Polym. Bull. (2009) 63:509–515
DOI 10.1007/s00289-009-0118-z

ORIGINAL PAPER

Poly(dibenzodiazocine)s: analysis of low molecular weight fractions by MALDI-TOF MS

**Charles Hoppin · Robert B. Bates ·
Cristina G. Contreras · Arpad Somogyi ·
Matthew J. Streeter · H. K. Hall Jr.**

Received: 23 February 2009 / Revised: 27 May 2009 / Accepted: 15 June 2009 /

Abstract Poly(dibenzodiazocine)s, members of a new class of polyimines with high thermal stability and solubility in organic solvents, were synthesized from 2-amino-4′-fluorobenzophenone and three bisphenols. The high molecular weight polymers were shown by MALDI-TOF mass spectra to be accompanied by low molecular weight linear oligomers with the expected end group combinations and low molecular weight cyclic oligomers. The yields of the smaller cyclics were raised using a pseudo-dilution polymerization method.

Keywords Polyimines · MALDI-TOF mass spectra · Synthesis

Introduction

Polyimines are an important class of polymers whose high thermal stability and optoelectronic properties make them attractive for a wide variety of applications [1–5]. Preparation of polyaromatic quinone imines by a polycondensation method was reported by Hall et al. [6, 7] using anthraquinone and aromatic diamines. The high molecular weight fractions were accompanied by low-molecular weight fractions that appeared to contain significant amounts of macrocyclic oligomers based on the lack of detectable end groups. More recently, Yamamoto revisited these macrocyclic aromatic imines as potential redox-driven molecular machines (“electric cyclophanes”) [8].

Poly(dibenzodiazocine)s (**4**) are a new class of polyimines (polyketanils) that have attractive properties, such as high T_g (280–300 °C), high thermal stability

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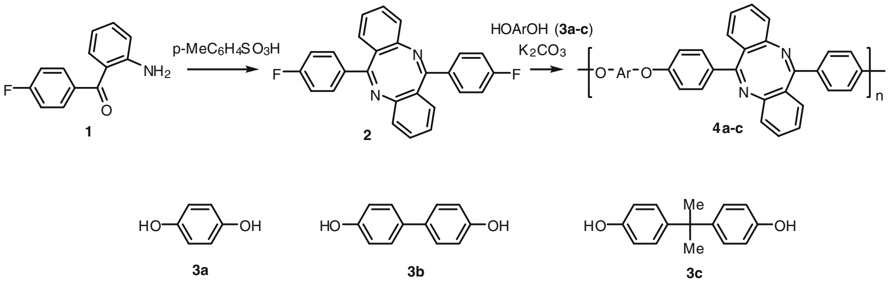
C. Hoppin
Solvay Advanced Polymers, LLC, 4500 McGinnis Ferry Road, Alpharetta, GA 30005, USA

R. B. Bates · C. G. Contreras · A. Somogyi · M. J. Streeter · H. K. Hall Jr. (✉)
Chemistry Department, University of Arizona, Tucson, AZ 85721, USA
e-mail: hkh@u.arizona.edu

($T_d^5 \sim 500$ °C) and solubility in common organic solvents, that make them potentially suitable for a variety of high-temperature electronics and other applications [9]. The tub-shaped eight-membered rings in both the monomer and polymer have recently been shown by Suga and Long [10] to undergo reversible *n*-type redox reactions under anaerobic conditions to form what is believed to be planar aromatic annulenes. This tub-planar interconversion makes this system a candidate for redox-driven flexing devices. The diazocine ring could also potentially form interesting metal coordination complexes or be incorporated into conducting polymer systems.



