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METHODS FOR THE PREPARATION OF SOME VINYL AND  
TRIFLUOROVINYL SUBSTITUTED HEXAFLUOROCUMINOLS(U) NAVAL  
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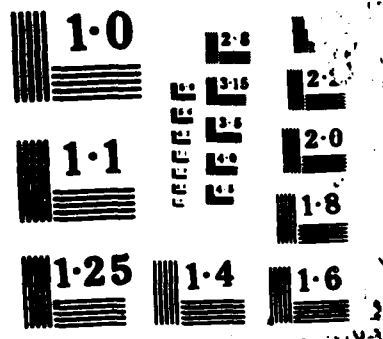
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FINAL TECHNICAL REPORT FOR THE  
ONT POSTDOCTORAL FELLOWSHIP GRANT

ENTITLED

" METHODS FOR THE PREPARATION OF SOME VINYL  
& TRIFLUOROVINYL SUBSTITUTED  
HEXAFLUOROCUMINOLS."

01 February 1988

Prepared by: Dr. Lee G. Sprague, Code 8120  
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For: American Society for Engineering Education  
11 DuPont Circle, Suite 200  
Washington, D.C. 20036

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**MEMORANDUM**

**TO:** Defense Technical Information Center

**FROM:** David Thornell *DT*  
Associate Program Manager, Projects and Federal Relations

**SUBJECT:** Final Technical Report, ONT Postdoctoral Fellow  
Contract N00014-83-D-0689

**DATE:** February 2, 1988

*Under the subject contract for administering the ONT Postdoctoral Fellowship Program final technical reports are to be submitted by participating Fellows at the conclusion of their tenure.*

Enclosed are twelve (12) copies of the final technical report for Dr. Joseph Thomas Guy relating to the research work completed at the Naval Research Laboratory.

Please do not hesitate to contact me if you have any questions.

## ABSTRACT

Synthetic methods which lead to both (1,1,1,3,3,3-hexafluoro-2-propanol) substituted styrenes and trifluorovinylstyrenes were developed. These styrenes were subsequently used to prepare homo and heteropolymers, and a correlation between monomer structure and polymer properties was examined.

This report summarizes the research results which have been recorded in Naval Research Laboratory Record Books #6999 and 7391. These laboratory record books are on permanent file in Building 222 of the Naval Research Laboratory.

Some of the research results funded by this grant, have been presented at the 1987 Scientific Conference on Chemical Defense Research, Aberdeen, Maryland, and will be published as a result of this conference in an article entitled Synthesis and Evaluation of Hexafluorodimethylcarbinol Functionalized Polymers as SAW Microsensor Coatings. These results will also be incorporated into articles which will be submitted to referred journals for which both ONT and NRL will be credited.

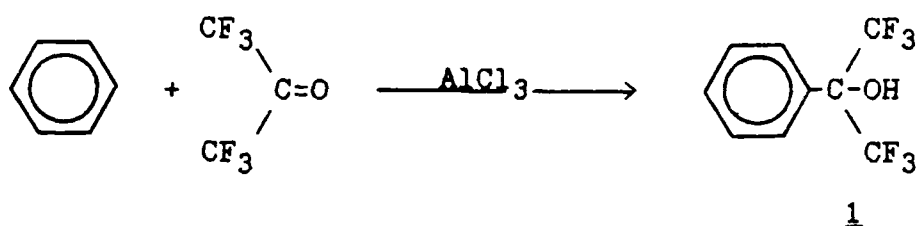
### ISOMERIC ETHENYL- $\alpha,\alpha$ -BIS(TRIFLUOROMETHYL)BENZENEMETHANOLS

$\alpha,\alpha$ -Bis(trifluoromethyl)benzenemethanol (1) has been conveniently prepared by the Friedel-Crafts reaction of hexafluoroacetone (HFA) and benzene. However, styrene is not suited for a Friedel-Crafts type reaction and is

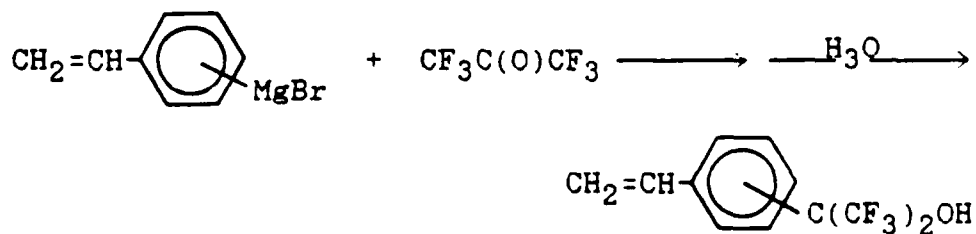


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anticipated to yield polystyrene rather than the monomer 2.



$\alpha,\alpha$ -bis(trifluoromethyl)methanolic aromatics may also be prepared by an alternate Grignard reaction with HFA. The derivative styrenes 2A, 2B, & 2C have been regioselectively synthesized by means of the reaction of the corresponding styryl Grignard reagent with hexafluoroacetone. Due to the limited availability of the starting material and the subsequent fair yield from the Grignard reagent, only a limited amount of the ortho isomer 2C was available for study.



2A	(para)	59%
2B	(meta)	52%
2C	(ortho)	43%

#### CHAIN TRANSFER CONSTANT

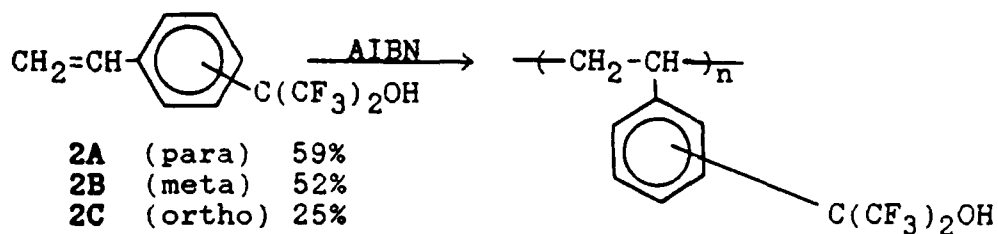
We have investigated the effect of the alcoholic hexafluoro-*i*-propanol functionality on the radical polymer-

ization of styrene. During the course of its polymerization the intermediate polystyrene radical may suffer a premature demise via the abstraction of a hydrogen atom from the alcohol to yield a dead polymeric chain and a new radical. The new radical may then initiate a new polymeric chain. This process is called chain transfer, and if it is reasonably efficient the average polymer will be unsuitably short. We have experimentally determined the chain transfer constant for this process to be  $10^{-4}$  to  $10^{-5}$ . A chain transfer constant of this magnitude indicates that chain transfer is negligible and that very high molecular weight molecules may be obtained.

