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Ethynyl terminated bisquinazolone
A new thermosetting heat resistant resin

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SUMMARY

The reaction of -2(-4 ethynylphenyl)-4H-1,3 benzoxazin-4 one with bis-2,6(3-aminophenoxy pyridine leads to a soluble ethynylated bisquinazolone. The latter starts to polymerize at 150°C to yield a network which exhibits a Tg at 290°C. This network is stable in air up to 405°C.

Introduction

Ethynyl end-capped heterocycle oligomers have received considerable attention in recent years (1-3). The aim was to develop heat resistant thermosetting resins for structural applications such as matrixes, adhesives, and electronic applications planarizing coatings (4).

The cured resins display excellent resistance to solvents and high softening temperatures (> 300°C) (5). However, the polymerization of acetylenic fonctions starts at low temperature, and most acetylenic resins really do not melt before crosslinking, so that the processability window is very narrow.

The attractive high temperature dimensional stability of polyarylquinazolone is well known (6-7). Our purpose was to prepare a low melting point soluble bis acetylenic quinazolone and to examine the behavior of the corresponding crosslinked network after curing at moderate temperature. A recent patent (8), concerning the preparation of 2,6-diamino-phenoxypyridine prompted us to publish our results obtained with the diamine.

The acetylenic bisquinazolone was synthetized by condensation of 2-(4-ethynylphenyl) benzoxazinone 4, with bis 2-6(3-aminophenoxy)pyridine 7 prepared for the purpose.

The reaction of 4-bromobenzoylchloride 2 with isatoic anhydride 1 gave 2-(4-phenyl)benzoxazinone 3 which was condensed with trimethylsilylacetylene (TMSA) according to the standard procedure (9).

On the other hand, 3-aminophenol 5 was condensed with 2,6-dichloropyridine 6 in order to obtain the diamino ether 7

The sylilated acetylenic bis-quinazolone 8a was formed using a Yamazaki modified condensation (13) and free acetylenic groups were obtained by potassium carbonate in methanol leading to the free acetylenic compound 8b

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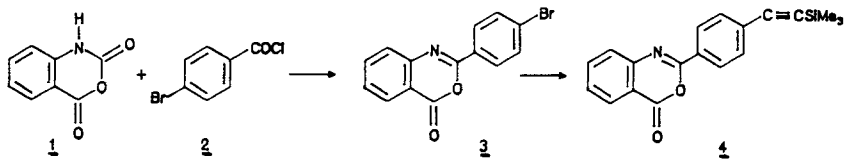

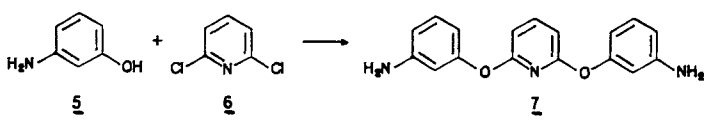

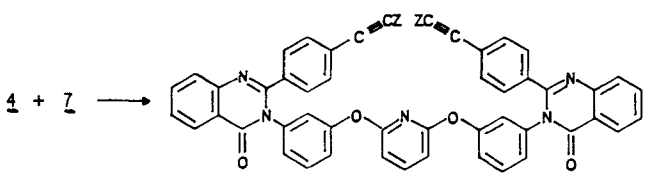

8a Z = $SiMe_3$
8b Z = H

EXPERIMENTAL

Solvents and starting materials

All the chemical reagents used to synthesize bisquinazolone were supplied by Janssen Chemicals. Isatoic anhydride was recrystallized from pyridine. Pyridine was distilled over KOH and kept on molecular sieve type 4 Å. The another solvents and reagents were used without further purification.

Physical methods

The following equipment was used :
. Perkin-Elmer 398 for infrared spectra recording (KBr disk)
. Brucker WP 80 spectrometer for ^1H NMR (with deuteriated chloroform as solvent and TMS or dioxan as internal reference).
. Du Pont 910 thermal analyzer for Differential Scanning Calorimetry (DSC)
. Mettler thermomechanical analyzer (TMA 40)
. Setaram thermobalance

Synthesis of 2-(4-bromophenyl)-4H-1,3 benzoxazin-4 one: 3

30.4 g (0.138 mole) of 4-bromobenzoylchloride was added dropwise to a solution of 22.6 g (0.138 mole) of isatoïc anhydride in 70 cc of pyridine at 80°C under argon (precipitation occured before the end of the addition). The reaction was continued for 1 hour at the same temperature, then cooled and kept at room temperature for 10 hours. The white crystalline precipited was filtered, washed twice with water and methanol and dried at 120°C (15 mm Hg) to give 38.1 g (91%) of pure product Mp 186°C (DSC, heating rate 2° K/min), (Lit. (10) Mp 184°C).

^{1}H NMR (in ppm from TMS): 7.2-7.85 (m, 5H), 7.92-8.22 (m, 3H).