Results and discussion

The poly(dibenzodiazocine)s for this study (**4a-c**) were made from 6,12-bis(4-fluorophenyl)dibenzo[b,f][1,5]diazocine (**2**, prepared from 2-amino-4′-fluorobenzophenone, **1**), a bisphenol (hydroquinone, HQ, **3a**; biphenol, BP, **3b**; or bisphenol A, BA, **3c**), and potassium carbonate. Methyl chloride was added to end cap phenols in all but one case. Using a "traditional" polycondensation method, both monomers were added at the beginning of the reaction and the total monomer concentration in the solvent, dimethylacetamide, was 20% w/v. All three high-molecular weight polymers were amorphous; their molecular weights (GPC) and glass transition temperatures (T_g, DSC) are given in Table 1.

Formation of macrocycles during such stepwise condensation polymerizations is well known [11–16]. Colquhoun and Hodge found that the amount of macrocyclic oligomers increases as the monomer concentration decreases during the preparation of polyphenyl ether sulfones (e.g., Radel R®) using a similar potassium carbonate-based polycondensation method [17]. They also used a "pseudo-dilution" method to prepare higher amounts of macrocyclic oligomers [18]. We used MALDI-TOF mass spectra [19] to semi-quantitatively determine the relative amounts of cyclic diazocine aryl ether oligomers formed under both traditional polycondensation and Colquhoun–Hodge "pseudo-dilution" conditions.

The main peaks in all the mass spectra came from protonation of expected products. Protonated cyclic monomers (designated BD, from one of the three bisphenols **4a–c** and diazocine **2**) were not observed because they would be too

Table 1 Molecular weights and glass transition temperatures of polymers prepared in this study

Polymer	Bisphenol	Method	M_w/1,000[a]	T_g (°C)[b]	CH$_3$Cl end cap
4a	HQ (**3a**)	Traditional	67	298	Y
		Dilute	2.7	232	Y
4b	BP (**3b**)	Traditional	30	297	Y
		Dilute	3.7	227	Y
		Dilute	3.7	234	N
4c	BA (**3c**)	Traditional	38	260	Y
		Dilute	3.6	217	Y

[a] GPC, relative to polystyrene standards

[b] DSC, 2nd heat

strained, but the largest peak in each spectrum was due to the protonated cyclic dimer (B_2D_2).

Figure 1 shows a section of the mass spectrum of the polymer **4b** (dilute, methyl chloride cap) and Table 2 shows the calculated and observed masses of the cations from cyclic and linear trimers in Fig. 1. The relative amounts of cyclics decreased rapidly with increasing molecular weight (Fig. 1), while the protonated linear species (designated in Fig. 1 by their end groups) decreased much more slowly.

Table 3 summarizes the results from the MALDI-TOF mass spectra. These results are only semiquantitative, since some molecules ionize much better than others and low molecular weight species show better than high molecular weight ones. The amounts of compounds come from the intensities of the peaks of their protonated ions.

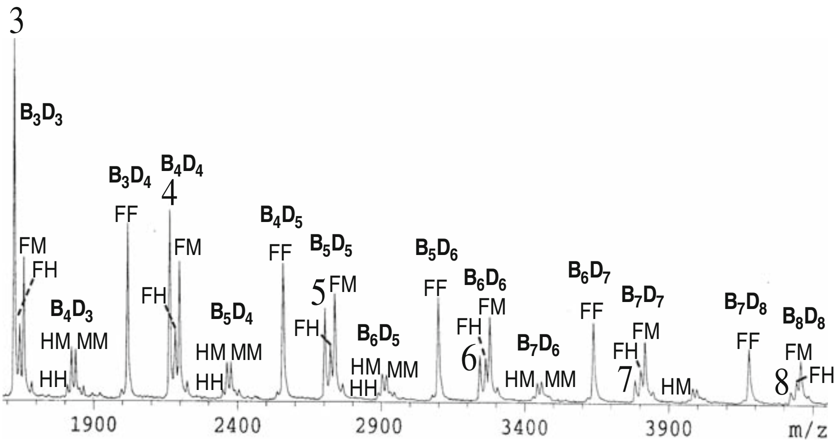


Fig. 1 1,600–4,450 *m/z* range of the MALDI-TOF mass spectrum of products **4b** from polymerization of diazocine **2** with biphenol **3b** under dilute conditions with MeCl as end-capping agent. *Numbers 3–8* refer to peaks from protonation of cyclic trimer through cyclic octamer; *B* biphenol unit, *D* diazocine unit. End groups on linear oligomers: *F* fluorine, *H* OH, *M* OMe

