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Synthesis and Properties of a New Polyether Ketone

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SUMMARY

A new polyether ketone has been synthesized (via addition polymerization) by reacting N,N'-bispropargyl-4,4'-diaminobenzophenone and Bisphenol A. The polymer is soluble in both polar and ketonic solvents. The inherent viscosity data indicates the molecular weight of the polymer to be low and thermogravimetric analysis suggests it to be a fairly thermostable polymer.

INTRODUCTION

The first aromatic polyether ketone was reported by Bonner (BONNER 1962) and more recently some polyether ketones have been prepared by Attwood (ATTWOOD et al. 1981). The polyether ketone and polyether are both in the same class of engineering plastics. Most polyethers or polyether ketones are prepared by oxidative coupling reaction (HAY 1962, COOPER et al. 1969) or by Friedel-Crafts polycondensation reaction (IWAKURA et al. 1968, MARKS 1969). In this communication we wish to report the synthesis and properties of a new polyether ketone via the addition polymerization technique.

EXPERIMENTAL

Materials - Propargylbromide was obtained from Aldrich Chemical Company (USA) and was used without further purification. Bisphenol A (4,4'-isopropylidenediphenol) was obtained from Aldrich Chemical Company (USA) and was recrystallized from toluene; N-methyl-2-pyrrolidone (NMP) was distilled and stored over 4 Å molecular sieves prior to use.

Monomer Synthesis: Compound I, 4,4'-diaminobenzophenone, was prepared in 61% yield from 4,4'-diaminodiphenylmethane according to the method of Bell (BELL 1976). N,N'-Bispropargyl-4,4'-diaminobenzophenone(IV) was prepared according to the method of Wolfe (WOLFE 1980) and after recrystallization from 95% ethyl alcohol, a 95% yield was obtained.

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Polymer Synthesis: Bisphenol A (20.8 g) was dissolved in 20 ml NMP and a few drops of triethylamine added. To this was slowly added a solution of 6 g of N,N'-bispropargyl-4,4'-diaminobenzophenone in 40 ml of NMP under nitrogen atmosphere. The reaction temperature was raised to 150°C, maintained for 3 hrs., and then raised to 220°C over a period of 2 hrs. In the last 30 minutes of reaction, vacuum was applied to distil excess solvent and Bisphenol A from the reaction pot. The reaction was quenched by pouring into methanol at the gel point, and the polymer thus obtained was purified by dissolving in DMF and reprecipitating with methanol. The polymer was dried in a vacuum dessicator at 60°C.

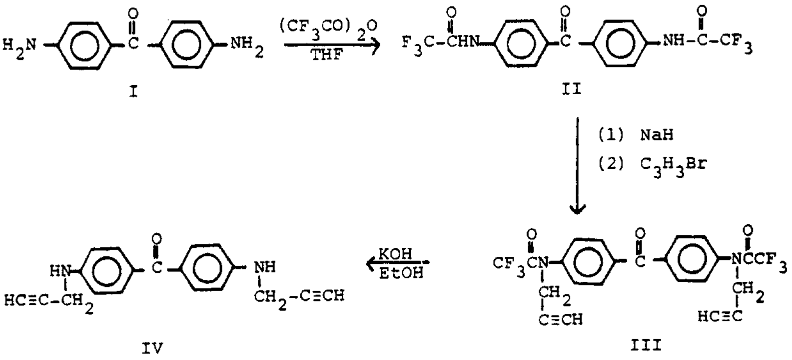
Characterization of monomer and polymer: The IR spectra was obtained with a Perkin-Elmer model 421 in KBr pellet, the NMR spectrum with a Varian HA-100, and the mass spectrum with a AIE 12 Mass spectrometer. Thermogravimetric analyses were carried out using a DuPont 950 Thermogravimetric Analyzer and were recorded in air at a heating rate of 6°C/min. Viscosity measurements were determined using a 0.5% (g/ml) solution of the polymer in tetrahydrofuran (THF) at 28°C using a Ubbelohde viscometer.