I.R. (in cm^{-1}): 1760 (ν, C=O), 1620 (ν, C=N), 1060 (ν, C-O-C) (11).

Elem. anal. for $C_{14}H_8BrNO_2$

%	C	H	N	O	Br
Calc.	55,65	2,67	4,63	10,6	26,45
Found	55,6	2,7	4,7	10,66	26,35

Synthesis of 2-(4-(trimethylsilylethynyl)phenyl)-4H-1,3 benzoxazin-4 one: 4

15 g (0.05 mole) of 3 was dissolved in 150 cc of THF triethylamine mixture (70/30, v/v) at 67°C (the solvents were degassed). 7.36 g (0.075 mole) of trimethylsilylacetylene was added dropwise to the solution. At beginning of the addition of acetylene 0.225 g of bistriphenylphosphine palladium dichloride, 0.4 g of triphenylphosphine and 0.075 g of cuprous iodide were added. The temperature of the reaction mixture was maintained at 60°C for 8 hours. The solution was filtered to separate the triethylamine hydrobromide. After the solvent was removed under reduced pressure, 15.7 g of the crude product was collected. Recristallization from hexane gave a pale yellow powder (yield 75%), Mp 99°C.

^{1}H NMR (in ppm from TMS as external reference): 0.2 (s, 9H, Si-CH_3), 7,2-7,85 (m, 5H, aromatic), 7.92-8.22 (m, 3H, aromatic).

IR (in cm^{-1}): 2960 (ν, CH_3), 2150 (ν, C≡C-Si(CH_3)$_3$), 1760 (ν, C=O), 1610 (ν, C=N-).

Elem. anal. for $C_{19}H_{17}NO_2Si$

%	C	H	N	Si
Calc.	71.44	5.37	4.38	8.79
Found	71.15	5.38	4.46	8.3

Synthesis of bis-2.6 (3-aminophenoxy) pyridine: 7

A mixture of 29.6 g (0.2 mole) of 2.6 dichloropyridine, 45.8 g (0.42 mole) of 3-aminophenol and 62 g of K_2CO_3 was stirred in DMSO toluene (200/40 cc) at 135°C for 24 hours under argon, with water removal by azeotropic distillation. After toluene and a part of DMSO evaporation under reduced pressure, the reaction mixture was poured into basic water. The crude product was filtered, washed with water and dried to yield 55 g (94%). After double recrystallization in methanol and one treatment with charcoal, a white powder was isolated (Yield 65%) Mp 120°C.

^{1}H NMR (in ppm from TMS) 4.85 (s, 4H, NH_2) 6.35-6.8 (m, 8H, aromatic) 7.05-7.35 (m, 2H, aromatic phenyl) 7.8-8.1 (t, 1H, aromatic pyridine).

IR (in cm^{-1}): 3320-3440 (ν, NH_2).

Elem. anal. for $C_{17}H_{15}N_3O_2$

%	C	H	N	O
Calc.	69.62	5.16	14.32	10.9
Found	69.65	5.22	14.26	11.13

Synthesis of acetylene bisquinazolone: 8a, 8b

A mixture of 4 (7.2 g, 0.022 mole), diamine 7, (3.04 g, 0.01 mole), triphenylphosphite (5 g) and pyridine (40 ml) was heated under argon at 100°C for 10 hours. Most of the pyridine was removed by distillation at reduced pressure. The crude product was dissolved in methanol and a amount of water was added to initiate the precipitation of a pale yellow solid. After filtration, the solid was dried at 70°C for 12 hours (15 mm Hg). The trimethylsilyl group was removed using K_2CO_3 in methanol THF at room temperature (1 hour). The solution was then poured into methanol to precipitate a white solid. The solid was filtered and dried under vacuum for 12 hours. Compound 8b was isolated after treatment with charcoal and recrystallisation from hexane (Yield 75%).

^{1}H NMR (in ppm) 3.17 (s, 2H, C≡C-H), 6.4 (d, 2H) 7.02-8.12 (m, 23H aromatic (12), 8.57 (d, 2H).

IR (in cm^{-1}) 3285 (ν, ≡CH), 2100 (ν, C≡C), 1685 (ν, C=O).

RESULTS AND DISCUSSION

As previously observed (13), the condensation of acid chloride on isatoic anhydride is a convenient synthetic method to produce arylbenzoxazinone, and very high yields were obtained for the bromophenylbenzoxazinone 3 The substitution of an aromatic bromine by protected acetylene is well documented, but it is interesting to observe that the benzoxazinone ring is stable enough to support the basic medium needed for the reaction.

Concerning the preparation of the diaminophenoxypyridine 7, as expected (14), the pyridine ring enhances the reactivity of the halogen in positions 2 and 6, so that dichloropyridine can be used with a good yield for the nucleophilic substitution by the aminophenoxide ion.

Finally, the modified Yamazaki method described for the preparation of quinazolone (15) was used successfully to synthesize the ethynyl end-capped bisquinazolone 8a The ortho substitution on the quinazolone ring and the meta pyridylene ether linkage allow good solubility in many solvents as shown in Table 1.