### POLYMERS

The styrenes 2A & 2B were polymerized with radical initiation to yield brittle, colorless polymers. The differential scanning calorimetry of 2A revealed a glass transition point ( $T_g$ ) of  $125^{\circ}\text{C}$  (Figure 1). In our hands the ortho isomer 2C, [2-Ethenyl- $\alpha,\alpha$ -bis(trifluoromethyl)benzene-methanol], polymerized poorly and only a trivial amount of polymer was available for study.

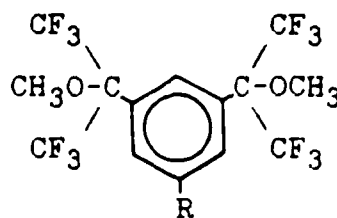
These polymers have been applied as thin films to Surface Acoustical Wave microsensory devices. The initial evaluation of these polymers for the detection of simulant vapors such as dimethyl(methyl)phosphonate was of encouragement, and suggests that further study is warranted.



The radical copolymerization of 2A with isoprene yielded polymers in which 2A constituted the bulk of the polymer regardless of the percentage of isoprene in the feed.

#### TRIALKYLSILANE PROTECTING GROUPS

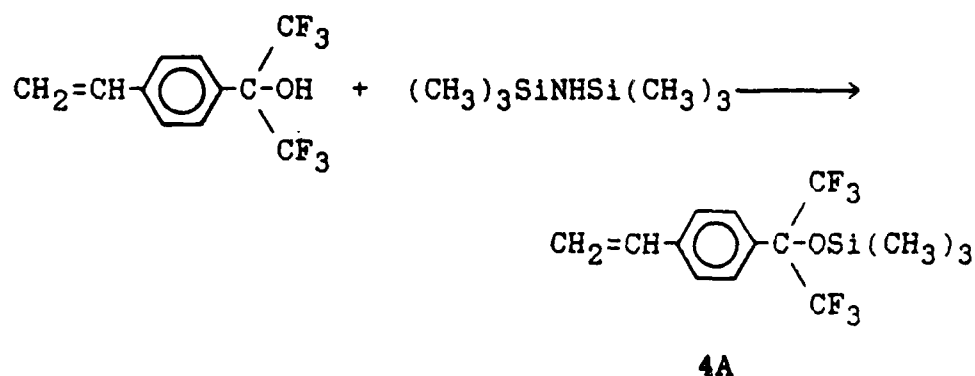
Copolymers of styrene and isoprene are prepared on large commercial scales by anionic initiation. However the alcoholic functionality of 2A prevents its anionic polymerization without prior protection. A common method for the protection of alcohols from incompatible reagents and their chemistry is to introduce either an alkyl or silyl ether functionality. Alkyl ethers such as 3 have been previously used at NRL; however, once in place it is difficult to remove the methyl group to regain the alcoholic functionality.



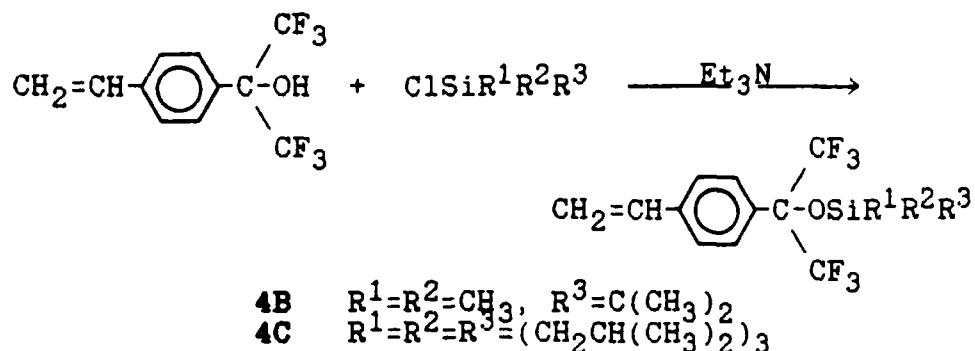


Silyl ethers offer varying degrees of limited protection, but conversely are much easier to remove when protection is no longer desired. We have prepared several silyl ethers from 2A, but have found that the simplest and easiest of these to prepare, the trimethylsilyl ether (4A), provides very good protection against some harsh reagents.

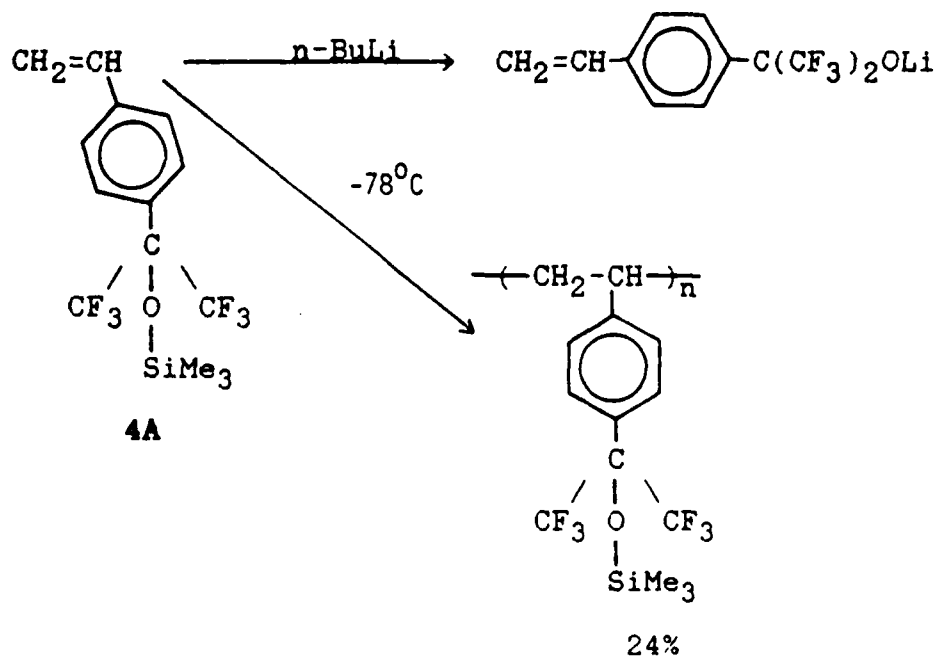
[4-ethenyl- $\alpha,\alpha$ -bis(trifluoromethyl)benzenemethoxy]-trimethylsilane (4A) may be prepared from 2A,  $\text{ClSiMe}_3$ , and triethylamine. However, a route which proved vastly superior involves stirring 2 equivalents of 2A with hexamethyldisilazane under mild heat. Hexamethyldisiloxane,  $\text{Me}_3\text{SiOSiMe}_3$ , did not react with 2A to any appreciable extent.



The protection a silyl ether will afford is related to the steric hinderence of the silane used. Dimethyl-*t*-butylsilyl ethers are commonly used for protection against alkyl-lithium reagents. The silyl ethers 4B & C have been prepared as outlined in the equations below. An excess of the chlorosilane must be used as an insoluble complex is formed with triethylamine.

