

1,3-bis(4-ethynylbenzoyl)benzene

Synthesis and polymerization

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SUMMARY

1,3-Bis(4-ethynylbenzoyl)benzene was prepared in a three steps synthesis. This compound exhibits a maximum of the exotherm of polymerization at 222°C. This temperature shifted to 198°C in presence of dicumyl peroxide. The polymerization was followed by DSC analysis and was found to be faster when it was initiated by peroxide.

INTRODUCTION

Monomers and oligomers containing ethynyl groups have been widely studied as precursors for high performance materials (1,2,3,4).

The ethynyl group can polymerize without evolving volatile by-products, leading in the case of diethynyl monomers to thermoset materials.

Thermally induced polymerization generally occurs in the 160-250°C range. In order to reduce the temperature of curing, a promoted radical polymerization could be under consideration.

In this paper we report the synthesis of a diethynyl monomer, the 1,3-bis(4-ethynylbenzoyl)benzene. Curing of this compound was conducted at different temperatures in isothermal conditions. An approach of radical initiated polymerization is related.

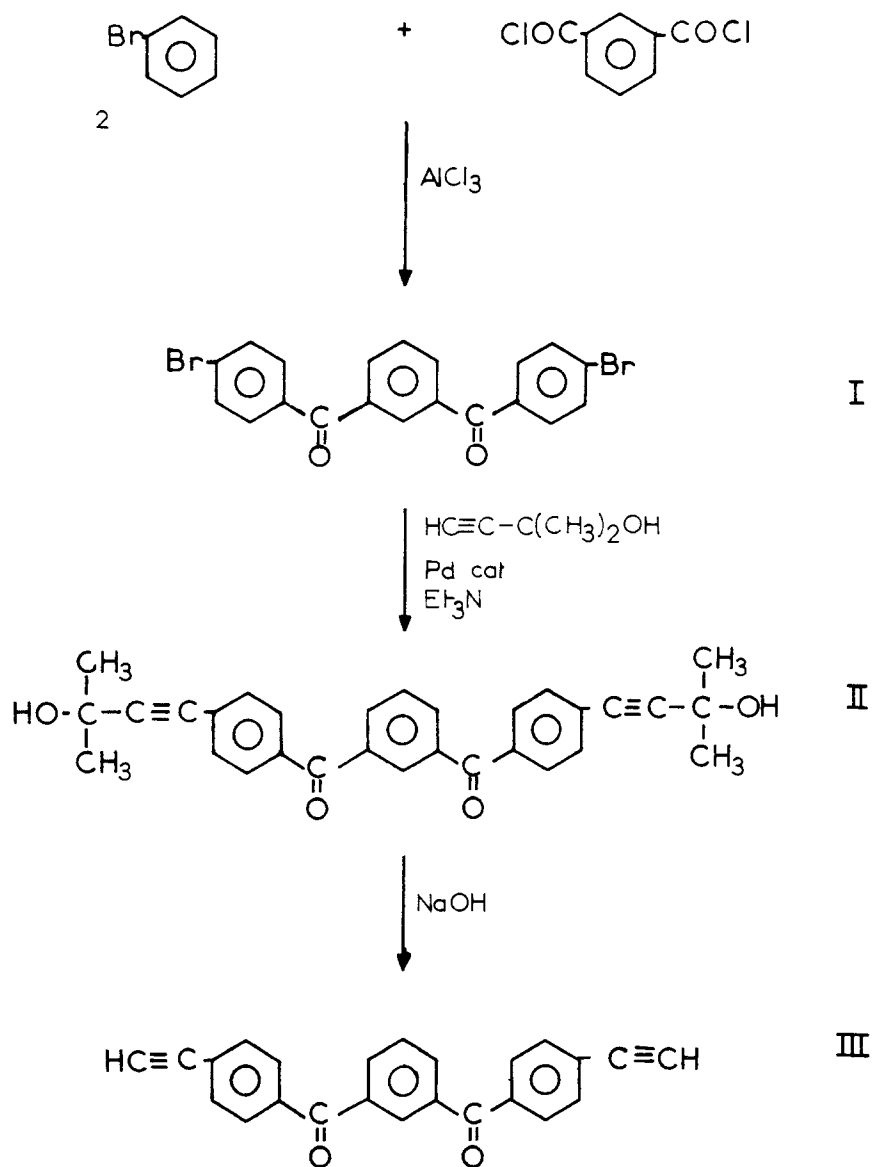
EXPERIMENTAL

Materials

Isophthaloyl chloride, 2-methyl-3-butyn-2-ol were supplied from Fluka. Bromobenzene was supplied from Aldrich Chemical and was distilled before use. Dicumylperoxide was obtained from Merck.

