Polymer Bulletin 26, 1–6 (1991)

Polymer Bulletin

1,2-bis(3-propargyloxyphenoxy)ethane

Synthesis and polymerization

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SUMMARY

1,2-Bis(3-propargyloxyphenoxy)ethane was prepared by phase transfert catalyzed etherification. This monomer exhibits a maximum of the exotherm of polymerization at 280°C. When the reaction was initiated by cupric chloride and by cupric sulfate this temperature respectively shifted to 186°C and 217°C. Conversion of the propargyl group was followed by DSC at different temperatures and increased significantly in the presence of cupric catalysts.

INTRODUCTION

Acetylene terminated monomers and oligomers are known to be good candidates for thermosetting materials (1). Phenylacetylene end-capping group has been the most widely studied (2,3,4).

Propargyl ether is another very attractive acetylenic reactive group mainly because its preparation is easy. Indeed an only one etherification step is required when starting from phenol and propargyl bromide or propargyl chloride (5,6).

In this paper we report the synthesis of a new dipropargyl ether monomer the 1,2-bis(3-propargyloxyphenoxy) ethane. Curing was followed by DSC. An attempt to promote the polymerization of this monomer was effected in order to improve processability. In this way cupric salt catalysis was considered.

EXPERIMENTAL

Material

1,2-Bis(3-hydroxyphenoxy)ethane was obtained from Aldrich Co and was recrystallized from chlorobenzene then from a methanol-water mixture. Propargyl chloride was obtained from Fluka.

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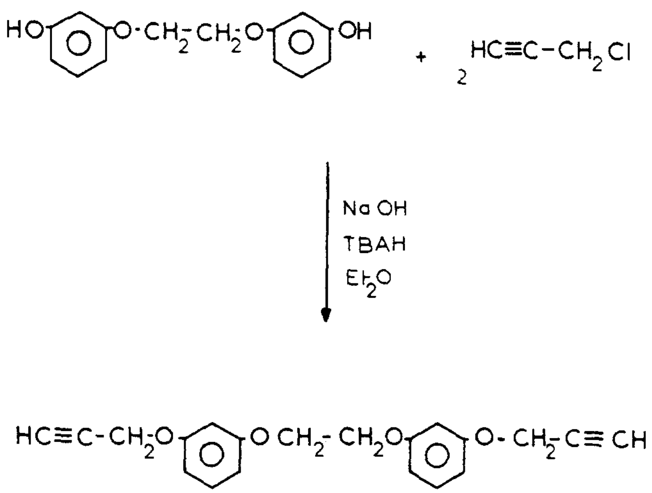
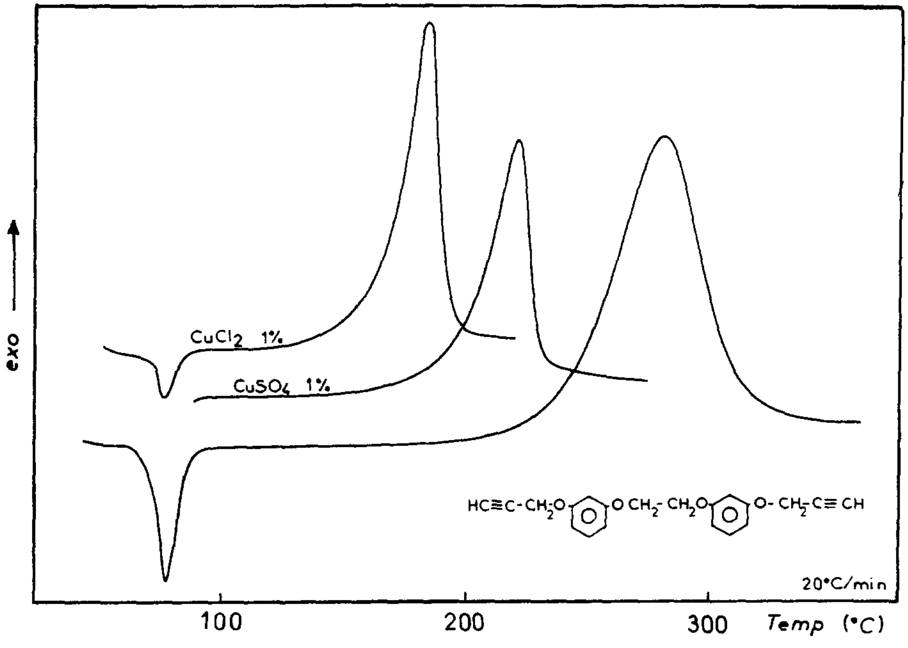


Scheme 1. Synthesis

Fig.1 DSC behaviour of propargylether



Differential Scanning Calorimetry was performed on a DuPont 990 Thermal Analyzer at 20°C/min.