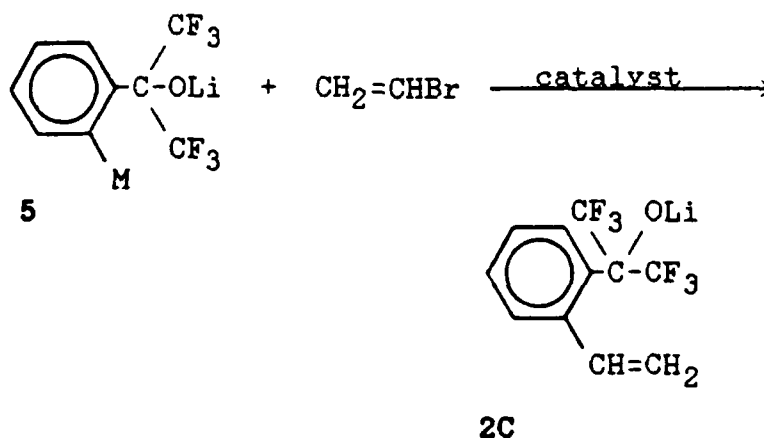


Anionic polymerization of **4A** with *n*-BuLi did not yield polymer at room temperature or 60°C. At the higher temperature a small amount of desilylated monomer was produced as determined by <sup>19</sup>F NMR spectroscopy. A 24% yield of homopolymer was obtain with a relatively large amount of initiator after an extended period at -78°C. Thus, the chain lenght is thought to be short, as characterized by differential scanning calorimetry (Figure 2).



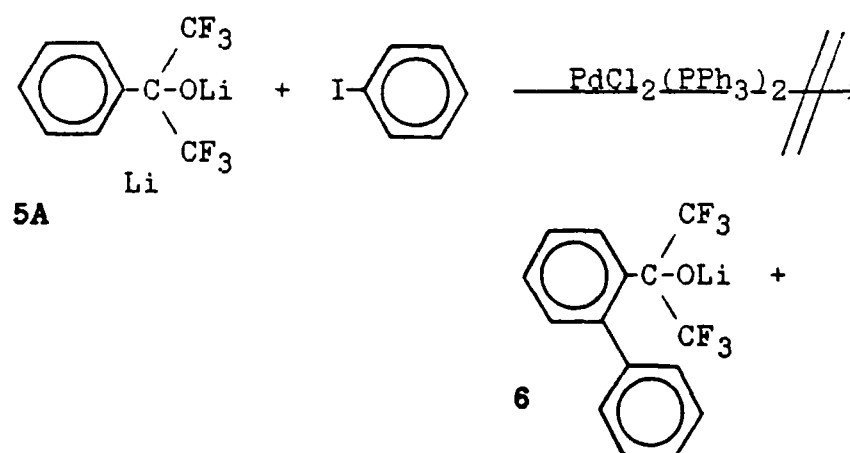
## TRANSITION METAL CATALYZED COUPLING REACTIONS

Attempts to prepare a useful amount of 2C via the transistion metal salt mediated coupling of organometallic 5 with vinylbromide gave poor yields at best. Lithium 1-lithio- $\alpha,\alpha$ -bis(trifluoromethyl)benzenemethoxide (5A) was prepared by the reaction of 1 with two equivalents of *n*-butyllithium while the *o*-organocuprate 5B was readily prepared by the reaction of 5A with cuprous cyanide.

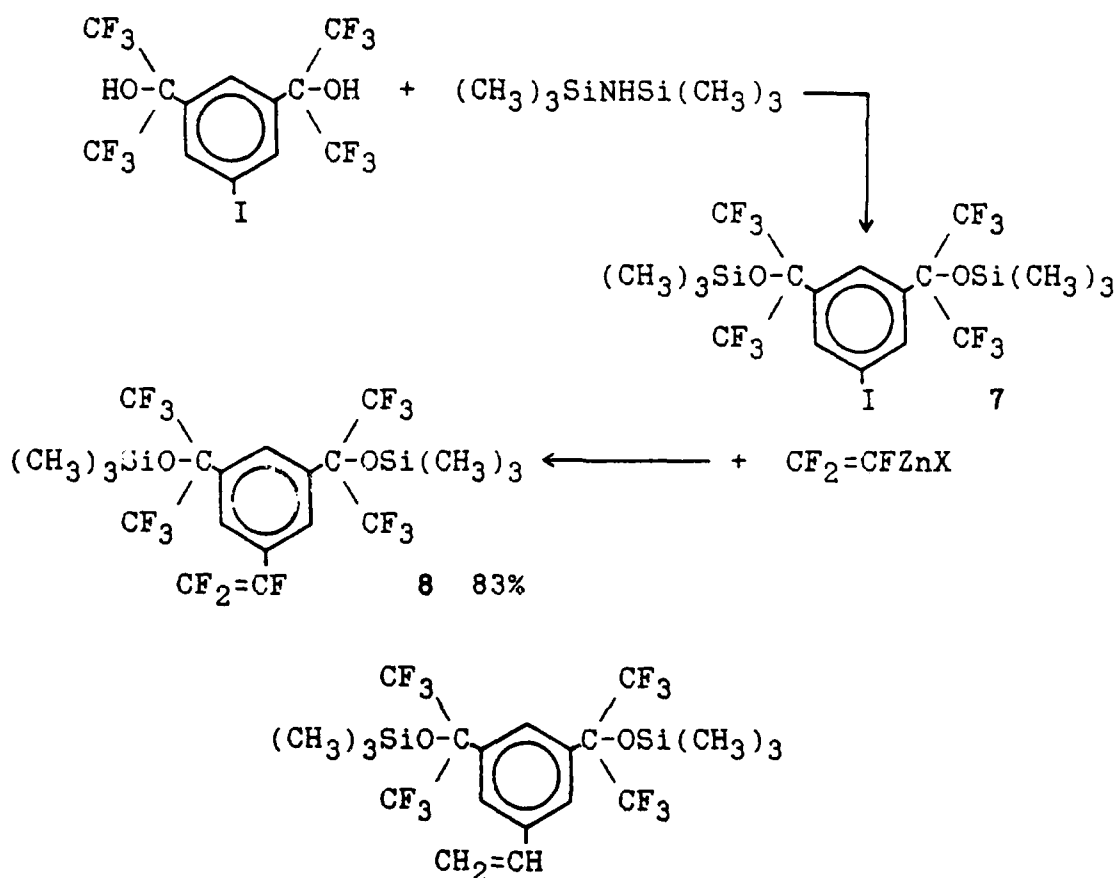


The Coupling Reaction of 5 with Vinyl Bromide			
	M	Catalyst	Percent conversion
5A	Li	$\text{NiCl}_2(\text{PPh})_3$	No rxn
5A	Li	$\text{PdCl}_2$	No rxn
5A	Li	$\text{PdCl}_2(\text{PPh})_3$	trace
5A	Li	$\text{Pd}(\text{PPh}_3)_4$	trace
5B	$1/2(\text{Cu Li})$	--	8%

The best result was obtained from the organocuprate 5B as it is less basic than phenyl lithium 5A, however the poor yield is thought to be due to steric hinderance. It is curious that iodobenzene coupled with 5A to produce biphenyl,  $C_6H_5-C_6H_5$ , rather than 6, as determined by GLPC analysis.



