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2,2 bis (4-ethynylphenyl) hexafluoropropane

Synthesis and preliminary study of thermal polymerization

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SUMMARY

The 2,2 bis(4-ethynylphenyl)hexafluoropropane is prepared via an original synthesis's process using a substitution of 2,2 bis(4-triflatephenyl) hexafluoropropane by trimethylsilyl acetylene. In this process ZnO is used to remove the triflate anion formed during the reaction.

This diacetylenic compound melts at 37-38°C, exhibits an onset of polymerization at 120°C. After thermal treatment at 250°C, the obtained network shows a softening point at 300°C. This network remains stable in air up to 435°C.

INTRODUCTION

Ethynyl end-capped oligomers have already received considerable attention (1, 2, 3, 4).

Classical methods for the synthesis of terminal aryl acetylenes in general involve the formation of an intermediate dihalide as described by LAU (5).

Recently A. Y. CHEN and Z.Y. YANG published the substitution of phenyl triflate by trimethylsilyl acetylene using experimental conditions very closed to the classical ethynylation reaction starting from aromatic bromocompounds (6).

This paper deals with synthesis of 2,2 bis (4-ethynylphenyl) hexafluoropropane starting from the bisphenol A.F using the following sequence: (see scheme 1)

- Synthesis of 2,2 bis (4-triflate-phenyl) hexafluoropropane.
- Synthesis of 2,2 bis (4-(trimethylsilyl ethynyl) phenyl) hexafluoropropane.
- Removal of the trimethylsilyl group to give the desired product.

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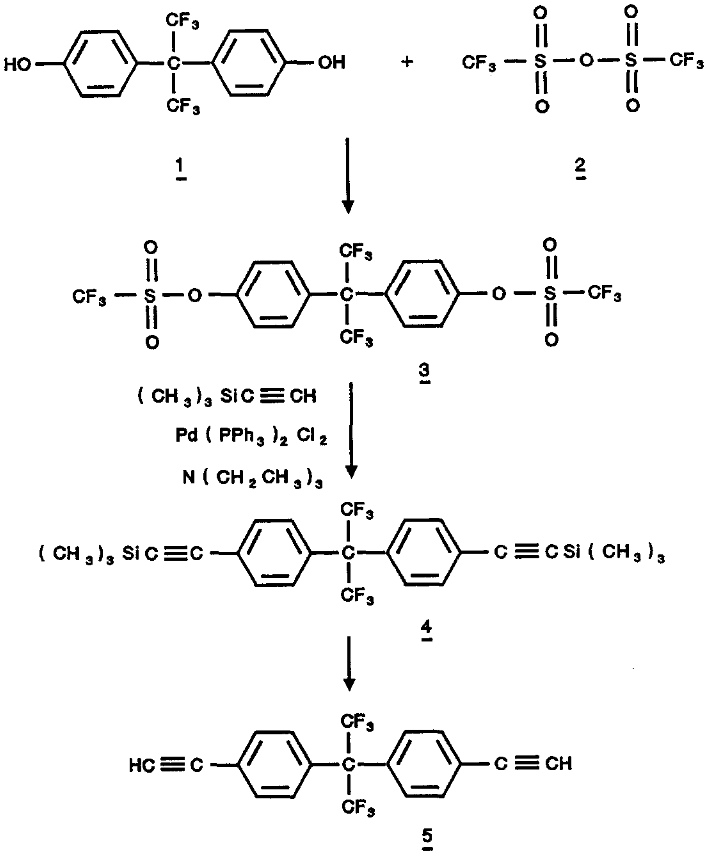

Scheme 1

EXPERIMENTAL

Solvents and starting materials

Trifluoromethanesulfonic anhydride was supplied by Aldrich Chemicals.

Dimethylformamide was kept on molecular sieve. The other solvents and reagents were used without further purification.

Physical methods

The following equipment was used:

- Perkin-Elmer 398 for infrared spectra recording (KBr disk).
- Mettler thermomechanical analyzer (TMA 40).
- Mettler TC 10A and Du Pont 990 thermal analyzer for Differential Scanning Calorimetry (DSC).
- Setaram thermobalance for thermogravimetric analysis.
- Brucker A.C 250 MHz spectrometer for ^{1}H NMR.

Synthesis of 2,2 bis(4-triflate-phenyl) hexafluoropropane 3

This product was synthesized according to the procedure described by LAU (3).

After drying, a white crystalline product was obtained which was purified by crystallization from hexane.

Yield: 93%

Mp: 98.5°C

^1H NMR (deuteriated acetone and TMS as internal reference): 7.6 ppm (m, aromatic)

IR (in cm^{-1}): 1510 (ν, C=C), 1410-30 (ν,SO_2), 1150-1250, 890 (ν , CF_3)

Synthesis of 2,2 bis(4-trimethylsilyl ethynyl)phenyl) hexafluoropropane 4

20 g (0.033 mole) of 3 was dissolved in 150 cc of (DMF/NEt_3) mixture (5/1) at 90°C (the solvents were degassed).

8 g (0.098 mole) of dried ZnO was added.

9,8 g (0.099 mole) of trimethylsilylacetylene was added dropwise to the solution. At the beginning of the addition of acetylene, 0.833 g (0.0011 mole) of bistriphenylphosphine palladium dichloride was added.

The temperature of the reaction mixture was maintained at 90°C for 6 hours.

