MI, Nm	0.68	0.40	0.79
ts ₂ , mins	2.5	3.5	2.5
MH, Nm	4.6	3.2	3.1
MH-ML, Nm	4.0	2.8	2.3

PROPERTIES	O-Rings ¹	Dumb Bells ²	O-Rings ¹	Dumb Bells ²	O-Rings ¹
Tensile D1708					
M50, MPa	4.24		4.18	4.45	
M100, MPa	7.24	8.39	7.14	7.42	10.8
Tb, MPa	10.4	17.1	10.5	9.54	18.2
Eb, %	167	240	186	157	200
Comp. Set 204°C/ 70 hr D1414	54		58	60	

¹Post-cured at 305°C/42 h under nitrogen (PCN42)

²Post-cured at 225°C/24 hr in air

EXAMPLE 29

- 5 Viton[®] GF (a copolymer of vinylidene fluoride, hexafluoropropylene, tetrafluoroethylene and bromotrifluorobutene available from E. I. du Pont de Nemours and Company, Wilmington, DE, U.S.A.) was used in this Example. The formulation described in Table 3 was used.

TABLE 3

TRIS(VINYLTETRAFLUOROETHYLENE)TRIAZINE (TVTFET) AND
TRIS(VINYLDIFULOROMETHYLENE)TRIAZINE (TVDFMT) AS
COAGENTS IN THE PEROXIDE CURING OF VITON[®] GF

	<u>A</u> (TAIC)	<u>B</u> (TVTFET)	<u>C</u> (TVDFET)	<u>D</u> (TVDFMT)
COMPOUND				
Polymer	100	100	100	100
MT Black	30	30	30	30
MgO	3	3	3	3
Luperc [®] 101XL	3	3	3	3
TAIC	3	----	----	----
TVTFETriazine	----	3	1.5	----
TVDFMTriazine	----	----	----	1.5
ODR 177°/3° Arc D2084				
ML, Nm	1.0	0.90	0.90	0.90
ts ₂ , mins	1.5	5.5	5.0	3.5
MH, Nm	4.3	2.4	2.6	2.4
MH-ML, Nm	3.3	1.5	1.7	1.5

PROPERTIES (O-Rings¹) D1414

M50, MPa	2.95	2.34		2.18
M100, MPa	8.06	4.83		4.43
Tb, MPa	14.6	14.1		11.7
Eb, %	143	215		202

Comp. Set 204°C/ 70 h D1414	53	73	79	58
--------------------------------	----	----	----	----

(Dumbbells²) D1708

M100, MPa	5.58	3.50	3.36	3.89
Tb, MPa	22.4	22.5	22.7	22.1
Eb, %	230	400	400	360

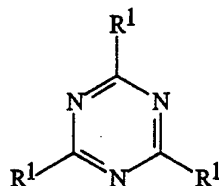
¹Post-cured at 260°C/48 h under nitrogen (PCN260)

²Post-cured at 225°C/24 h in air

CLAIMS

What is claimed is:

1. A compound of the formula



5

(I)

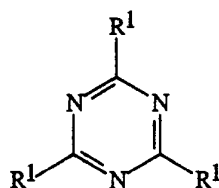
wherein R^1 is $CH_2=CH(CF_2)_n-$, $CH_2=CHCH_2(CF_2)_n-$,
 $CH_2=CHCF_2CF(CF_3)OCF_2CF_2-$ or
 $CH_2=CHCF_2CF_2CF(CH=CH_2)OCF_2CF(CF_3)OCF_2CF_2-$, and n is an integer of 1
 10 to about 10.

2. The compound as recited in Claim 1 wherein when R^1 is
 $CH_2=CH(CF_2)_n-$ and n is 1 or 2.

3. The compound as recited in Claim 1 wherein R^1 is
 $CH_2=CHCH_2(CF_2)_n-$ and n is 1.

4. The compound as recited in Claim 1 wherein R^1 is
 $CH_2=CHCF_2CF(CF_3)OCF_2CF_2-$ or
 $CH_2=CHCF_2CF_2CF(CH=CH_2)OCF_2CF(CF_3)OCF_2CF_2-$.

