Poly(p-Benzoquinono)Diimidazoles from Two-Ring Aromatic Dicarboxylic Acids

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Synopsis

New poly(p-benzoquinono)diimidazoles have been synthesized by one-stage polycondensation in polyphosphoric acid of 2,3,5,6-tetraamino-p-benzoquinone with diphenyl-4,4'-dicarboxylic acid, diphenylmethane-4,4'-dicarboxylic acid, 4,4'-oxydibenzoic acid, and 4,4'-sulfonyldibenzoic acid. The polymers were characterized by infrared and ultraviolet spectral study, viscometric measurements, and thermal analysis. The effects of introducing flexibilizing links such as —CH$_2$—, —O—, and —SO$_2$— in the backbone of the polymers, on their thermal stability and solubility were studied.

INTRODUCTION

In our previous work[1,2] we reported the preparation of poly(p-benzoquinono)diimidazoles of phenylene[1] and aliphatic[2] dicarboxylic acids by thermal polycyclodehydration of the corresponding poly(amino-p-benzoquinone)amides, in an effort to obtain new redox thermally stable polymers. The prepared polymers showed good thermal stability which could undergo reversible reduction-oxidation reactions, but were compeltely insoluble in organic solvents and strong acids. It was found[2] that the presence of a flexible aliphatic chain in the main chain of the polymer decreased the thermal stability of the corresponding poly(p-benzoquinono)diimidazoles and did not affect the solubility of them, but it facilitated the thermal cyclodehydration of their precursors poly(amino-p-benzoquinone)amides, which occurred more easily (maximum rate at 280°C) than that of the corresponding aromatic ones (maximum rate at 380–405°C, accompanied by decomposition). It was thought that the use of two-ring aromatic dicarboxylic acids containing flexible linking units such as —CH$_2$—, —O—, —SO$_2$— might allow the preparation under mild conditions of poly(p-benzoquinono)diimidazoles with as much aromaticity as possible to preserve thermal stability but with decreased rigidity of the chain and degree of crosslinking, and therefore, with some solubility in organic solvents and strong acids. It must be mentioned here that work on polybenzimidazoles had indicated that when methylene, ether, or sulfone groups were incorporated into the main chain by the use of m-phenylenediacetic acid[3] or 3,3',4,4'-tetra-aminobiphenyl ether or sulfonyl,[4,5] the solubility of the polymer was increased.

This paper is concerned with the preparation of polymers **IIa–e** (Scheme 1) by one-stage polycondensation reaction in polyphosphoric acid at

200°C of 2,3,5,6-tetraamino-1,4-benzoquinone (TABQ) with dicarboxylic acids **Ia–e**.
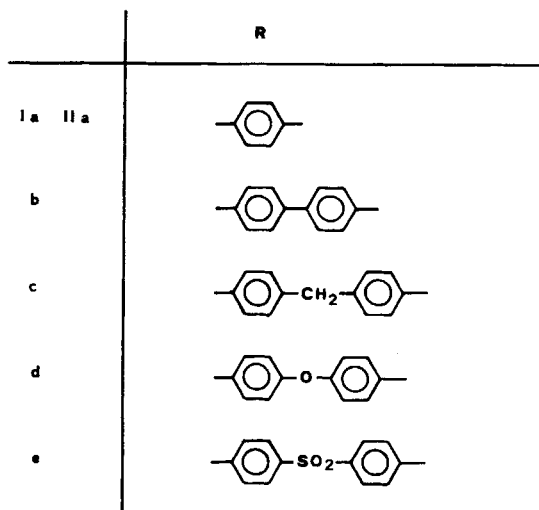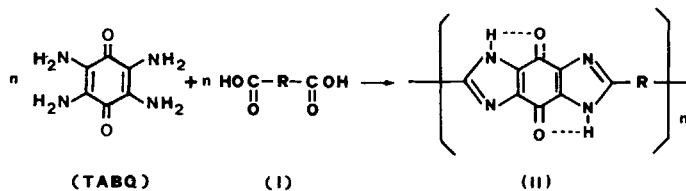
Poly(p-benzoquinono)diimidazole of diphenyl-4,4'-dicarboxylic acid and terephthalic acid, although the preparation of the latter has been reported earlier,[1] were synthesized under identical conditions with other polymers for the comparative study.