Just after reaction ethylene diamine was added in order to complex the catalytic residue and the mixture was treated on charcoal.

After filtration, ethylene diamine was evaporated.

The mixture was poured into water and extracted with hexane/diethyle oxide (100:2).

After drying and removal of the solvent, the product was passed through silica gel (5-6 times) with the same eluent.

After evaporation, a white crystalline product was obtained with a yield of 33%.

MP: 107°C

^1H NMR ($CDCl_3$ in ppm TMS): 7.3-7.4 ppm (m, aromatic), 0,2 ppm (s, $Si-(CH_3)_3$)

IR (in cm^{-1}): 2150 (ν , $C{\equiv}CSi(CH_3)_3$), 1150-1250, 890 (ν , CF_3)

Synthesis of 2,2 bis(4-ethynylphenyl) hexafluoropropane 5

7,49 g of <u>4</u> are dissolved in a THF/CH_3OH mixture with K_2CO_3 at ambient temperature in order to remove the trimethylsilyl group.

After filtration and removal of the solvent, the product was filtered through a bed of silica gel with hexane/diethyle oxide (100:2).

After evaporation, a white crystalline product was obtained.

Yield: 94%

Mp: 37-38°C

^1H NMR ($CDCl_3$ in ppm TMS): 7.4-7.5 ppm (m, aromatic), 3,1 ppm (s, $C\equiv CH$)

Elem. anal. for $C_{19}H_{10}F_6$

%	C	H	F	S
Calc.	64.77	2.84	32.38	
Found	64.34	2.88	32.36	0.10

RESULTS AND DISCUSSION

The triflate of bisphenol A.F was obtained according to the data of the litterature. More surprising was the bistriflate behaviour during the ethynylation. The following table 1 summarize different runs :

Table 1: Effect of experimental conditions on the extent of acetylenic fonction.

$nPd(PPh_3)_2Cl_2$ (mmol)	n PPh_3 (mmol)	n CuI (mmol)	ZnO (mol)	DMF (ml)	NEt_3 (ml)	Δ t (h)	%f
0.238	-	-	-	25	5	10	90
0.238	-	-	0.0196	25	5	6	98
0.059	0.5	0.055	0.0196	25	5	10	60
0.059	0.5	0.0275	0.0196	25	5	10	80
0.059	0.5	-	0.0196	25	5	10	50
0.238	-	-	0.0196	30	-	10	80

All these syntheses were lead in the following conditions:

n bistriflate = $6.66.10^{-3}$ mole, n $HC\equiv CSi(CH_3)_3$ = 0.02 mole, T = 90°C

Three main observations have to be discussed :

- Instead of the classical ethynylation reaction using an halogen as a starting group (7), the best results were obtained using $Pd(PPh_3)_2Cl_2$ alone.

- The formation of triflate anion during the reaction destroyed rapidly the catalytic system and a base giving an insoluble salt is needed for the complete removal of the triflate anion.

- The polar solvent used with NEt$_3$ has a strong influence and the best results were obtained with dimethylformamide.

The formation of the free acetylene end-capped by potassium carbonate was performed with very good yield giving the product with a good purity (98% from GPC and ^{1}H NMR, ^{13}C MNR determination).

Analysis of 2,2 bis (4-ethynylphenyl) hexafluoropropane by DSC showed one exotherm with a maximum at 209°C attributed to the polymerization of the acetylene groups. A ΔH polymerization per acetylenic mole of 131 kJ was measured which accords with litterature (120 kJ), (8).

The thermo-oxidative stabilities of the crosslinked network were evaluated by thermogravimetric analysis. Onset of weight loss under air or argon occured at 435°C as shown in figure 1 where the evolution of the degradation can be followed. The isothermal aging was checked at 300°C under air. The resin losts only 2% of initial weight after 70 h.

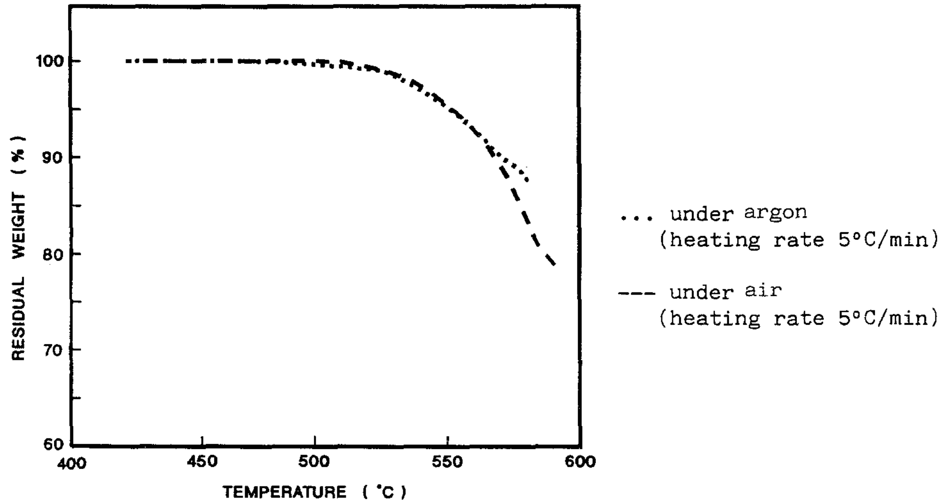

Figure 1: Thermogravimetric analysis of 2,2 bis (4-ethynylphenyl) hexafluoropropane

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