The aromatic iodide 7 may be prepared in quantitative yield from the reaction of hexamethyldisilazane and 5-Iodo-1,3- $\alpha, \alpha, \alpha', \alpha'$ -tetrakis(trifluoromethyl)benzenedimethanol. The subsequent palladium catalyzed reaction with trifluoroethenylzinc produced [1,3- $\alpha, \alpha, \alpha', \alpha'$ -tetrakis(trifluoromethyl)-5-( $\alpha, \alpha, \beta$ -trifluoroethenyl)benzenedimethoxy]bis-(trimethylsilane)] (8) in good isolated yield. It is anticipated that 9 could be similarly synthesized from the reaction with tributylvinyltin.



## EXPERIMENTAL

General. The reaction flasks and other glass equipment were stored in an oven at 130°C overnight and assembled under a stream of dry nitrogen. All boiling points were determined during fractional distillation and are uncorrected. NMR spectra were recorded on a Varian EM-390 spectrometer.  $^{19}\text{F}$  NMR spectra are referenced against external  $\text{CFCl}_3$  and  $^1\text{H}$  NMR spectra against internal tetramethylsilane. FTIR spectra were recorded as thin films on a Perkin-Elmer instrument. Mass Spectral data was recorded on

a CVC instrument at 70 ev by Dr. Alan Berry. Bromo- and chlorostyrenes were obtained from Aldrich Chemical Co. and were distilled prior to use. THF was distilled from sodium metal immediately prior to use.

#### 4-Ethenyl- $\alpha,\alpha$ -bis(trifluoromethyl)benzenemethanol (2A).

A Grignard reagent was initiated by addition of 4-bromostyrene (2.0 g, 0.011 moles) in one portion to a stirred slurry of Mg (1.0 g, 0.04 mole) in 2 mL of THF. An immediate exothermic rxn resulted which produced a green solution and caused the solvent to briefly reflux. On cooling, additional Mg (5.0 g, 0.21 mole) in 10 mL of THF was added to the reaction mixture. Neat 4-chlorostyrene (33.1 g, 0.239 mole) was placed in an addition funnel and introduced to the reaction mixture in a dropwise manner. When the reaction mixture again began to become warm, 10 mL of THF was syringed into the reaction mixture while the remaining 4-chlorostyrene was diluted with 25 mL of THF. After each 10 mL portion of the 4-chlorostyrene/THF solution had been added, 12-13 mL of fresh THF was syringed directly into the reaction mixture. The complete addition of 4-chlorostyrene required 3/4 hours and produced a very darkly colored green solution. The Grignard reagent was stirred at room temperature for an additional 1 hour before hexafluoroacetone (42.8 g, 0.258 mole) was added via a gas inlet. Upon complete HFA addition the reaction mixture was stirred at room temperature for 1 hour and poured into 100 mL 3N HCl to produce a bright yellow colored oil above the aqueous

phase. The phases were separated in a separatory funnel, the aqueous phase was extracted with 50 mL  $\text{CHCl}_3$ , the organic phases were combined, reduced by rotary evaporation, and poured into 200 mL of 10% (w/v) NaOH solution. The NaOH solution was rotary evaporated over a warm  $\text{H}_2\text{O}$  bath for 6 minutes and diluted with 200 mL of 6N HCl. The resultant yellow oil was separated from the aqueous phase in a separatory funnel, the aqueous phase was thrice extracted with 60 mL  $\text{CHCl}_3$ , the organic phases were combined, dried over anhydrous  $\text{Na}_2\text{SO}_4$ , decanted, rotary evaporated, and flash distilled to yield a pale yellow distillate which contained 9% residual THF (by normalized GLPC analysis) which could not be removed by further fractional distillation. The distillate was again dissolved in 250 mL 10% (w/v) NaOH, rotary evaporated for 8 minutes over a warm  $\text{H}_2\text{O}$  bath, diluted with 200 mL 3N HCl, separated in a separatory funnel, the aqueous phase extracted with 100 mL  $\text{CHCl}_3$ , the organic phases combined, dried over anhydrous  $\text{Na}_2\text{SO}_4$ , decanted, reduced by rotary evaporation, and vacuum distilled to yield 39.9 g (0.148 moles, 59% yield, 99% GLPC purity) of the title compound: bp  $61-63^\circ\text{C}/3$  mmHg;  $d^{20}_4$  1.374;  $n^{24}_D$  1.4530;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) 4.1 ppm (s, 1H, -OH), 5.7 ppm (d, 1H, cis- $\text{HC}=\text{CHPh}$ )  $^3J_{\text{H,H}}=11$  Hz, 6.4 ppm (d, 1H, trans- $\text{CH}=\text{CHPh}$ )  $^3J_{\text{H,H}}=17$  Hz, 7.1 ppm (dd, 1H,  $=\text{CHPh}$ )  $^3J_{\text{H,H}}=11$  & 17 Hz, 8.0 ppm (AABB, 4H,  $\text{C}_6\text{H}_4$ );  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ ) -76.5 ppm (s); FTIR (Neat film, KCl block) 3605 (40%), 3545 (45%), 3093 (64%), 3052 (66%), 3017 (67%), 2341 (72%), 1918 (73%), 1844

blocks) 3676 (0.017), 3649 (0.017), 3604 (0.021), 3465 (0.021), 3041 (0.021), 2993 (0.017), 2929 (0.017), 2855 (0.022), 1615 (0.017), 1514 (0.019), 1455 (0.017), 1425 (0.018), 1371 (0.019), 1270 (0.044), 1215 (0.047), 1171 (0.039), 1153 (0.033), 1104 (0.031), 1021 (0.018), 971 (0.030), 950 (0.025), 927 (0.030), 832 (0.024), 741 (0.019), 711 (0.034), 574 (0.026); UV (MeOH) 252 (absorptivity = 0.8053), 257 (0.8171), & 219 nm (1.1946).

Analytical. Calculated for  $(C_{11}H_8F_6O)_x$ : C, 48.90%; H, 2.99%; F, 42.19%. Found: C, 49.21%; H, 3.02%; F, 23.55%.