Table 2 Calculated and observed masses of the oligomers from mass 1,600–2,100 in Fig. 1

Symbol	Composition		Calculation	Cation	Mass	
					CALCD	OBSD
B_3D_3	Cyclic	B_3D_3	$B_3D_3 + H^+$	$C_{114}H_{73}N_6O_6{}^+$	1,621.6	1,621.9
FH	Linear		$B_3D_3 + HF + H^+$	$C_{114}H_{74}N_6O_6F^+$	1,641.6	1,641.9
FM			$B_3D_3 + HF + CH_2 + H^+$	$C_{115}H_{76}N_6O_6F^+$	1,655.6	1,656.0
HH		B_4D_3	$B_3D_3 + \mathbf{3b} + H^+$	$C_{126}H_{83}N_6O_8{}^+$	1,807.6	1,808.1
HM			$B_3D_3 + \mathbf{3b} + CH_2 + H^+$	$C_{127}H_{85}N_6O_8{}^+$	1,821.6	1,822.1
MM			$B_3D_3 + \mathbf{3b} + 2CH_2 + H^+$	$C_{128}H_{87}N_6O_8{}^+$	1,835.7	1,836.3
FF		B_3D_4	$B_3D_3 + \mathbf{2} + H^+$	$C_{140}H_{89}N_8O_6F_2{}^+$	2,015.7	2,016.5

Table 3 Percentages of cyclics and end groups of linear species from MALDI-TOF mass spectra

Polymer	Method	% of cyclics					% of linear ends						% end types		
		2	3	4	5	6	HH	HF	FF	HM	FM	MM	H	F	M
4a	Traditional	25	22	17	12	8	0	20	75	0	5	0	10	85	5
	Dilute	30	24	17	12	7	12	0	0	42	0	46	33	0	67
4b	Traditional	38	27	17	8	4	23	22	11	26	11	7	47	28	25
	Dilute	62	18	9	5	3	2	13	35	12	26	11	15	55	30
	Dilute[a]	57	25	11	5	2	25	37	38	–	–	–	44	56	–
4c	Traditional	27	27	21	12	7	41	24	0	31	2	2	69	13	18
	Dilute	41	30	15	7	4	18	38	38	4	2	0	39	58	3

Percentages of cyclic dimers (2) through hexamers (6) out of the total cyclics are given

H phenolic end group, *F* fluorine end group, *M* methoxyl end group. See text for details

[a] Uncapped by MeCl

The "% of cyclics" column gives the percentages of the smallest five cyclics out of the total cyclics (which were observed out as far as $B_{18}D_{18}$ for the traditional hydroquinone (**4a**) polymerization). As expected, the more dilute polymerizations gave more of the smaller cyclics than did the traditional polymerizations.

The last columns in Table 3 show the relative amounts of various end groups in the linear oligomers. The percentages are based on all the linear oligomers which were seen (out to M_w 16,000 in one case). The last column shows that end capping of the phenols with methyl chloride was far from complete, with the highest methylation to only 67%. The relative amounts of the three end groups varied greatly, probably due to variations in the stoichiometry, reaction completeness, and degree of polymerization. Small peaks 14 and 28 mass units higher than MM peaks may be due to one or two C-methylations on positions ortho to OH followed by O-methylations.

Future studies will focus on the effects of different bases and solvents used during polymerization on cyclic formation as well as ring-opening polymerizations on the high-cyclic containing oligomers.

Experimental

General

Polymerization-grade bisphenols **3a–c** were oven-dried before use. 2-Amino-4′-fluorobenzophenone (**1**) purchased from Unibest (China) was found to be 99.5% GC area purity with 0.2% of 2-aminobenzophenone and was used without purification. Potassium carbonate was purchased from Fisher Scientific, ground to <100 microns, and dried in a vacuum oven at 120 °C. Dimethylacetamide, toluene, mixed xylenes, and *p*-toluenesulfonic acid-hydrate were supplied by Fisher Scientific and stored under nitrogen.