EXPERIMENTAL

Materials

2,3,5,6-Tetraamino-p-benzoquinone (TABQ), was synthesized and purified as described earlier.[1] Terephthalic acid (**Ia**) (Fluka AG) was recrystallized twice from methanol, while diphenyl-4,4'-dicarboxylic acid, diphenylmethane-4,4'-dicarboxylic acid, 4,4'-oxydibenzoic acid, and 4,4'-sulfonyldibenzoic acid (**Ib–e**) (K&K Laboratories) were used as received. Polyphosphoric acid (PPA) (Fluka AG, P_2O_5 content 84%) was used as received.

MEASUREMENTS

Infrared (IR) spectra were recorded on a Perkin-Elmer 281-B spectrophotometer in KBr pellets. Ultraviolet (UV) spectra were recorded on a PYE

UNICAM SP 8000 spectrophotometer using concentrated sulfuric acid as the solvent. Elemental analyses were performed with a Perkin-Elmer model No. 240 analyzer.

The solubility measurements were carried out at ambient temperature. A 0.02 g portion of the polymer was placed in 10 mL of the desired solvent (DMF, DMAc, DMSO, ethylene glycol, formic acid, methanesulfonic acid, and concentrated sulfuric acid) and the mixture was stirred for 10 hr. The reductive solubilization of the polymers was carried out according to the literature.[6] Polymer inherent viscosities were measured in formic acid solutions, prepared as described earlier,[7] in an Ubbelohde viscometer at 25°C.

The thermal stability of the prepared polymers was studied on a Perkin-Elmer TGS-2 Thermobalance (ΔT = 5°C/min). Polymer samples of 5 ± 2 mg were taken for each experiment and heated at 200°C for 10 min before carrying out the runs, because it was observed that the samples lost 7–9% of their weight during heating up to 200°C, regain their former weight during cooling to 50°C under dried nitrogen atmosphere. This increase of weight on cooling could be attributed to the absorbance of nitrogen by the samples. Differential scanning calorimetry (DCS) was performed on a Perkin-Elmer DSC-2.

POLYMERIZATIONS

Poly[(1,4,5,8-tetrahydro-4,8-dioxobenzo[2,3-d:5,6-d′] diimidazole-2,6-diyl)-1,4-phenylene]
(IIa)

TABQ (1.68 g, 0.010 mole) was dissolved in 167 g PPA and Ia (1.66 g, 0.010 mole) was added to the solution (50°C) and allowed to react under nitrogen for 3 hr at 200°C. The polymer was precipitated with water, collected, added, and remained overnight in 5% aqueous ammonium carbonate solution, stirred for 2 hr in 5% aqueous potassium hydroxide and washed thoroughly with water. Extracted in a Soxhlet extractor for 1 day with ethanol and dried under vacuum (150°C/0.1 mmHg). It gave 2.20 g (84% yield) of a brown powder with an inherent viscosity 1.4 dL/g (c = 0.08%). IR (KBr): 3400 (br NH), 1650 (C=O), 1630, 1600 (C=N, C=C), 1425, 1500, 1250, 1170, 1100, 1070 (br), 950, 750 (trisubst. imidazole ring) and 850 (p-subst.) cm^{-1}. UV (H$_2$SO$_4$): λ_{max} 260 and 310 nm.

Anal. calcd. for (C$_{14}$H$_6$N$_4$O$_2$)$_n$: C, 64.12%; H, 2.31%, N, 21.36%. Found: 63.17%; H, 2.45%; N, 19.23%.

All the polymerizations below were carried out as described above.

Poly[(1,4,5,8-tetrahydro-4,8-dioxobenzo[2,3-d:5,6-d′] diimidazole-2,6-diyl)-4,4′-biphenylene]
(IIb)

Polycondensation of TABQ (1.68 g, 0.010 mole) and Ib (2.42 g, 0.010 mole) in 200 g PPA gave 2.70 g (80% yield) of a black powder with an inherent viscosity 1.22 dL/g (c = 0.07%). IR (KBr): 3400 (br NH), 1650 (C=O), 1630,

1600 (C=N, C=C), 1510, 1400, 1240, 1180, 1070 (br), 950, 730 (imidazole ring) and 830 (p-subst.) cm^{-1}. UV (H$_2$SO$_4$): λ_{max} 262 and 318 nm.