**Poly[3-Ethenyl- $\alpha,\alpha$ -bis(trifluoromethyl)benzenemethanol].**

In a similar manner, 3-bromostyrene (5.11 g, 0.028 mole), Mg (0.7 g, 0.029 g-atom), 30 mL of THF, and hexafluoroacetone (4.3 g, 0.026 mole) yielded 2B (3.90 g, 52%): bp 40-43°C / 0.1 mmHg;  $d^{20}_4$  1.364;  $n^{23}_D$  1.4488;  $^1H$  NMR ( $CDCl_3$ ) 4.10 ppm (bs, 1H, -OH), 5.31 ppm (d, 1H)  $^3J_{H,H}=11$  Hz, 5.77 ppm (d, 1H)  $^3J_{H,H}=18$  Hz, 6.78 ppm (dd, 1H), 7.30-7.80 ppm (m, 4H);  $^{19}F$  NMR ( $CDCl_3$ ) -75.3 ppm (s); FTIR (Neat film, NaCl block)  $cm^{-1}$  (absorbance) 3604 (0.199), 3542 (0.174), 3209 (0.157), 3094 (0.166), 2986 (0.153), 2884 (0.122), 1835 (0.082), 1720 (0.075), 1634 (0.110), 1605 (0.146), 1584 (0.110), 1488 (0.144), 1440 (0.124), 1406 (0.152), 1367 (0.166), 1288 (0.589), 1267 (0.853), 1208 (0.926), 1154 (0.744), 1126 (0.419), 1090 (0.270), 1055 (0.159), 1001 (0.203), 989 (0.307), 970 (0.641), 916 (0.298), 802 (0.339), 749 (0.423), 725 (0.738), 711 (0.303), 665 (0.194).



The monomer (3.44 g, 0.013 mole) was polymerized with AIBN initiator (0.011 g, 0.0008 mole) in 10 mL of benzene at 60°C to yield the titled polymer (2.23 g, 65%):  $n_{\text{inh}}$  in acetone at 30°C, 0.02;  $^{19}\text{F}$  NMR ( $\text{CD}_3\text{COCD}_3$ ) -75.7 ppm (bs);  $^1\text{H}$  NMR ( $\text{CD}_3\text{COCD}_3$ ) 0.30 to 1.30 ppm (broad hump, 4H), 2.58 ppm (s, 1H), 5.86 ppm (broad hump, 1H), 6.46 ppm (broad hump, 2H), 6.71 ppm (broad hump, 1H); FTIR (Neat film, NaCl blocks, absorbance), 3606 (0.267), 3528 (0.174), 3045 (0.089), 2928 (0.189), 2855 (0.102), 2364 (0.068), 1996 (0.066), 1959 (0.067), 1893 (0.070), 1709 (0.073), 1608 (0.125), 1591 (0.099), 1491 (0.170), 1451 (0.154), 1365 (0.173), 1269 (0.562), 1206 (0.599), 1152 (0.504), 1124 (0.347), 1088 (0.287), 1002 (0.170), 970 (0.418), 903 (0.177), 795 (0.230), 744 (0.221), 722 (0.572), 703 (0.229), & 668  $\text{cm}^{-1}$  (0.163).

**Poly[2-Ethenyl- $\alpha,\alpha$ -bis(trifluoromethyl)benzenemethanol]**  
(3C). In a similar manner, 2-bromostyrene (1.55 g, 0.009 mole), Mg (0.22 g, 0.010 g-atom), 8.5 mL of THF, and hexafluoroacetone (3.0 g, 0.018 mole) yielded 2C (0.99 g, 43%), which smelled strongly of phenol: bp 35-37°C / 0.1 mmHg;  $n_{\text{D}}^{24}$  1.4492;  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ ) -74.2 ppm (s);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) 4.32 ppm (s, 1H, -OH), 5.45 ppm (dd, 1H)  $^3J_{\text{H,H}}=10.8$  & 1.5 Hz, 5.52 ppm (dd, 1H)  $^3J_{\text{H,H}}=17.6$  & 1.5 Hz, 7.33 to 7.78 ppm (m, 5H); FTIR (Neat film, NaCl blocks, absorbance) 3588 (0.207), 3526 (0.264), 3091 (0.160), 3074 (0.158), 2990 (0.120), 2884 (0.098), 1626 (0.155), 1571 (0.151), 1489 (0.209), 1446 (0.198), 1412 (0.193), 1366 (0.223), 1301

(0.406), 1258 (0.572), 1224 (0.591), 1203 (0.605), 1177 (0.550), 1151 (0.496), 1110 (0.487), 1060 (0.271), 1030 (0.210), 995 (0.261), 965 (0.485), 951 (0.494), 927 (0.487), 841 (0.121), 785 (0.233), 767 (0.471), 749 (0.457), 713 (0.578), 662 (0.309), & 631  $\text{cm}^{-1}$  (0.193);

The monomer (0.96 g, 0.004 mole) was polymerized with AIBN initiator (0.0032 g, 0.0003 mole) in 3 mL of benzene at 60°C to yield the titled polymer (0.24 g, 25%):  $^{19}\text{F}$  NMR ( $\text{CH}_3\text{COCH}_3$ ) -75.0 ppm (bs); FTIR (Neat film, NaCl blocks, absorbance) 3588 (0.078), 3353 (0.181), 3066 (0.100), 2963 (0.129), 2932 (0.122), 2874 (0.079), 1607 (0.065), 1581 (0.075), 1488 (0.179), 1472 (0.076), 1456 (0.193), 1372 (0.080), 1255 (0.568), 1230 (0.763), 1176 (0.592), 1147 (0.324), 1118 (0.295), 1061 (0.181), 965 (0.234), 950 (0.232), 924 (0.219), 898 (0.077), 804 (0.055), 755 (0.322), 712 (0.382), & 660  $\text{cm}^{-1}$  (0.074).

[4-Ethenyl- $\alpha,\alpha$ -bis(trifluoromethyl)benzenemethoxy]-trimethylsilane (4A). Hexamethyldisilazane (3.4 g, 0.021 mole) was added to 2A (5.1 g, 0.019 mole) and  $\text{NH}_4\text{Br}$  (0.1 g). The reaction mixture was stirred at 55°C for 2 days, the low boiling point components were removed at room temperature in vacuo, and residue was distilled through a short path apparatus to yield 4.4 g (0.013 mole, 68%) of the titled compound: bp 64-70°C / 0.1 mmHg;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) 0.23 ppm (s, 9H), 5.31 ppm (d, 1H)  $^3\text{J}_{\text{H,H}}=10$  Hz, 5.73 ppm (d, 1H)  $^3\text{J}_{\text{H,H}}=18$  Hz, 6.73 ppm (dd, 1H), 7.57 ppm (AABB pattern, 4H);

$^{19}\text{F}$  NMR ( $\text{CDCl}_3$ ) -73.9 ppm (s); FTIR (Neat film, NaCl block)  $\text{cm}^{-1}$  (absorbance), 3807 (0.212), 3587 (0.223), 3093 (0.223), 2964 (0.272), 1634 (0.267), 1514 (0.306), 1409 (0.291), 1305 (0.486), 1296 (0.572), 1280 (0.587), 1259 (0.703), 1219 (0.730), 1206 (0.808), 1202 (0.807), 1191 (0.693), 1153 (0.591), 1127 (0.412), 1033 (0.285), 1020 (0.291), 988 (0.381), 973 (0.550), 944 (0.595), 915 (0.373), 879 (0.617), 849 (0.627), 812 (0.335), 762 (0.408), 743 (0.358), 713 (0.571), 693 (0.310); MS ( $m/z$ ) 342 (22%,  $\text{M}^+$ ), 273 (16%,  $\text{M}^+ - \text{CF}_3$ ), 231 (41%), 203 (14%), 153 (23%), 131 (72%,  $\text{CH}_2=\text{CHC}_6\text{H}_4\text{CO}^+$ ), 103 (14%,  $\text{CH}_2=\text{CHC}_6\text{H}_4^+$ ), 77 (100%,  $\text{C}_6\text{H}_5^+$ ), 73 (62%), 63 (19%), 49 (17%), 47 (15%), 45 (18%).

