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Ethynyl terminated ethers. Synthesis and thermal characterization of 2,2 bis (ethynyl-4-phenylcarbonyl-4-phenoxy-4-phenyl) propane and 2,2 bis (ethynyl-4-phenylsulfonyl-4-phenoxy-4-phenyl) propane

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SUMMARY

Two ethynyl end-capped ethers 2,2 Bis [ethynyl-4-phenylsulfonyl-4-phenoxy-4-phenyl] propane and 2,2 Bis [ethynyl-4-phenylcarbonyl-4-phenoxy-4-phenyl] propane have been prepared by a three steps synthesis each. They exhibit melting point followed by the thermal polymerisation of the ethynyl groups in the 200-250°C range. Curing lead to thermoset materials where Tg are respectively of 240°C and not detectable.

INTRODUCTION

Ethynyl end-capped oligomers and polymers have been widely studied as heat resistant thermosetting materials (1,2,3,4).The acetylenic group can be thermally polymerized without evolving volatile by products.

Because of their good thermal stability and their solubility in most common solvents before curing, ethynyl end-capped aromatic ethers are good candidates for reactives oligomers (5,6).

In this paper we report the synthesis by a three steps sequence of two ethynyl end-capped aromatic ethers, starting from the bisphenol A and including sulfone or benzophenone unit.

The general reaction is illustrated in scheme 1.

EXPERIMENTAL

Materials

4-Bromo-4'-fluorobenzophenone was prepared by the classical Friedel-Crafts acylation of bromobenzene with 4-fluorobenzoylchloride. 4-Bromo-4'-fluoro diphenylsulfone was prepared by the Friedel-Crafts sulfonylation of bromobenzene with 4-fluorobenzene sulfonylchloride. Bisphenol A and 2-methyl 3-butyn-2-ol were obtained from Fluka and were used as received.

Synthesis

2,2 Bis [bromo-4-phenylsulfonyl-4-phenoxy-4-phenyl] propane (Ia)

In a flask fitted with a Dean-Stark apparatus 5.7g (25 m.mol) of bisphenol A, 4.83g (35 m.mol) of potassium carbonate, 75 cc of N-methyl

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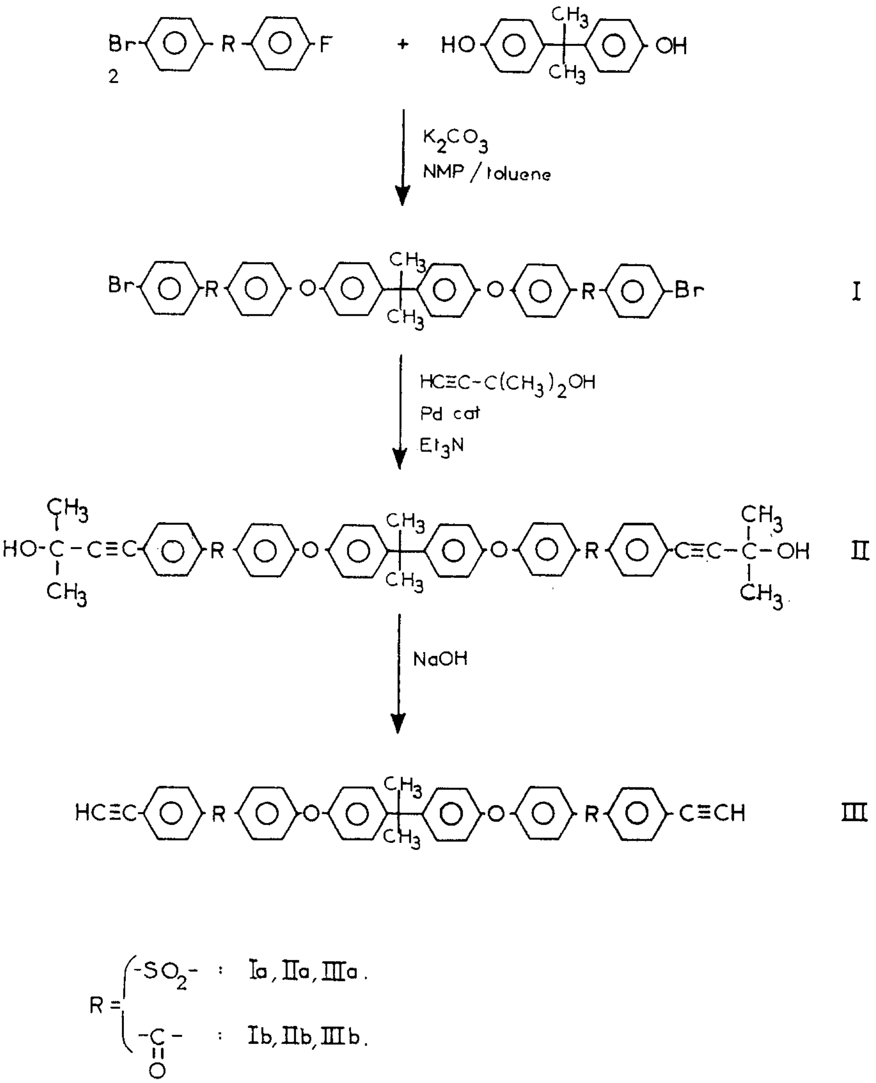