Table 1: Solubility of acetylenic bisquinazolone at room temperature

Solvent	Weight %	T = 0	Time (days)		
			1	2	3
Chloroform	20	S	S	**	
Methanol		I			
Ethyl acetate	30	S	S	*	**
THF	20	S	S	S	S
Cyclohexane		I			
Acetonitrile	30	S	S	S	*
Toluene	20	S	S	S	S
Diglyme	30	S	S	S	S
DMF	50	S	S	S	S

**precipitated *onset of precipitation S = soluble I = insoluble

Analysis of the acetylenic bisquinazolone by DSC (Figure 1) showed a softening point at 90°C and two exotherms. The first strong exotherm with an onset at 150°C and a peak at 228°C was attributed to the polymerisation of the acetylene groups. The second, very weak, which appeared near 300°C with a peak at 320°C, was not identified.

The resin was cured for 2 h at 230°C and 1 h at 330°C under argon and analyzed by TMA with a scan rate of 10°C/min. The resin exhibited a first weak transition at 290°C, probably due to the Tg of quinazolone ether groups. A second transition occurring at a temperature above 350° was attributed to the deformation of the network.

A dynamic thermal gravimetric analysis (TGA) curve is shown in Figure 2. In air or nitrogen, the values obtained were the same with the initial weight loss at 405°C and 10% weight loss occurring at 517°C. The isothermal aging of the cured resin was checked at 280°C and 350°C. At 280°C, the resin only losts 0.8% of initial weight after 100 hours. On the other hand, the Tg value remains nearly constant. For an aging temperature (T = 350°C) higher than the Tg of the cured resin, the sample exhibited a weight loss of 2% in 9 hours and 5% in 40 hours

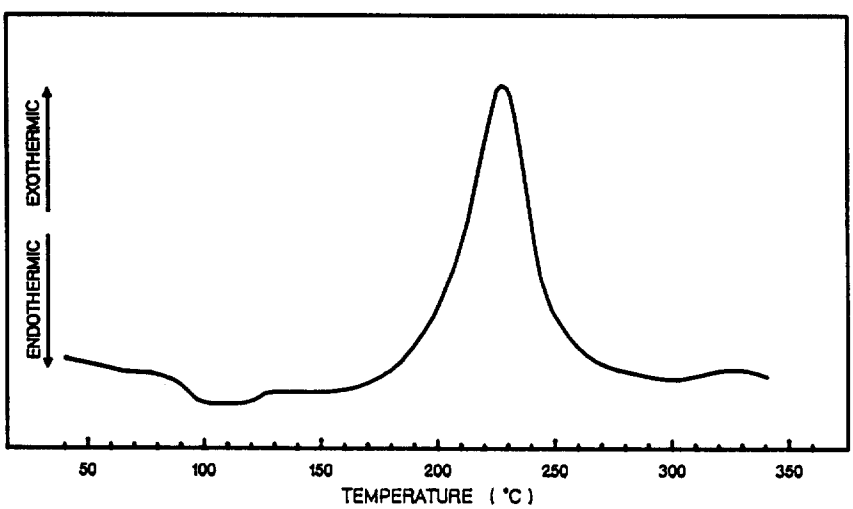

FIGURE 1 : DSC thermogram of bisquinazolone 8b (scan rate 10°C/min, under argon)

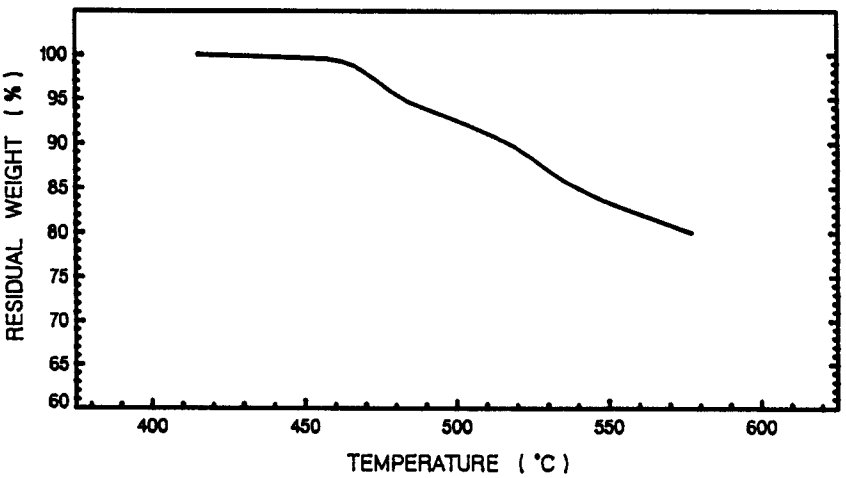

FIGURE 2 : Thermogravimetric analysis curve of bisquinazolone 8b (heating rate 10°C/min under air)

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