Differential scanning calorimetry (DSC) was performed on DuPont 990 Thermal Analyzer.

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Scheme 1. Synthesis.

Synthesis1,3-Bis (4-bromobenzoyl) benzene (I)

Anhydrous powdered aluminium chloride (32.04 g, 0.24 mol) was added under nitrogen to a well stirred solution of isophthaloyl chloride (20,3 g, 0,1 mol) in bromobenzene (196.2 g, 1.25 mol) during 20 min at room temperature and the reaction mixture was stirred for 1 hour. Then the mixture was heated to 80°C and stirred for 4 hours. After cooling the reaction mixture was poured in cold aqueous hydrochloric acid. The organic layer was separate diluted with dichloromethane, washed twice with water and dried over magnesium sulfate. Then the solvents were removed and the crude product was recrystallized from chlorobenzene to afford 24.9 g of white crystals.

Yield = 56%. mp = 221°C.

Anal Calcd for $C_{20}H_{12}Br_2O_2$: C, 54.05% ; H, 2.70%. Found : C, 54.18% ; H, 2.52%.

1,3-Bis (4 (3-hydroxy-3-methyl-1-butynyl) benzoyl) benzene. (II)

I (14 g, 31.5 m.mol), 2-methyl-3-butyn-2-ol(10.6 g, 0.126 mol), bistrisphenylphosphine palladium dichloride (64mg), triphenyl phosphine (122 mg) and cuprous iodide (122 mg) in triethylamine (100 cc) and toluene (150 cc) were stirred at 90°C for 6 hours. After cooling the hydrobromic salt was filtered, the solvents were removed and the crude product was washed with ether to afford 10.5 g of white solid.

Yield = 75%. mp = 188°C.

H-NMR ($CDCl_3$) : 1.6 ppm (s, 12H, CH_3) ; 2.2 ppm (s, 2H, -OH) ; 7.4-8.1 ppm (m, 12H, aromatic).

^{13}C -NMR ($CDCl_3$) : 31.4 ppm (CH_3) ; 65.7 ppm ($-C-$) ; 81.4, 97.5 ppm ($C\equiv C$) ; 127.7, 128.7, 129.9, 131.0, 131.7, 133.5, 136.2, 137.8 (aromatic) ; 194.9 ($C=O$).

IR (KBr) cm^{-1} : 3350 (-OH), 2100 ($C\equiv C$) 1700 ($C=O$)

Anal Calcd for $C_{30}H_{26}O_4$: C, 80.0% ; H, 5.78%. Found : C, 79.75% ; H, 5.73%.

1,3-Bis (4-ethynylbenzoyl) benzene. (III)

To a suspension of sodium hydroxide (3,78 g, 94.5 m.mol) in chlorobenzene (100 cc) was added a solution of II (10 g, 22,2 m.mol) in chlorobenzene (100 cc). The mixture was stirred at 100°C for 1 hour under a nitrogen atmosphere, then poured into water. The organic layer was succesively washed with diluted hydrochloric acid and water. After drying over magnesium sulfate, the solvent was removed and the crude product was recrystallized from toluene to afford 6.5 g of a light yellow solid.

Yield = 88%.

H-NMR ($CDCl_3$) : 3.2 ppm (s, 2H, $HC\equiv$) ; 7.5-8.2 ppm (m, 12 H, aromatic).

Figure 1. DSC of ethynyl monomers.

