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(12) (A)

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2003 09 11

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60/389,790

2002 03 01
2002 06 19

(US)
(US)

(71) (19898) 1007

(72) 19807 7

, , .3
19806 2407

, '
01532 35

(74)

:

(54)

(UV)

가 , 193 nm 157 nm

< >

가
60/361,124

2002 6 19

가 60/389,790

2002 3 1

nm)

(, 193 nm 157

(UV)

가

(feature)
. 193 nm

가
157 nm

. 193 nm

. 0.100 μm

, 0.18 0.13 μm

157 nm

WO 00/67072

62186907 A2)

(3,444,148

193 nm,

157 nm

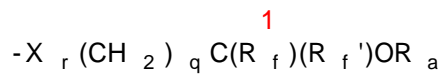
< >

a. 1

1 ;

b. 2

2

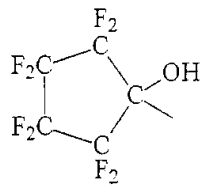


$R_f, R_{f'} \text{ (10)}$, $(CF_2)_n$ (, n 2)
 $X \text{ S, O, N, P}$,
 $q = 0, r = 0$, $q = 1, r = 0, 1$,
 $R_a \text{ H}$ - - (labile) ,
 R' 1 4 1 4 ,
 $R \text{ H, F,}$ 1 5 1 5 .

가

< >

$R_f, R_{f'} \text{ (10)}$, $(CF_2)_n$ (, n 2)
 $R_f, R_{f'} \text{ (10)}$, $R_f, R_{f'} \text{ (10)}$, $R_f, R_{f'} \text{ (10)}$

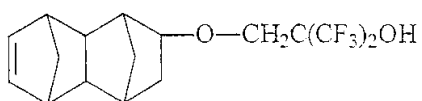
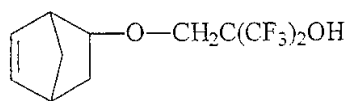
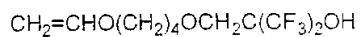
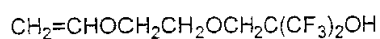
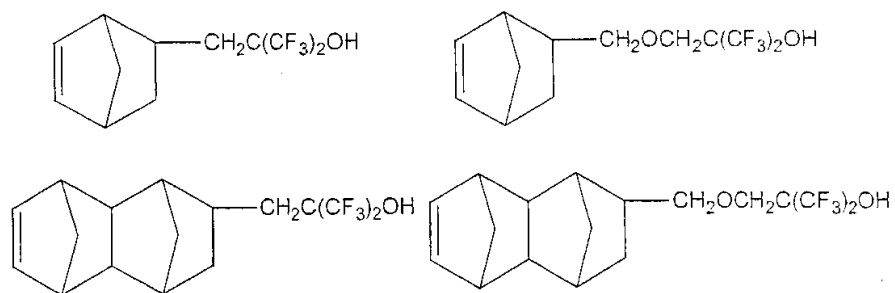


$R_f, R_{f'} \text{ (10)}$ 가 (-OH) , $R_f, R_{f'} \text{ (10)}$ 가 5 11 pKa 1 5 , 가
 (CF_3) .

< 1 >

$-X_r(CH_2)_qC(R_f)(R_{f'})OR_a$

$R_f, R_{f'} \text{ (10)}$, $X \text{ S, O, N, P}$ 1 10 , $q = 0, r = 0$, $(CF_2)_n$ (, n 2)
 R_a - - () , $q = 1, r = 1$.



2

< 2 >



R' 1 4

1 4

R H, F, 1 5

1 5

R' 3 4, R')

R'

(

, $-(\text{CH}_2)_m\text{OH}$ (, m 1, 2, 3 4)

R' 1

R 3 5, R)
H

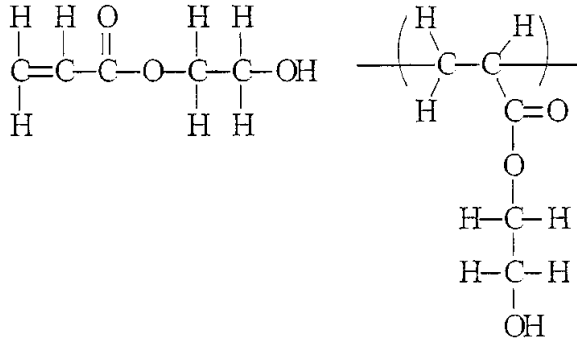
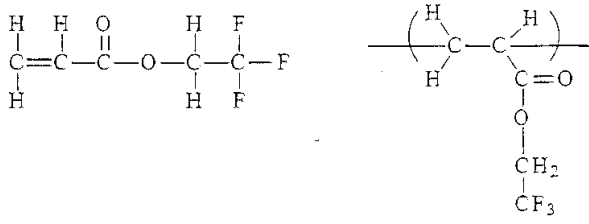
. R