Scheme 1 - Synthesis

pyrrolidone and 25 cc of toluene were heated under nitrogen atmosphere until the water and the toluene were removed from the trap. Then, the temperature was stabilized at 160°C and 15.75 g (50 m.mol) of 4-bromo-4'-fluoro diphenyl sulfone in 25 cc of toluene were introduced. The reaction was allowed to continue at this temperature for 3 hours.

After filtration the solvent was removed under reduced pressure and the residue was washed with a n hexane-acetone mixture to yield 17 g of the expected product as a light brown solid. Yield = 83%. mp = 178°c.

H-NMR ($CDCl_3$) : 1.7 ppm (s,6H, CH_3), 6.7-7.9 ppm (m,24 H, aromatic).

2,2 Bis [(3-hydroxy-3-methyl-1-butynyl)-4-phenylsulfonyl-4-phenoxy-4-phenyl] propane (IIa)

15 g (18.3 m.mol) of Ia, 5.04g (60 m.mol) of 2-methyl-3-butyn-2-ol, 37 mg of bistriphenylphosphine palladium dichloride, 74 mg of triphenyl phosphine, and 74 mg of cuprous iodide in 100 cc of triethylamine and 150 cc of toluene were stirred at 90°C for 6 hours. After cooling, the hydrobromic salt was filtered, the solvent was removed and the residue was washed with hot n hexane to afford the expected product with a nearly quantitative yield. This material will be used without further purification.

H-NMR ($CDCl_3$) : 1.6 ppm (s, 12H,- C $(CH_3)_2$ O-),1.7 ppm(s,6H, Ø-C$(CH_3)_2$-Ø), 6.9-7.8 ppm (m,24H, aromatic).

2,2 Bis [ethynyl-4-phenylsulfonyl-4-phenoxy-4-phenyl] propane (IIIa)

To a suspension of 2.2 g (55 m.mol) of sodium hydroxyde in 50 cc of chorobenzene was added 15 g (18.3 m.mol) of IIa in 50 cc of chlorobenzene. The mixture was stirred at 110°C for 1 hour under nitrogen atmosphere, then pourred into water. The organic layer was successively washed with dilute hydrochloric acid and water. After drying over magnesium sulfate the solvent was removed and the residue was recrystallized from ethanol to give 10.4 g of light yellow crystals. Yield = 80%. mp = 154°c.

H-NMR ($CDCl_3$): 1.7 ppm (s, 6H, -C $(CH_3)_2$-), 3.2 ppm (s, 2H, $\equiv$ C-H), 6.9-7.9 ppm (m,24H, aromatic).

IR (KBr) cm^{-1} : 3280 ($\equiv$ C-H), 2960 (CH_3-),2100 ($C\equiv C$),1330 (SO_2), 1240 (C-O-C).

Anal calcd for $C_{43}H_{32}O_6S_2$ = C (72.88%), H (4.52%). Found : C(72.62%), H (4.66%).

2,2 Bis [bromo-4-phenylcarbonyl-4-phenoxy-4-phenyl] propane (Ib)

Ib was synthesized according to the same procedure than for the preparation of Ia using 4-bromo-4'-fluorobenzophenone instead of 4-bromo-4'-fluoro diphenylsulfone.

Yield = 81 %. mp = 86°C.

H-NMR ($CDCl_3$) = 1.7 ppm (s, 6H, CH_3), 6.9-7.8 ppm (m, 24H, aromatic).

2,2 Bis [(3-hydroxy-3-methyl-1-butynyl)-4-phenylcarbonyl-4-phenoxy-4-phenyl] propane. (IIb)

IIb was prepared according to te procedure described for the synthesis of IIa. Yield = 91%. mp = 190°c.

H-NMR ($CDCl_3$) = 1.6 ppm (s, 12H,$-C(CH_3)_2$ O-), 1.7 ppm (s, 6H,Ø $-C(CH_3)_2$-Ø), 6.9-7.8 ppm (m,24H, aromatic).

2,2 Bis [ethynyl-4-phenylcarbonyl-4-phenoxy-4-phenyl] propane (III b)

IIIb was prepared according to the procedure described for the preparation of IIIa. Yield = 81% mp = 183°C.

H-NMR ($CDCl_3$ = 1.7 ppm (s, 6H, $- C(CH_3)_2-$), 3.2 ppm (s 2H, ≡ C-H).