Synthesis

1,2-Bis(3-propargyloxyphenoxy) ethane

1,2-Bis(3-hydroxyphenoxy)ethane (6.15g, 25m.mol), propargyl chloride (5.59g, 75 m.mol) were dissolved in 100 cc of diethyl ether. To the mixture was added tetrabutylammonium hydrogen sulfate (1.7g, 5m.mol) then 50 cc of a 20 % aqueous sodium hydroxide solution. The mixture was vigouresly stirred at room temperature for 4 hours. Then the organic layer was separated, diluted with 100 cc of diethyl ether, washed with diluted hydrochloric acid and twice with water, dried over magnesium sulfate and finally evaporated to afford 5.9 g of the expected product.
Yield : 73%. mp : 80°C.

H-NMR ($CDCl_3$) : 2.5 ppm (t, 2H, HC≡) ; 4.3 ppm (s,4H, $-OCH_2-CH_2O-$) ; 4.6ppm (d, 4H, $OCH_2-C\equiv$) ; 6.5-7.2 ppm (m, 8H, aromatic).

IR (KBr)cm^{-1} : 3260, 3280 (≡C-H), 2100 (C≡C).

Anal Calcd for $C_{20}H_{18}O_4$: C, 74.53% ; H, 5,59%. Found : C,74.48% ; H, 5.42%.

RESULTS AND DISCUSSION

The synthesis is illustrated in the scheme 1. The etherification could be conducted by refluxing the phenol and the propargyl bromide in acetone in presence of potassium carbonate for 72 hours (7). In the phase transfert catalyzed etherification presented herein, the reaction occurs at room temperature for few hours. Moreover, this way can be carried out using propargyl chloride less expensive and less versatile than propargyl bromide (8). Etherification was performed using tetra alkylammonium salt as transfert agent according to the classical reported phase transfert catalysis conditions (9,10,11).

The mechanism of thermally induced polymerization of propargyl ether is not yet clearly elucidate. Rearrangement of aromatic propargyl ether into chromene ring has been recently reported (8). In this case, the chromene ring might be the reactive species during the polymerization stage.

Elsewhere, catalyzed polymerization of alkynyl groups has been widely investigated (12,13, 14). Among the mentioned catalysts, cupric salts were found to initiate oxidative coupling leading to diynes. This reaction was observed with a large requirement of cupric chloride while catalytic amount of this salt was found to be efficient on coupling in a pyridine-methanol medium (15).No specific effect of cupric salt catalysis on bulk polymerization of dipropargyl ether was reported.

1,2-Bis(propargyloxyphenoxy) ethane presented herein is solid at room temperature. The DSC thermogram represented in figure 1 shows an endotherm corresponding to the melting point at 80°C, and an exotherm attributed to the polymerization of the propargyl groups. This reaction starts about 200°C and the maximum of intensity was pointed at 280°C. The enthalpy of reaction was estimate to 169 KJ/acetylenic mole.

In order to reduce the temperature of curing of this monomer, an attempt to catalyze the polymerization by cupric salt has been effected. The monomer was respectively associated to 1 % of cupric chloride dihydrate and to 1 % of cupric sulfate pentahydrate. Each of the two blends was prepared by dissolving the monomer and the catalyst in a methanol-dichloromethane mixture, then by removing the solvents.

The DSC behaviour is shown in figure 1. For each catalyzed monomer evaluated, the exotherm is significantly shifted to lower temperature. In the $CuCl_2,2H_2O$ composition the reaction starts at 120°C and exhibits a maximum of intensity at 186°C, so about 100°C less than for the non catalyzed reaction. When $CuSO_4$, $5H_2O$ is involved the exotherm starts at 140°C with a maximum at 217°C. So, catalytic amount of such cupric salts was efficient to modify the thermal behaviour of the reaction.

The enthalpies are estimated to 166 KJ/acetylenic mole for the chloride salt composition and to 170 KJ/acetylenic mole for the sulfate one. This parameter does not seem to be affected by the presence of any of these two catalysts.