5. A process for the crosslinking of a fluoroelastomer, comprising,
 contacting a free radical generator, a fluoroelastomer which is capable of
 20 crosslinking with a polyolefin under free radical conditions, and a compound of the
 formula



(I)

25 wherein R^1 is $CH_2=CH(CF_2)_n-$, $CH_2=CHCH_2(CF_2)_n-$,
 $CH_2=CHCF_2CF(CF_3)OCF_2CF_2-$ or
 $CH_2=CHCF_2CF_2CF(CH=CH_2)OCF_2CF(CF_3)OCF_2CF_2-$, and n is an integer of 1
 to about 10, and provided said contacting is done at a temperature at which said
 free radical generator generates free radicals.

6. The process as recited in Claim 5 wherein said fluoroelastomer is a copolymer of hexafluoropropylene/vinylidene fluoride; tetrafluoroethylene/vinylidene fluoride/hexafluoropropylene; tetrafluoroethylene/perfluoro(alkyl vinyl ether) wherein the alkyl group contains 1 to 5 carbon atoms, or and tetrafluoro-
- 5 ethylene/perfluoro(alkyl vinyl ether) wherein the alkyl group contains one or more ether oxygen atoms and 2 to 20 carbon atoms.
7. The process as recited in Claim 5 wherein R^1 is $CH_2=CH(CF_2)_n$ - and n is 1 or 2, or R^1 is $CH_2=CHCH_2(CF_2)_n$ - and n is 1.
8. The product of the process of Claim 5.
- 10 9. The product of the process of Claim 6.
10. The process as recited in Claim 6 wherein said fluoroelastomer also contains 0.1 to 5 mole percent of a curesite monomer.
11. The product of the process of Claim 10.
12. The process as recited in Claim 5 wherein said fluoroelastomer
- 15 contains 0.1 to 5 mole percent of a curesite monomer.
13. The process as recited in Claim 5 wherein said fluoroelastomer is a tetrafluoroethylene/perfluoro(alkyl vinyl ether) copolymer wherein the alkyl group is methyl or propyl.
14. The process as recited in Claim 13 wherein said fluoroelastomer
- 20 contains 0.1 to 5 mole percent of a curesite monomer.
15. The product of the process of Claim 7.
16. The product of the process of claim 14.

INTERNATIONAL SEARCH REPORT

Interr. al Application No
PCT/US 96/12384

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C07D251/24 C08J3/24 C08K5/3492

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C07D C08J C08K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US,A,3 847 916 (DOW CORNING CORPORATION) 12 November 1974 * complete document *	1-3,5
Y	US,A,3 532 696 (DOW CORNING CORPORATION) 6 October 1970 * complete document *	1-3,5
Y	US,A,3 810 874 (MINNESOTA MINING AND MANUFACTURING COMPANY) 14 May 1974 * example 6; complete document *	1-3,5
Y	US,A,3 654 273 (PCR, INC.) 4 April 1972 * complete document *	1-3,5
	-/--	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *&* document member of the same patent family

Date of the actual completion of the international search

8 October 1996

Date of mailing of the international search report

15.10.96

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Van Bijlen, H

INTERNATIONAL SEARCH REPORT

Intern al Application No

PCT/US 96/12384

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US,A,4 320 216 (E.I. DU PONT DE NEMOURS AND COMPANY) 16 March 1982 cited in the application see column 1-2	1
A	--- US,A,4 035 565 (E.I. DU PONT DE NEMOURS AND COMPANY) 12 July 1977 cited in the application * complete document * -----	1

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 96/12384

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A-3847916	12-11-74	US-A- 3884875	20-05-75
		BE-A- 733948	02-12-69
		DE-A- 1928050	11-12-69
		FR-A- 2014152	17-04-70
		NL-A- 6908387	05-12-69
		US-A- 3532696	06-10-70