Mass spectra were run on a Bruker Reflex III MALDI-TOF instrument in linear low power mode at a wavelength of 337 (N_2 laser, attenuation 28%). The dithranol matrix and analyte were dissolved in dichloromethane in a ratio of about 50:1.

6,12-Bis(4-fluorophenyl)dibenzo[b,f][1,5]diazocine (2)

In a 1 L four-neck round-bottom flask fitted with a Dean-Stark trap, condenser, and overhead stirrer with a PTFE blade were placed 2-amino-4′-fluorobenzophenone (**1**, 200 g, 0.93 mole), *p*-toluenesulfonic acid-hydrate (8.9 g, 0.047 mole), and mixed xylenes (200 mL). The mixture was stirred under nitrogen and warmed to reflux for 7 h while collecting water. The dark mixture was cooled to 90 °C and poured slowly into methanol (3 L) with rapid stirring. The slurry was allowed to stand overnight and the solid isolated by filtration, washed 4 times with methanol, and soaked in methanol (500 mL) at 50 °C for 3 h. The solid was isolated by filtration, washed with fresh methanol (3×), recrystallized from CH_2Cl_2/methanol, and dried in a vacuum oven to afford 153 g (82% yield) of **2** as a yellow crystalline solid. GC/MS: 99.6% ($m/z = 394$), 0.25% ($m/z = 376$, monofluorodibenzodiazocine). T_m (DSC) = 196 °C. IR (ATR): 1,622 (C=N), 960, 935 cm^{-1}.

Traditional polycondensation method (illustrated with biphenol, 3b)

In a four-neck, 500 mL round-bottom flask fitted with an overhead stirrer, Dean-Stark trap, and condenser, were placed biphenol (**3b**, 11.56 g, 0.06208 moles), 6,12-bis(4-fluorophenyl)dibenzo[b,f][1,5]diazocine (**2**, 24.00 g, 0.06085 moles), anhydrous potassium carbonate (9.01 g, 0.0652 moles), DMAc (180 mL), and toluene (50 mL). The mixture was stirred and warmed to reflux (143–145 °C) using an oil bath. After 5 h, the trap was drained and the remaining toluene removed by distillation. The mixture was heated at 160–162 °C for an additional 16 h. The viscous mixture was cooled to 120 °C and methyl chloride (10 g) was slowly bubbled in with stirring over 15 min. After purging the reaction vessel with nitrogen and cooling to 40–50 °C, the mixture was diluted with dimethylacetamide (100 mL) and filtered through a 2.7 μm glass-fiber filter. The clear filtrate was added slowly to methanol (1.5 L) with rapid stirring to precipitate the polymer as a porous solid. The solid was washed extensively with methanol and dried in a vacuum oven overnight. Yields of polymer **4b** were near quantitative. The glass transition temperature (T_g) determined by a standard DSC method was 297 °C (2nd heat).

Pseudo-dilution method (illustrated with biphenol, 3b; after Ref. [18])

In a four-neck, 500 mL round-bottom flask purged with nitrogen and fitted with overhead stirrer, constant pressure addition funnel, Dean-Stark trap, and condenser, were placed DMAc (200 mL), toluene (50 mL) and potassium carbonate (1.40 g, 10.1 mmol). The slurry was stirred and warmed to reflux for 20 min while filling the trap. A solution containing 6,12-bis(4-fluorophenyl)dibenzo[b,f][1,5]diazocine (**2**, 3.94 g, 10.0 mmol) biphenol (**3b**, 1.86 g, 10.0 mmol) in DMAc (90 mL) was added dropwise to the refluxing reactor contents over 4–5 h. The mixture was stirred an additional 2 h at 155 °C, cooled to 120 °C, methyl chloride (3 g) was added over 10 min, cooled to room temperature, filtered through a 2.7 μm glass-fiber filter, and the filtrate poured into methanol (500 mL) with stirring to precipitate the polymer. The solid was isolated by filtration and washed with methanol several times before drying in a vacuum oven for several hours to afford 4.6 g of polymer **4b** as a porous, pale-yellow solid with T_g (DSC, 2nd heat) 234 °C.