**[4-Ethenyl- $\alpha,\alpha$ -bis(trifluoromethyl)benzenemethoxy]-dimethyl- $\underline{t}$ -butylsilane (4B).**  $\underline{t}$ -Butyldimethylsilyl chloride (0.60 g, 0.004 mole), 2A (1.03 g, 0.004 mole), and 5 mL of triethylamine were stirred at room temperature for 90 hr (100% conversion by GLPC). The reaction mixture was gravity filtered, the solvent removed in vacuo, and the residue was distilled in vacuo through a short path apparatus to yield 0.53 g (37%, 100% GLPC purity) of the titled compound: bp 75-78°C / 0.1 mmHg;  $d^{21}$  1.170;  $n^{23}$  1.4558;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) 0.15 ppm (s, 6H), 1.00 ppm (s, 9H), 5.35 ppm (d, 1H)  $^3\text{J}_{\text{H,H}}=11$  Hz, 5.81 ppm (d, 1H)  $^3\text{J}_{\text{H,H}}=18$  Hz, 6.72 ppm (dd, 1H), 7.60 ppm (AABB pattern, 4H);  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ ) -72.7 ppm (s); FTIR (Neat film, NaCl blocks) 3854 (0.221), 3587 (0.232), 3090 (0.225), 2961 (0.362), 2934 (0.381), 2899 (0.286), 2863 (0.352), 1696 (0.238), 1635 (0.260), 1612

(0.251), 1539 (0.246), 1515 (0.300), 1474 (0.365), 1465 (0.323), 1409 (0.291), 1392 (0.283), 1364 (0.293), 1306 (0.435), 1295 (0.491), 1280 (0.508), 1259 (0.577), 1219 (0.616), 1202 (0.652), 1190 (0.588), 1152 (0.539), 1127 (0.385), 1034 (0.278), 1020 (0.281), 1006 (0.289), 988 (0.370), 971 (0.499), 943 (0.526), 915 (0.363), 867 (0.524), 841 (0.567), 797 (0.377), 785 (0.518), 754 (0.296), 744 (0.348), 713 (0.528), & 677  $\text{cm}^{-1}$  (0.356).

**[4-Ethenyl- $\alpha,\alpha$ -bis(trifluoromethyl)benzenemethoxy]tri-*i*-butylsilane (4C).** Chlorotri-*i*-butylsilane (13.98 g, 0.060 mole), 2A (8.88 g, 0.033 mole), and 30 mL of triethylamine were heated to reflux for 66 hr (47% conversion by GLPC), although no change had occurred in 48 hr as determined by GLPC analysis. The reaction mixture was gravity filtered, the solvent removed in vacuo, the residue was gravity filtered, and the filtrate distilled in vacuo through a short path apparatus to yield 2.56 g (91% GLPC purity) of the titled compound: bp 99-100°C / 0.1 mmHg;  $d^{20}_D$  1.078;  $n^{25}_D$  1.4603;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) 0.70 ppm (d, 6H)  $^3J_{\text{H,H}}=6$  Hz, 0.96 ppm (d, 18 H)  $^3J_{\text{H,H}}=6$  Hz, 1.87 ppm (m of seven signals, 3H), 5.30 ppm (d, 1H)  $^3J_{\text{H,H}}=11$  Hz, 5.75 ppm (d, 1H)  $^3J_{\text{H,H}}=17$  Hz, 6.72 ppm (dd, 1H)  $^3J_{\text{H,H}}=17$  & 11 Hz, 7.57 ppm (AABB pattern, 4H);  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ ) -72.7 ppm (s).

**[5-Iodo-1,3- $\alpha,\alpha,\alpha',\alpha'$ -tetrakis(trifluoromethyl)benzene-dimethoxy]bis(trimethylsilane) (7).** Hexamethyldisilazane (24.8 g, 0.154 mole) and 5-Iodo-1,3- $\alpha,\alpha,\alpha',\alpha'$ -tetrakis-

(trifluoromethyl)benzenedimethanol (50.58 g, 0.094 mole) were heated together at 94°C for 64 hr, the excess disilazane was removed in vacuo at room temperature, and the residue distilled through a short path apparatus to yield 63.05 g (0.096 mole, 101%) of the titled compound as a clear and colorless oil: bp 99-105°C / <0.1 mmHg (100% GLPC purity);  $d^{20}_D$  1.496;  $n^{27}_D$  1.4284;  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ ) -73.3 ppm;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) 0.22 ppm (s, 18 H), 8.03 ppm (s, 1 H), 8.10 ppm (s, 2 H); FTIR (Neat film, NaCl blocks) 3101 (0.069), 2953 (0.156), 2906 (0.082), 1599 (0.086), 1572 (0.181), 1441 (0.128), 1433 (0.123), 1423 (0.122), 1298 (0.338), 1260 (0.422), 1218 (0.431), 1204 (0.465), 1156 (0.343), 1039 (0.193), 1028 (0.251), 998 (0.148), 973 (0.361), 956 (0.145), 880 (0.347), 848 (0.363), 819 (0.183), 762 (0.261), 727 (0.339), 707 (0.284), 701 (0.269), & 633  $\text{cm}^{-1}$  (0.219).