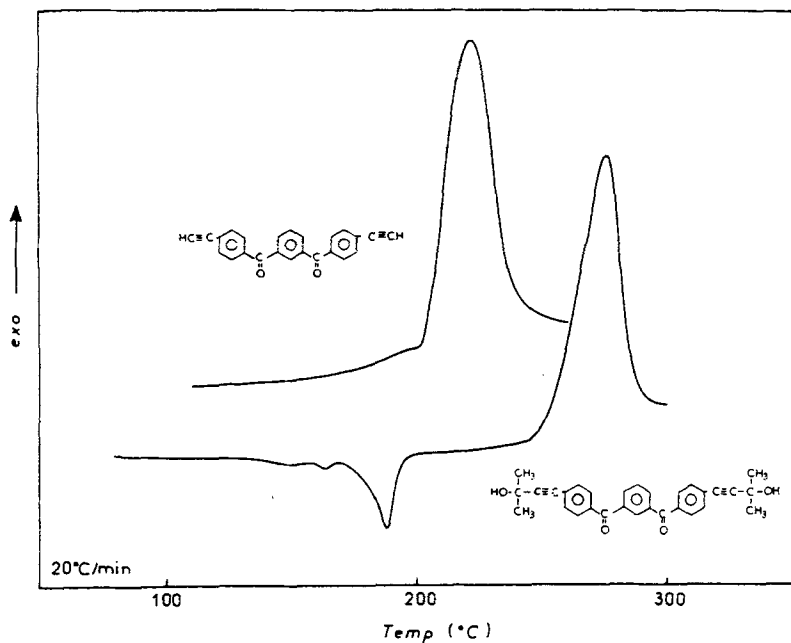
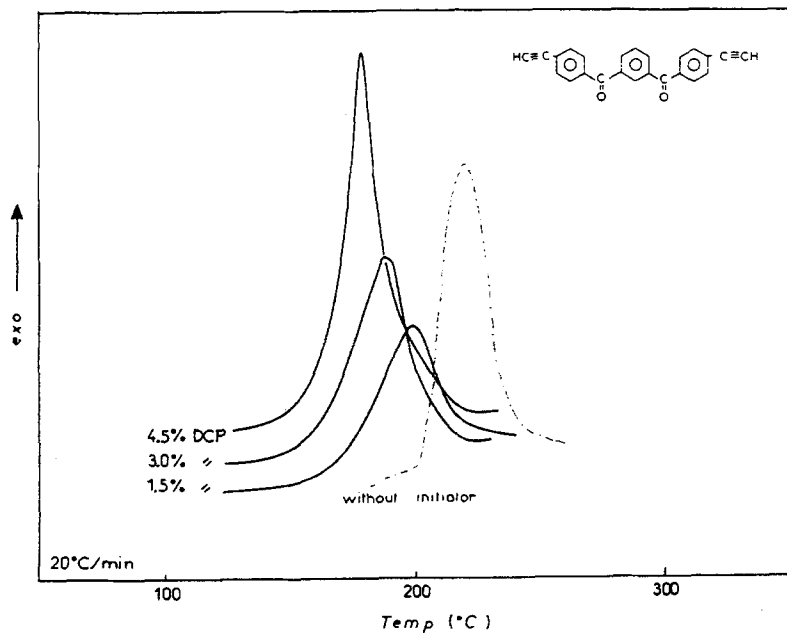


Figure 2. Influence of dicumyl peroxide (DCP) on DSC data



^{13}C -NMR (CDCl_3) : 80.4 ppm ($\text{HC}\equiv$) ; 82.8 ppm ($\equiv\text{C} - \text{O}$); 127.0, 128.7, 129.9, 130.9, 132.3, 133.5, 136.9, 137.8 ppm (aromatic); 194.8 ppm ($\text{C}=\text{O}$).

IR (KBr) cm^{-1} = 3275 ($\equiv\text{C}-\text{H}$), 2100 ($\equiv\text{C}$), 1710 ($\text{C}=\text{O}$).

Anal Calcd for $\text{C}_{24}\text{H}_{14}\text{O}_2$: C, 86.21% ; H, 4.22%. Found : C, 86.10% ; H, 4.31%.

RESULTS AND DISCUSSION

1,3-Bis (4-ethynylbenzoyl) benzene was obtained according to the three steps synthesis illustrated in scheme 1.

The first step is a classical Friedel-Crafts acylation using aluminium chloride leading to dibromo compound. Ethynylation was performed by bromo displacement using 3-methyl-2-butyne-3-ol under palladium catalysis as reported in literature (5,6). Cleavage of the isopropanol group under strong basic medium like sodium hydroxide leads to ethynyl terminated product. This synthesis required very common and no expensive starting materials, and leads to high purity product.

Figure 1 illustrated the thermal behaviour of compounds II and III, where end-chains are respectively isopropanol substituted ethynyl groups and pure ethynyl ones.

Both exhibit exotherm of polymerization of acetylenic function, but pure ethynyl group presents a better reactivity with a beginning of reaction at about 180°C and a maximum of the exotherm at 222°C . Isopropanol substituted ethynyl group starts to react at $230\text{--}240^\circ\text{C}$ with a maximum of intensity at 275°C .

So the isopropanol group decrease consequently the reactivity, and unsubstituted ethynyl group will be preferred as reactive function. Enthalpies of polymerization were estimated at 85 KJ/acetylenic mole for II, and at 103 KJ/acetylenic mole for III. These values seem slightly lower than the reported data (7).

The reaction of polymerization of such ethynyl compound and the structure of the resulting thermoset material are not clearly elucidated yet. However, a thermally induced radical polymerization might be considered. In order to increase the reactivity, a radical initiator like dicumyl peroxide (DCP) was associated to the monomer. Monomer and DCP compositions were obtained by evaporation of dichloromethane solutions.