H

, 가

(

가



가 (2,2-1,3-), R_f 'OCF=CF_2 (2-4-1,3-), CF_2

가 () 가
 가 ()
 가 (4-tert-)
 0 psig 200 1,000 psig 50 10,000
 40 80 30 120
 1,1,1,3,3- 1,1,2-

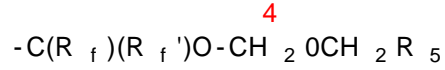
-1 157 nm 3.0 μm⁻¹ 157 nm 4.0 μm⁻¹ 157 nm 2.51 μm⁻¹ 3.5 μm

PAC

(PAC)
 (, -C(R_f)(R_f')OR_a ,
 R_a H가)
 (R_a)
 (, -C(R_f)(R_f')OR_a , R_a H)

(, R_a = OR_b, R_b = C₁₁-C₁₁)
 (MOM)

4



R_f R_{f'} 1 10 (CF₂)_n (, n 2
 10) ,

R₅ H, 1 10 3 10
 , 3

MEEMA (, B) , C) A) 3 , D) - 3 , E) - , F) 가
 가 , (anchimeric assistance) 가

A) t- , 2- -2-

(PAC)

(photoacid generator: PAG)
 (photobase generator: PBG)

(PAC) 1
 PAC
 PAC
 가 WO 00/66575

가

(193 nm) (DI) 가 DI 가 / 가 WO 00/66575
 가

가

가

가

, , , , 가 T_g () 가 ,

/ _____

bs

NMR

g

NMR

¹H NMR NMR

¹³C NMR -13 NMR

¹⁹F NMR -19 NMR

s

sec.

m

mL

mm

T_g

M_n

M_w

P=M_w/M_n

AC = A/b (, A Log₁₀ (1/T) , b μm , T

nm) (T) , (

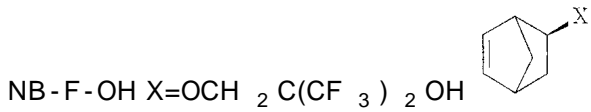
/ _____

DMF

HFIBO

2HEtA 2- ((Aldrich Chemical C
ompany))

NBE ()
 (Perkadox,) 16N
 -(4-tert-mical Corp.)) (Noury Che
 (Solkane) 365 mfc
 1,1,1,3,3- (Solvay Fluor))
 t-BuAc tert- ()
 TCB ()
 TFE (E. I. du Pont de Ne
 mours and Company))
 TFEtA 2,2,2- ()
 THF ()
 (Vazo,) 52
 2,4- -2,2'- () ()



10 nm 200 nm
 200 nm 300 nm
 10 nm 390 nm
 300 nm 390 nm

etry)) (T_g) , 20 / 가 DSC ((differential scanning calorim
 (TA Instruments) 가 DSC2910 DSC
 157 nm , 157 nm (Lambda-Physik Compex) 102
 가 , D2 (McPherson)
 CaF₂
 1. (Brewer Cee) () / 100CB ,

- a) 2 4 (2000, 3000, 4000, 6000 rpm) 120 (30 (bake) 가
(Gaertner Scientific) () L116A (Ellipsometer) (400 120
0) CaF₂ 2가
- b) 2 CaF₂ (1 X 0.80) 632 (Deuterium Source), 658
(photomultiplier) 485 (Keithley 485 picoammeter)
() 234/302
- c) a) 2가 (2000 4000 rpm) CaF₂
120 30
CaF₂
- d) , 386 (GRAMS386) (KALEIDAGRAPH)
(CaF₂ CaF₂) μm (abs/mic)

< 1>

NB-F-OH

95 % 가 가 19.7 g (0.78 mol)
500 mL DMF 5 , 80.1 g (0.728
mol) -5- -2- 가 15 . 0.5
HFIBO (131 g, 0.728 mol) 가 . ()
40 mL) 가 DMF 200 mL pH가 8
.0 가 3 X 150 mL 3 X 1
50 mL 150 mL
0.15 0.20 torr 30 60 (Kugelrohr) 190.1 (90 %)
. ¹H NMR (, CD₂Cl₂) 1.10-1.30 (m, 1H), 1.50 (d, 1H), 1.55-1.65 (m, 1H), 1.70 (s, 1H), 1.75 (d, 1
H), 2.70 (s, 1H), 2.85 (s, 1H), 3.90 (d, 1H), 5.95 (s, 1H), 6.25 (s, 1H).
. C₁₁H₁₂F₆O₂ : C, 45.53; H, 4.17; F, 39.28. : C, 44.98; H, 4.22; F, 38.25.