[1,3- $\alpha,\alpha,\alpha',\alpha'$ -Tetrakis(trifluoromethyl)-5-(a,a,b-trifluoroethenyl)benzenedimethoxy]bis(trimethylsilane)] (8). Zn (6.6 g, 0.10 g atom), bromotrifluoroethene (20.8 g, 0.13 mole), and 50 mL of dry DMF were used to prepare the trifluoroethenylzinc halide in a manner similar to that of Burton and Heinze (J. Fluorine Chem. 1987). The excess  $\text{CF}_2=\text{CFBr}$  was removed in vacuo, the residue was Schlenk funnel filtered (course frit), tetrakis(triphenylphosphine) (0.9698 g, 1%) and 7 (51.7 g, 0.078 mole) added and the reaction mixture stirred at 50°C for 21 hrs. The product was separated as a clear oil to yield 40.5 g (0.065 mole,

83%) of the crude titled compound which was distilled through a 10 cm vigreux column: bp 63-65°C / <0.1 mmHg; 100 % GLPC purity;  $d^{20}_D$  1.334;  $n^{25}_D$  1.4014; FTIR (Neat film, NaCl blocks) 3128 (0.053), 2966 (0.178), 2907 (0.067), 1611 (0.090), 1573 (0.063), 1462 (0.119), 1451 (0.122), 1413 (0.110), 1302 (0.637), 1260 (0.680), 1203 (0.684), 1156 (0.611), 1146 (0.549), 1077 (0.357), 1071 (0.325), 1032 (0.293), 974 (0.635), 951 (0.097), 891 (0.569), 877 (0.617), 849 (0.623), 762 (0.400), 738 (0.266), 728 (0.593), 705 (0.439), 693 (0.161), 634 (0.267), & 629  $\text{cm}^{-1}$  (0.281).

Analytical. Calculated for  $\text{C}_{18}\text{H}_{21}\text{F}_{15}\text{O}_2\text{Si}_2$ : C, 34.62%; H, 3.39; F, 45.64%.

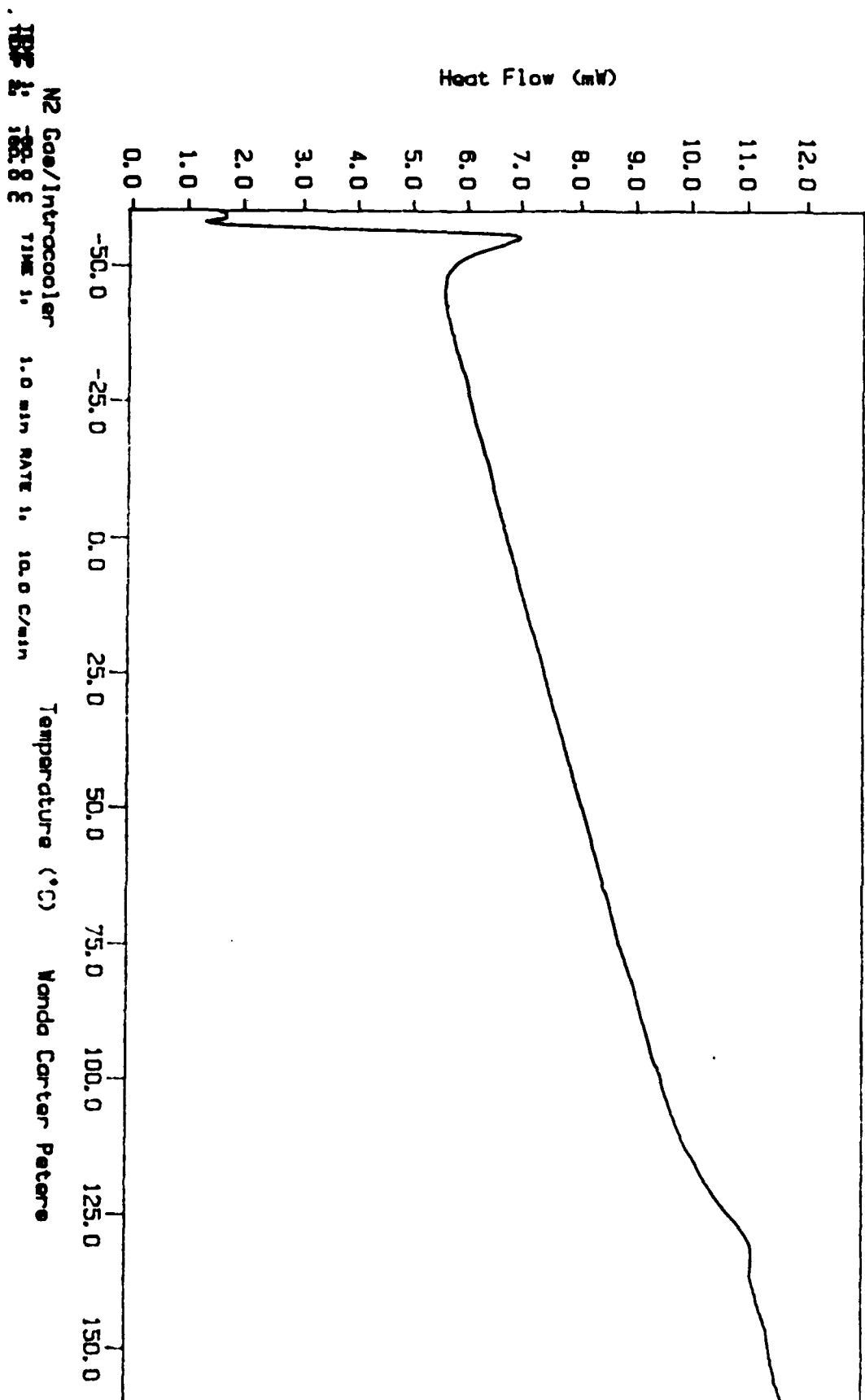
DSC Data File: w066

Sample Weight: 24.618 mg

Tue Jun 16 15:30:09 1987

LS-1-020 2nd Heat Scan Same Sample

Figure 1. DSC of poly[4-ethenyl-a,a-bis(trifluoro-methyl)benzenemethanol] from radical initiation. T<sub>g</sub> of 125°C.



DSC Data File: wos8  
Sample Weight: 9.781 mg  
Wed Jun 17 13:58:21 1987  
LS-1-087 2nd Heat Scan Same Sample

Figure 2. DSC of poly[4-ethenyl-a,a-bis(trifluoro-methyl)benzenemethanol] from n-butylolithium initiation.