Figure 2 shows the DSC behaviour at three concentrations. The reactivity increases clearly with the concentration of peroxide confirming a radical initiated polymerization of ethynyl groups. In the 1.5% peroxide composition, the exotherm is shifted about 25°C to lower temperatures with a maximum at 198°C . This displacement reaches 40°C with an unusually high concentration of 4.5% of peroxide. In this case the exotherm peaks at 180°C .

Figure 3. Polymerization of 1,3-bis (4-Ethynylbenzoyl)benzene followed by DSC.

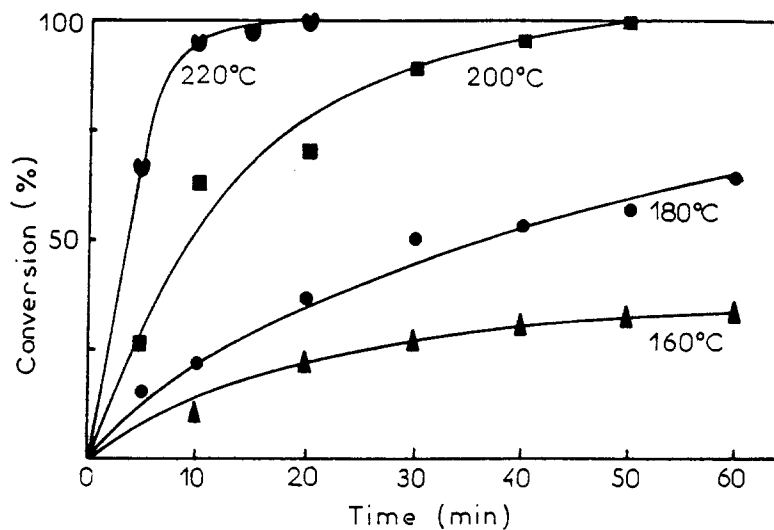
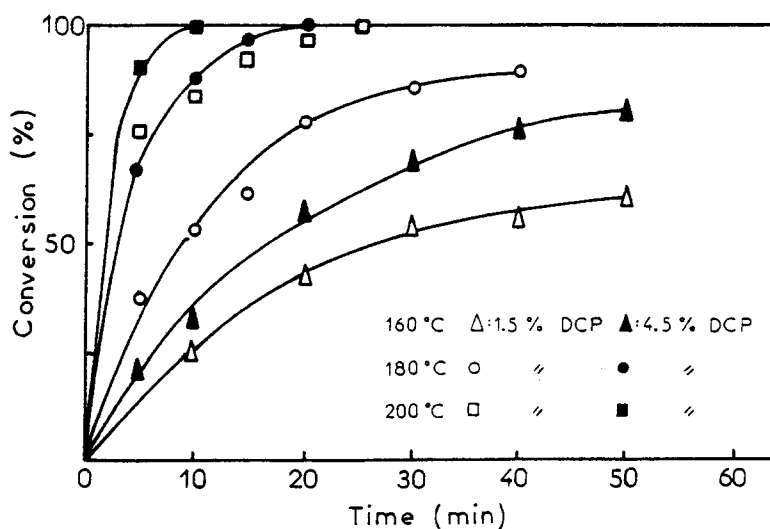


Figure 4. Dicumyl peroxide initiated polymerization followed by DSC.



The enthalpies of polymerization are respectively estimated to 118, 124 and 127 KJ/acetylenic mole for the 1.5%, 3,0% and 4,5% peroxide concentrations.

Polymerization has been followed by DSC analysis for uncatalyzed monomers. Conversions were determined using the ΔH residual : ΔH initial ratio.

Figure 3 shows the evolution of conversion of the free initiator monomer in isothermal conditions at 4 temperatures. Complete conversion was achieved at 200°C for 50 min and at 220°C for 20 min. When polymerization was radical initiated the reactivity increases significantly as shown in figure 4. With a 1.5% proxide concentration, the conversion became complete after 25 min at 200°C. Complete curing was observed at this temperature after only 10 min when peroxide concentration was 4.5%. In all compositions studied no glass transition temperature were detected by DSC.

These results seem to indicate that peroxide initiation in polymerization of ethynyl monomers could be a way to reduce the time and temperature of curing. However in our experiments, conversion means only disappearance of the exotherm attributed to the consumption of ethynyl groups, and does not include eventual additional transformations. Further investigations will include mechanical and structural analysis, in order to evaluate the influence of initiator on nature of polymerization reaction, degree of reticulation and physical properties of the materials.

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