< 2>

TFE, NB-F-OH, t-BuAc 2HEtA

270 mL 70.33 g NB-F-OH, 0.64 g tert- , 0.29 g 2HEtA
25 mL 365 , -15 , 400 psig 가 ,
50 가 . TFE 340 psig 가 , TFE 가 ,
340 psig 365 mfc 100 mL , 80.56 g
NB-F-OH, 6.22 g tert- 2.42 g 2HEtA 12 0.10 mL/
() 16N 45 mL 6 2.0 mL/ , 8 , 6.3 g 0.08 mL/
. 16 가 , 1
THF 365 mfc 가 ,
56.1 g . ¹³C N
MR , 35 % TFE, 42 % NB-F-OH, 18 % t-BuAc 5 % 2HEtA
DSC: T_g = 134 . GPC: M_n = 5400; M_w = 9100; M_w/M_n = 1.67. : C, 44.74; H, 4.17; F, 38.7
9.

< 3>

TFE, NB-F-OH, t-BuAc 2HEtA

70.33 g NB-F-OH, 0.85 g tert-
 2 , 0.096 g 2HEtA 25 mL 365
 OH, 8.71 g tert- 0.97 g 2HEtA 365 mfc 100 mL , 78.55 g NB-F-
) 16N 60 mL 6 , 365 mfc 75 mL 12 0.10 mL/
 2.0 mL/ , 7.3 g (0.1 mL/
 . 16 , 1 가 , 1 .
 THF 365 mfc 가 ,
 , , 46.4 g . ¹³C NMR
 33 % TFE, 46 % NB-F-OH, 16 % t-BuAc 5% 2HEtA . DSC: T_g =
 145 . GPC: M_n = 5300; M_w = 8400; M_w/M_n = 1.57. : C, 45.51; H, 4.35; F, 37.28.

< 4>

TFE, NB-F-OH, t-BuAc 2HEtA

68.15 g NB-F-OH, 1.76 g tert-
 2 , 0.145 g 2HEtA 25 mL 365
 OH, 12.13 g tert- 1.09 g 2HEtA 365 mfc 100 mL , 70.49 g NB-F-
 60 mL 6 , 365 mfc 100 mL , 7.3 g () 16N
 2.0 mL/ , 8 0.1 mL/
 . 16 , 1 가 , .
 THF 365 mfc 가 ,
 , , 49 g . ¹³C NMR
 28 % TFE, 35 % NB-F-OH, 30 % t-BuAc 6 % 2HEtA . DSC: T_g = 150 . G
 PC: M_n = 6000; M_w = 11000; M_w/M_n = 1.82. : C, 46.42; H, 4.28; F, 36.13.

< 5>

TFE, NB-F-OH, t-BuAc 2HEtA

1 L 206.63 g NB-F-OH, 3.84 g tert-
 75 mL 365 , -15 , 0.87 g 2HEtA
 50 가 . TFE 320 psig 가 , 400 psig 가 ,
 320 psig 365 mfc 250 mL , 202.28 g
 NB-F-OH, 23.81 g tert- 5.39 g 2HEtA 12 0.28 mL/
) 16N 100 mL 6 6.0 mL/ , 18.45 g (0.24 mL/
 . 16 , 1 가 , .
 THF 365 mfc 가 ,
 , , 156.2 g . ¹³C NMR
 31 % TFE, 44 % NB-F-OH, 21 % t-BuAc 3 % 2HEtA . DS
 C: T_g = 139 . GPC: M_n = 4200; M_w = 8000 ; M_w/M_n = 1.87. : C, 45.92; H, 4.23; F, 36.83.

< 6>

TFE, NB-F-OH, t-BuAc TFEtA

70.33 g NB-F-OH, 0.64 g tert-
 2 , 0.39 g TFEtA 25 mL 365
 OH, 6.22 g tert- 3.21 g TFEtA 365 mfc 100 mL , 80.56 g NB-F-
) 16N 45 mL 6 , 365 mfc 75 mL 12 0.10 mL/
 2.0 mL/ , 6.3 g (0.08 mL/
 . 16 , 1 가 , .
 THF 365 mfc 가 ,

52.34 g ¹³C NMR
 36 % TFE, 41 % NB-F-OH, 19 % t-BuAc 4 % TFEtA . DSC:
 T_g = 136 . GPC: M_n = 5800; M_w = 9300; M_w/M_n = 1.59. : C, 44.39; H, 3.94; F, 39.96.

< 7 >

TFE, NB-F-OH, t-BuAc TFEtA

270 mL 70.33 g NB-F-OH, 0.85 g tert- , 0.13 g TFEtA
 25 mL 365 , -15 , 400 psig 가 ,
 50 가 . TFE 340 psig 가 , TFE 가 ,
 340 psig 365 mfc 100 mL , 78.54 g
 NB-F-OH, 8.71 g tert- 1.28 g TFEtA 12 0.10 mL/
) 16N 60 mL 6 , 365 mfc 100 mL , 7.3 g (
) 2.0 mL/ , 8 0.1 mL/
 . 16 , 1 .
 가 , , .
 THF 365 mfc 가 .