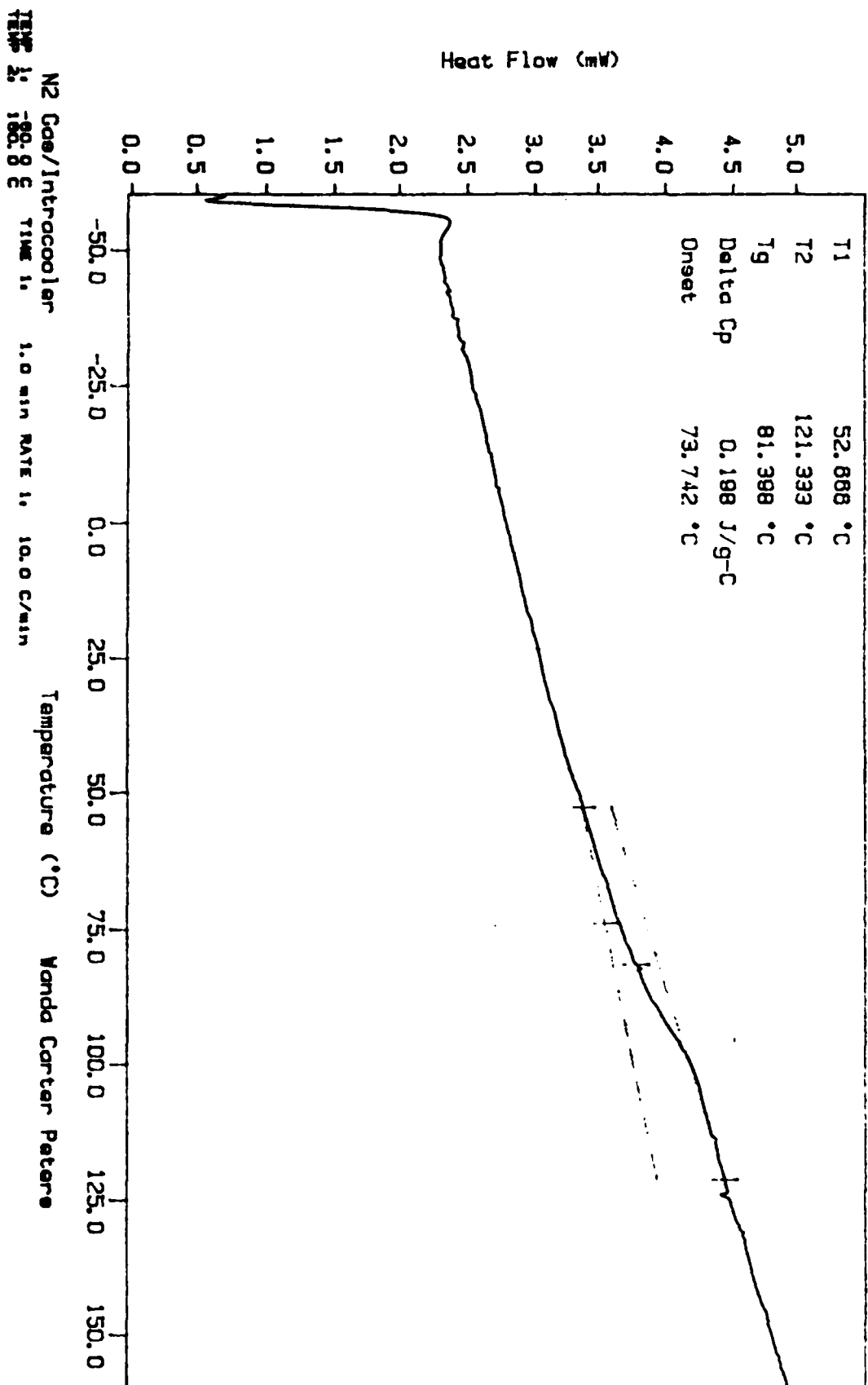
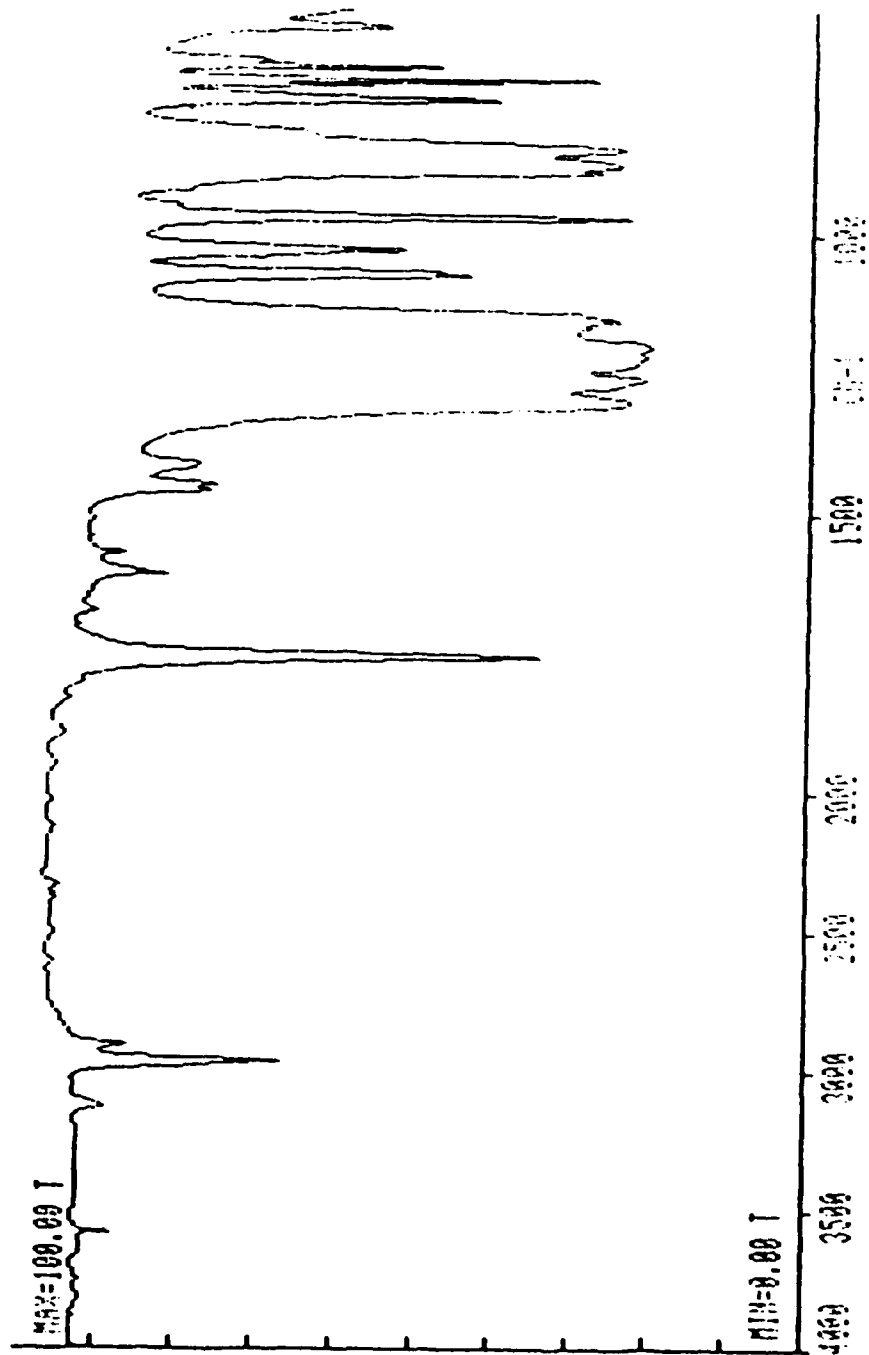




Figure 3. FTIR spectra of [1,3-a,a,a',a'-tetra-  
kis(trifluoromethyl)-5-(a,a,b-trifluoroethenyl)benzene-  
dimethoxy]bis(trimethylsilane)] (8).



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