No structural evidence about these polymerizations are yet available to indicate if the same reaction take place in a catalyzed process and in a non catalyzed one, leading to the same thermoset material or not. No glass transition temperatures were observed on cured materials to specify this point.

Conversion was followed by DSC at different temperatures in isothermal conditions using the ΔH residual : Δ initial ratio. This ratio means the conversion of the ethynyl group in despite of the nature of the polymerization reaction.

Figure 2 shows the evolution of conversion for non catalyzed monomer. Conversion was complete at 250°C for 40 min and at 280°C for 10 min. These observations confirm the lower reactivity of propargyl group compared with the phenyl acetylene one, for which such conversion rates are reached at temperature of curing at about 50°C less.

Conversions of catalyzed monomers are reported in figure 3. For cupric sulfate catalyzed composition, the conversion is achieved at 190°C for 30 min and at 220°C for 15 min. Complete conversion is reached more easily like 20 min at 160°C and 10 min at 190°C for cupric chloride catalyzed composition. After 1 hour at this last temperature, conversion was only 12% in a non catalyzed process.

These data indicate that cupric salt catalysis in propargyl ether polymerization could be considered to improve the processability of such monomers. Further investigations will include structural analysis of the thermoset materials.

Fig.2 Thermal polymerization of propargylether followed by DSC.

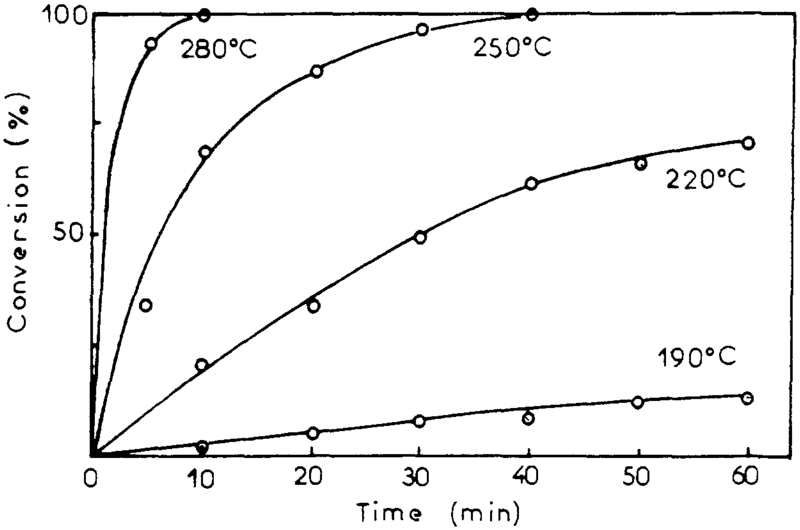
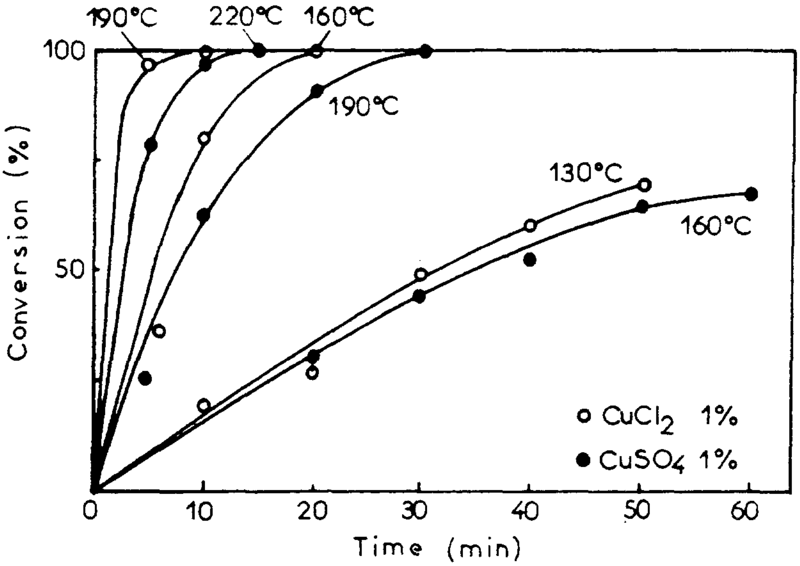


Fig.3 Catalyzed polymerization of propargylether followed by DSC.



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Accepted December 21, 1990 C