US-A-3532696	06-10-70	BE-A- 733948	02-12-69
		DE-A- 1928050	11-12-69
		FR-A- 2014152	17-04-70
		NL-A- 6908387	05-12-69
		US-A- 3847916	12-11-74

US-A-3810874	14-05-74	US-A- 3845051	29-10-74
		AU-B- 462798	10-07-75
		AU-A- 3317471	15-03-73
		AU-B- 469118	05-02-76
		AU-A- 3317671	15-03-73
		BE-A- 772308	07-03-72
		BE-A- 772309	07-03-72
		DE-A- 2145174	23-03-72
		DE-A- 2145176	16-03-72
		FR-A- 2106375	05-05-72
		FR-A- 2116364	13-07-72
		GB-A- 1373931	13-11-74
		GB-A- 1373932	13-11-74
		JP-C- 1408932	24-11-87
		JP-A- 59191721	30-10-84
		JP-B- 62014169	01-04-87
		JP-C- 1408933	24-11-87
		JP-A- 59191722	30-10-84
		JP-B- 62014170	01-04-87
		JP-A- 60034924	22-02-85
		JP-A- 59191723	30-10-84
		JP-C- 1408934	24-11-87
		JP-A- 59191724	30-10-84
		JP-B- 62014171	01-04-87
		JP-C- 1322347	11-06-86
		JP-A- 59191725	30-10-84
		JP-B- 60050823	11-11-85

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 96/12384

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A-3810874		JP-C- 1509565	26-07-89
		JP-A- 62048724	03-03-87
		JP-B- 63061336	29-11-88
		NL-A- 7111865	10-03-72
		NL-A,B 7112315	10-03-72
		US-A- 4094911	13-06-78
		US-A- 3972856	03-08-76
		US-A- 4085137	18-04-78
		BE-A- 747087	09-09-70
		CA-A- 960397	31-12-74
		DE-A- 2011774	17-09-70
		DE-B- 2066042	22-11-79
		FR-A- 2037807	31-12-70
		GB-A- 1309401	14-03-73
		GB-A- 1309402	14-03-73
		NL-A- 7002813	14-09-70

US-A-3654273	04-04-72	NONE	

US-A-4320216	16-03-82	US-A- 4299958	10-11-81
		AR-A- 223378	14-08-81
		BE-A- 883530	01-12-80
		CA-A- 1130035	17-08-82
		CA-A- 1139756	18-01-83
		DE-A- 3020185	11-12-80
		FR-A- 2457860	26-12-80
		GB-A,B 2052494	28-01-81
		JP-A- 60197712	07-10-85
		JP-C- 1327062	16-07-86
		JP-A- 56026970	16-03-81
		JP-B- 60052746	21-11-85
		NL-A- 8003117	02-12-80
		SE-B- 447900	22-12-86
		SE-A- 8002238	30-11-80
		SE-A- 8601617	10-04-86
US-A- 4303761	01-12-81		

US-A-4035565	12-07-77	AU-A- 1239876	13-10-77
		BE-A- 840099	27-09-76
		CA-A- 1076298	22-04-80

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 96/12384

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A-4035565		CA-A- 1094247	20-01-81
		DE-A- 2612360	30-09-76
		DE-C- 2659972	11-05-83
		FR-A- 2305462	22-10-76
		GB-A- 1528341	11-10-78
		GB-A- 1528342	11-10-78
		JP-C- 925455	22-09-78
		JP-A- 51129481	11-11-76
		JP-B- 53004115	14-02-78
		JP-C- 967146	26-07-79
		JP-A- 52081360	07-07-77
		JP-B- 54001585	26-01-79
		LU-A- 74645	28-01-77
		NL-A,B 7603217	29-09-76
		NL-A- 7810787	30-03-79
		SE-B- 410001	17-09-79