IR (KBr) cm^{-1} : 3280 (≡ C-H), 2960 (CH_3-), 2100 (C ≡ C), 1700 (C = 0), 1240 (C-0-C).

Anal Calcd for $C_{45}H_{32}O_4$ = C (84.91%), H (5.03%). Found : C (84,99%), H (5.10%).

RESULTS AND DISCUSSION

In the first step of the synthesis, etherification occurs quantitatively and selectively through fluoro displacement while bromo group does not react. Fluoro displacement is activated by the electron withdrawing sulfone and carbonyl groups.

Ethynylations were performed by bromo displacement using 2-methyl-3-butyn-2-ol under palladium catalytic system according to the literature procedure (7). Conversions of bromo derivatives were nearly quantitative using an excess of alkyne reagent.

Cleavage of the isopropanol group to produce free ethynyl end-groups is conducted with a strong base like sodium hydroxyde. During this reaction, the in-situ generated acetone will be continously removed from the mixture.

The two ethynyl ethers described are prepared with good yield each over the three steps : 75% for the ether-sulfone and 60% for the ether-ketone. These syntheses required common and available materials and lead to high purity products.

N°	mp	Exotherm*			Δ H
	(°C)	Ti	Tmax	Tf (°C)	(J/C≡C)
IIa	-	220	280	305	
IIIa	154	175	230	275	133
IIb	190	250	285	320	
IIIb	183	190	250	285	137

* temperatures of the exotherm = initial, at maximum, final.

Table 1. DSC data at 20°C/min.

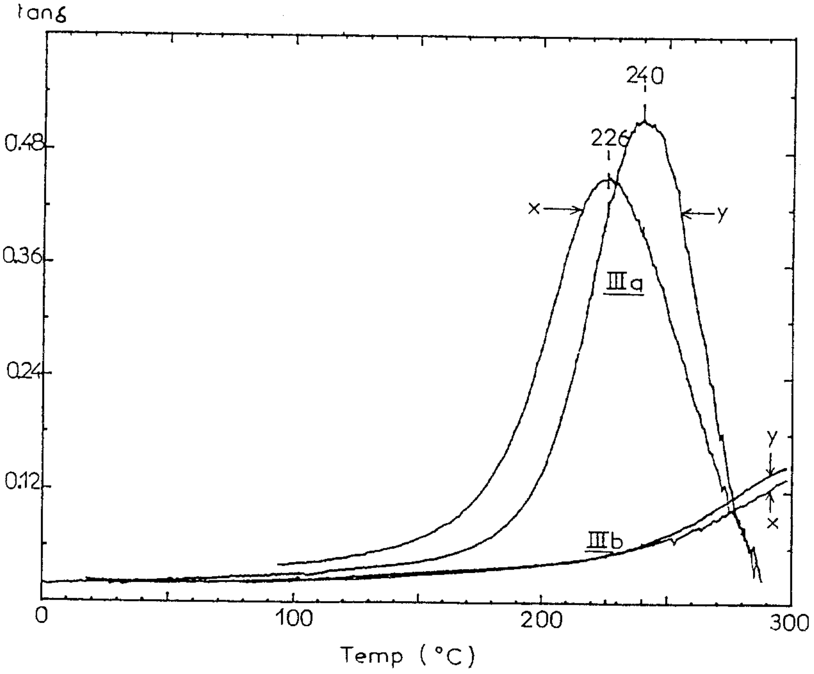

Fig.1 DMTA analysis (3°C/min).Tan δ versus temperature after a cure cycle of : x = 30 minutes at 230°C and y = 30 minutes at 230°+ 2 hours at 250°C.

The two ethynyl end-capped ethers are crystalline materials. Analysis by DSC showed an endotherm corresponding to the melting point followed by an exotherm attributed to the polymerisation of the ethynyl groups.

The DSC data are summarized in table 1.

Polymerisation of pure ethynyl groups starts at 175°C with a maximum at 230°C for the ether sulfone, and starts at 190°C with a maximum at 250°C for the ether ketone. The enthalpies of polymerisation are estimated at 133 and 137 KJ per acetylenic group. This is in accordance with published data (8).

When end-capping group is 2-methyl-2-ol-butynyl group the exotherms of polymerisation are shifted to higher temperature (about 30°C to 60°C).

The ethynyl ethers were cured at 230°C for 30 minutes in a compression mold to obtain 40 x 40 x 2 mm samples. On both materials no residual exotherm were detected by DSC analysis. Tg measurements by dynamical mechanical thermal analysis (DMTA) were performed at maximum tan δ .
The thermal behaviour of the cured materials is illustrated in fig.1.

The cured ethynyl ether sulfone exhibits a Tg at 226°C. This Tg moves to 240°C after a post-cure at 250° C for 2 hours, and it is not modified after an additional post cure at 300°C for 2 hours.

The thermoset ethynyl ether ketone presents no detectable Tg in DMTA (and in DSC as well) even after post-curing.

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