RESULTS AND DISCUSSION

Monomer Synthesis and Characterization:

The preparation of N,N'-bispropargyl-4,4'-diaminobenzophenone(IV) was accomplished as shown in Scheme 1, and it should be noted that St. Clair (ST.CLAIR et al. 1980) prepared the diphenylmethane analogue similarly. To avoid possible reduction of the carbonyl group of N,N'-bispropargyl-4,4'-bistrifluoroacetamidobenzophenone(II) by sodium hydride, the dianion reaction was performed at 0°C under nitrogen atmosphere.

REACTION SCHEME 1

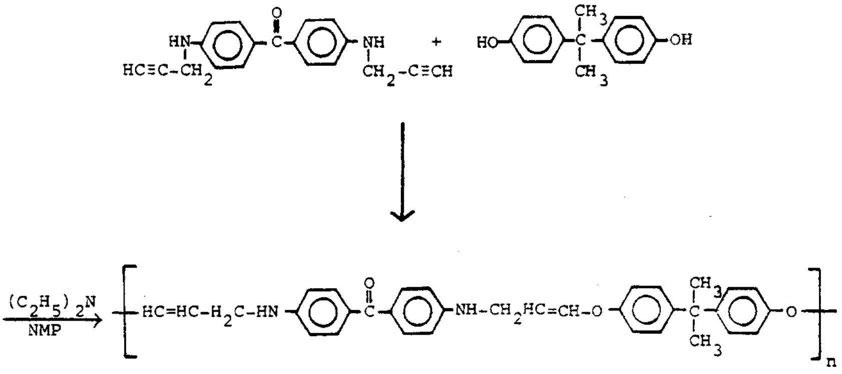


The infrared spectrum of IV contained a carbonyl stretching frequency at 1640 cm^{-1}, an N-H band in the region of 3400-3200 cm^{-1}, and a very weak absorption band was observed for -C≡CH at 2400 cm^{-1}. The weak absorption band for C≡C is usually not apparent by IR spectroscopy (DALE 1969). However, when there is a CH_2 group on one side of the triple bond, a relatively strong infrared band at 1325-1336 cm^{-1} is diagostic of this system (MANNION et al. 1961) and such a strong band was observed at 1325 cm^{-1}. The band was assigned to a CH_2 wagging, and its intensity was high, presumably due to the inductive effect of the C≡C bond. The proton NMR (D_6, DMSO) was consistent with structure IV showing resonances at 6.50 δ (4H, phenyl); 5.82 δ (4H phenyl); 5.20 δ (2H, N-H); 3.60 δ (2H, HC≡C-); 3.0 δ (4H, CH_2-C≡C). The mass spectrum indicated a molecular ion of M/Z = 288.

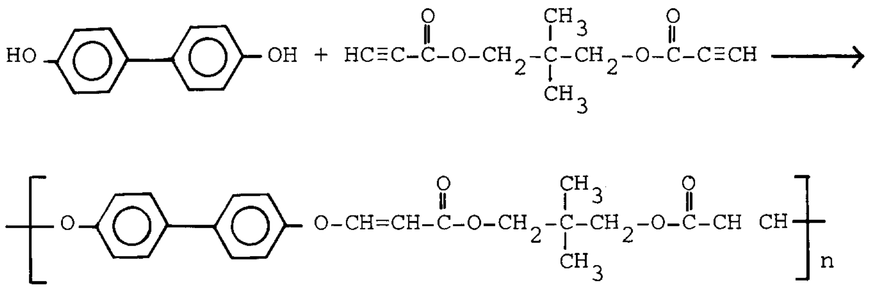
Polymer Synthesis and Characterizations:

The formation of polyether ketone is shown in Reaction Scheme 2.