55.4 g ¹³C NMR
 33 % TFE, 44 % NB-F-OH, 19 % t-BuAc 3 % TFEtA . DSC: T_g =
 138 . GPC: M_n = 5300; M_w = 8400; M_w/M_n = 1.59. : C, 44.98; H, 4.21; F, 38.80.

< 8 >

TFE, NB-F-OH, t-BuAc TFEtA

68.88 g NB-F-OH, 1.15 g tert- , 0.55 g TFEtA 25 mL 365
 가 7 . TFE 320 psig 가 , TFE
 75.52 g NB-F-OH, 8.00 g tert- 3.74 g TFEtA 12 0.10
 mL/ , 365 mfc 100 mL , 7.3 g
 () 16N 60 mL 6 2.0 mL/ , 8
 0.1 mL/ . 16 , 1
 가 , , .
 THF 365 mfc 가

51.3 g ¹³C NMR
 31 % TFE, 41 % NB-F-OH, 20 % t-BuAc 7 % TFEtA
 . DSC: T_g = 140 . GPC: M_n = 4300; M_w = 8500; M_w/M_n = 1.98. : C, 45.11; H, 4.05;
 F, 38.30.

< 9 >

TFE, NB-F-OH, t-BuAc 2HEtA

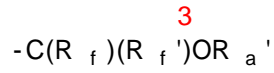
, 0.45 μm PTFE .

	(gm)
5 TFE/NB-F-OH/t-BuAc/2HEtA	1.507
2-	10.715
0.45 μm PTFE	0.778
6.82 %	

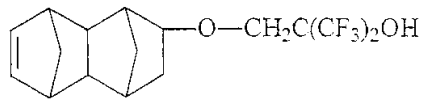
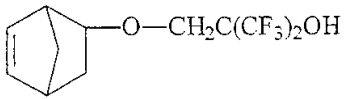
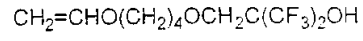
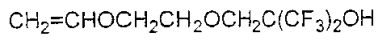
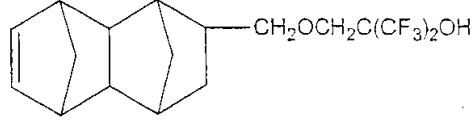
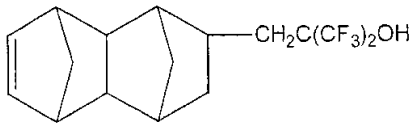
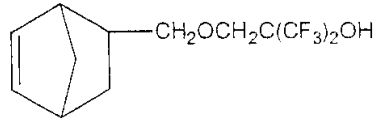
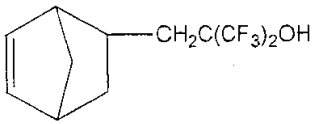
가 2125 8 Si 1992 rpm , 150 60 PAB
 157 nm sure) , 105 60 (Exitech)
 JEOL 7550 SEM . 13 mJ/cm² , 80 nm (post-expo)

(57)

- a. 1 ;
 - b. 2 2 .
- < 1>
 $-X_r(CH_2)_qC(R_f)(R_{f'})OR_a$
- < 2>
 $CH_2=CRCO_2CH_2R'$
- R_f $R_{f'}$ 1 10 , $(CF_2)_n$ (, n 2
 10) ,
- X S, O, N P ,
- q 0 r 0 , q 1 r 0 1 ,
- R_a H - - (labile) ,
- R' 1 4 1 4 ,
- R H, F, 1 5 1 5 .
2. 1 , 1 3 .
 3. 2 , 3 가 , , - (2,2- , -1,3-), - (2- -4- -1,3-
 10), $CF_2=CFO(CF_2)_tCF=CF_2$ (, t 1 2) $R_{f'}OCF=CF_2$ (, $R_{f'}$ 1
 4. 3 , 3 가 .
 5. 1 , R' - CF_3 - CH_2OH .
 6. 1 , R_a 가 H , 3



- 2, R_f, R_{f'} (10) , (CF₂)_n (n)
- R_{a'} H - - .
7. R_{a'}가 -CH₂OCH₂R₅ , R₅가 H, 1 10 3 1
8. 1 , 1 가
9. 8 , 1 가
10. 9 , 가
11. 10 , R'가 -CF₃ -CH₂OH .
12. 1 , t- .
13. 1 , - .
14. 1 , r 1 , q가 1 .
15. 1 , 1 가



16.

1 , 157 nm

가 3.5 μm^{-1}