References

1. Iwan A, Sek D (2008) Processible polyazomethines and polyketanils: from aerospace to light-emitting diodes and other advanced applications. Prog Polym Sci 33:289–345
2. Miyake J, Chugo Y (2008) The Aza-Wittig polymerization: an efficient method for the construction of carbon–nitrogen double bond-containing polymers. Macromolecules 41:5671–5673
3. Yang C-J, Jenekhe SA (1995) Conjugated aromatic polyimines. 2. Synthesis, structure, and properties of new aromatic polyazomethines. Macromolecules 28:1180–1196
4. Marvel CS, Hill YWJ (1950) Polyazines. Am Chem Soc 72:4819–4820
5. Hedrick JL, Labadie JW, Russell TP (1991) Imide-aryl ether phenylquinoxaline block copolymers. Macromolecules 24:4559–4566
6. Williams PA, Ellzey KA, Padias AB, Hall HK (1993) New polyaromatic quinone imines from anthraquinone. Macromolecules 26:5820–5821
7. Hall HK, Padias AB, Williams PA, Goasau J-M, Boone HW, Park D-K (1995) Novel polyaromatic quinone imines. Macromolecules 28:1–8
8. Kanazawa H, Higushi M, Yamamoto KJ (2005) An electric cyclophane: cavity control based on the rotation of a paraphenylene by redox switching. Am Chem Soc 17:16404–16405
9. Lee VJ, Wang L-S (2007) Compounds and methods to inhibit or augment an inflammatory response. US Patent 7238711, 3 July 2007
10. Suga T, Long T (2008) Synthesis of photosensitive poly(arylene imide sulfone)s. Polym Prepr 49:388–389
11. Hall AJ, Hodge P (1999) Recent research on the synthesis and applications of cyclic oligomers. React Funct Polym 41:133
12. Hodge P, Colquhoun HM (2005) Recent work on entropically-driven ring-opening polymerizations: some potential applications. Polym Adv Technol 16:84

13. Kricheldorf HR, Schwarz G (2003) Cyclic polymers by kinetically controlled step-growth polymerization. Macromol Rapid Commun 24:359–381
14. Kricheldorf HR, Schwarz GJ (2007) Cyclic and multicyclic poly(ether sulfone)s by polycondensation of 5,5′,6,6′-tetrahydroxy-3,3,3′,3′-tetramethylspirobisindane and 4,4′-difluorodiphenylsulfone. Polym Sci Part A Polym Chem 45:5597–5605
15. Kricheldorf HR, Böhme S, Schwarz G (2006) Competing cyclization and chain growth in tert-amine-catalyzed polycondensations of bisphenol A with bisphenol A bischloroformate. Macromolecules 39:3210–3216
16. Brunelle DJJ (2008) Cyclic oligomer chemistry. Polym Sci Part A Polym Chem 46:1151–1164
17. Ben-Haida A, Colquoun HM, Hodge P, Stanford JL (2005) A novel approach to processing high-performance polymers that exploits entropically driven ring-opening polymerization. Macromol Rapid Commun 26:1377–1382
18. Colquhoun HM, Lewis DF, Hodge P, Ben-Haida A, Williams DJ, Baxter I (2002) Ring–chain interconversion in high-performance polymer systems. 1. [Poly(oxy-4,4′-biphenyleneoxy-1,4-phenylenesulfonyl-1,4-phenylene)] (Radel-R). Macromolecules 35:6875
19. Somogyi A, Elandaloussi EH, Hall DE, Padias AB, Bates RB, Hall HK Jr (2007) Powerfully solvating matrices for MALDI-TOF spectroscopy of aromatic polyesters. Macromolecules 40:5311–5321