REACTION SCHEME 2



In a similar fashion, Miller (MILLER 1956) has reported the base catalyzed addition of CH_3OH to the triple bond of phenylacetylene while Butler (BUTLER et al. 1965) prepared several polyesters by adding (1) polyols to acetylenic diesters, or (2) a dipropriolate to hydroquinone, yielding an alkenylester polyether of the type shown:



The reaction conditions (temperature range of -10° to 125°C, using an acidic or basic catalyst in an inert solvent) can be characterized as mild since the triple bonds are activated by the ester groups which facilitate the addition of phenolic groups across the triple bonds. As indicated in Reaction Scheme 2, there are no such activating groups attached to the triple bonds of IV, thus requiring the higher temperature conditions (see Experimental).

The low yield (48%) conceivably results from the tendency of N,N'-bispropargyl-4,4'-diaminobenzophenone to crosslink via polycyclotrimerization of the acetylene groups (KORSHAK 1974).

The polymer was characterized by elemental analysis and IR spectroscopy. The IR spectrum contained the characteristic ether linkage at 1180 cm^{-1} and, on the basis of elemental analysis (Table 1) and IR spectrum, the structure of the polymer is proposed to be that shown in the Reaction Scheme 2 (vide supra).

Polymer Properties:

The general characteristics of the polymer are given in Table 1.

The polymer is soluble in polar solvents (DMF, DMAC, NMP and THF) and in ketones (acetone, methylethylketone and cyclohexanone). The inherent viscosity data suggest that the molecular weight of the polymer is low.

The thermogravimetric analysis (TGA) data of the polymer is shown in Fig. 1 and shows that the polyether ketone undergoes only 6% weight loss at 300°C, the maximum weight loss occurring at 400°C and the degradation of the polymer in air appears to occur in a three-stage process.

TABLE 1

Physical characteristics and elemental analysis of polyether ketone

Property		Observed
Color		light yellow
Inherent viscosity[a]		0.30
Yield[b] %		48
Analysis[c],	% carbon	79.48 (79.06)
	% nitrogen	3.90 (5.40)
	% hydrogen	6.53 (6.20)

[a] Inherent viscosity was measured in 0.5% solution in THF at 28°C. [b] Yield is calculated based on N,N'-bispropargyl-4,4'-diaminobenzophenone. [c] Numbers in parentheses are theoretical values.

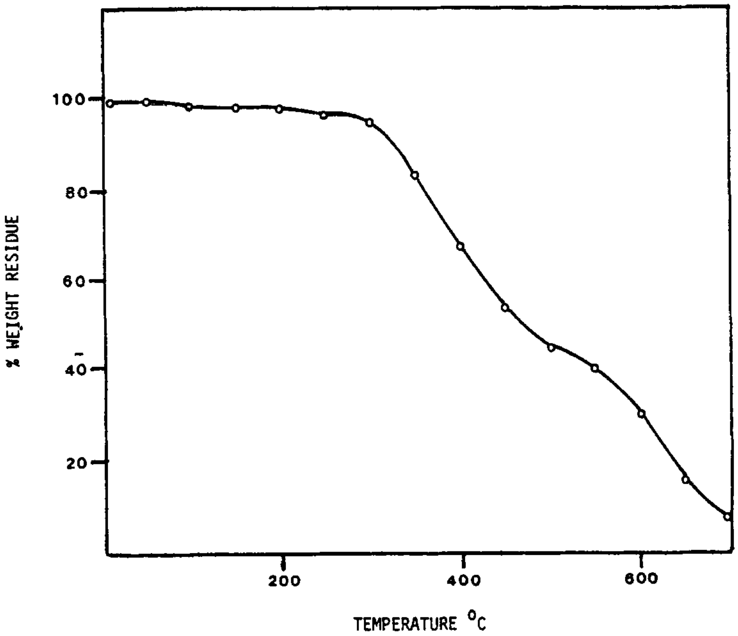


Fig. 1. Thermogravimetric analysis (TGA) of polyether ketone in air at heating rate 6°C/min

ACKNOWLEDGEMENT

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