Anal. calcd. for (C$_{20}$H$_{10}$N$_4$O$_2$)$_n$: C, 71.00%; H, 2.98%; N, 16.56%. Found: C, 70.12%; H, 3.17%; N, 15.23%.

Poly[(1,4,5,8-tetrahydro-4,8-dioxobenzo[2,3-d:5,6-d'] diimidazole-2,6-diyl)4,4'-methylenebiphenylene] (IIc)

Polycondensation of TABQ (0.84 g, 0.005 mole) with **Ic** (1.28 g, 0.005 mole) in 100 g PPA, gave 1.70 g (97% yield) of a brown powder with an inherent viscosity 2.10 dL/g (c = 0.16%). IR (KBr): 3400 (br NH), 2920, 2860 (CH$_2$), 1660 (C=O), 1630, 1610 (C=N, C=C), 1520, 1410, 1250, 1180, 1080 (br), 950, 710 (imidazole ring) and 855 (p-subst.) cm^{-1}. UV (H$_2$SO$_4$): λ_{max} 260, 307 nm.

Anal. calcd. for (C$_{21}$H$_{12}$N$_4$O$_2$)$_n$: C, 71.58%; H, 3.43%; N, 15.90%. Found: C, 71.12%; H, 3.46%; N, 15.64%.

Poly[(1,4,8-tetrahydro-4,8-dioxobenzo[2,3-d:5,6-d'] diimidazole-2,6-diyl)-4,4'-oxybiphenylene] (IId)

Polycondensation of TABQ (1.68 g, 0.010 mole) with **Id** (2.58 g, 0.010 mole) in 213 g PPA gave 3.04 g (86%) of a brown powder with an inherent viscosity 1.84 dL/g (c = 0.2%). IR (KBr): 3400 (br NH), 1600 (C=O), 1625, 1595 (C=N, C=C), 1410, 1230 (attributable and to —O—), 1170, 1075, 960, 730 (imidazole ring) and 835 (p-subst.) cm^{-1}. UV (H$_2$SO$_4$): λ_{max} 263, 313 nm.

Anal. calcd. for (C$_{20}$H$_{10}$N$_4$O$_3$)$_n$: C, 67.79%; H, 2.84%; N, 15.81%. Found: C, 67.22%; H, 2.93%; N, 15.68%.

Poly[(1,4,5,8-tetrahydro-4,8-dioxobenzo[2,3-d:5,6-d'] diimidazole-2,6-diyl)-4,4'-sulfonylbiphenylene] (IIe)

Polycondensation of TABQ (1.68 g, 0.010 mole) with **Ie** (3.06 g, 0.010 mole) in 237 g PPA gave 3.42 g (85%) of a brown powder with inherent viscosity 1.66 dL/g (c = 0.2%). IR (KBr): 3400 (br NH), 1650 (C=O), 1630, 1595 (C=N, C=C), 1370, 1130 (—SO$_2$—), 1410, 1230, 1160, 1070, 940, 730 (imidazole ring) and 835 (p-subst.) cm^{-1}. UV (H$_2$SO$_4$): λ_{max} 263, 313 nm.

Anal. calcd. for (C$_{20}$H$_{10}$N$_4$O$_4$S): C, 59.70%; H, 2.50%; N, 13.92%. Found: C, 59.62%; H, 2.58%; N, 13.14%.

## RESULTS AND DISCUSSION

Poly(p-benzoquinono)diimidazoles (**IIa-e**) were prepared as amorphous powders in good yields by one-stage polycondensation of equimolecular amounts of the corresponding monomers in PPA at 200°C. Excess of dicarboxylic acid was avoided, although it was reported that 1% excess of dicarboxylic acid[3] or 1–5% of dianhydride,[8] when commercial monomers were

used, gave correspondingly polybenzimidazoles[3] or polyimides[8] with higher inherent viscosity, in order to decrease the possibility of crosslinking during polycondensation. The monomers were added into PPA at 50°C, because it has been observed[7] that TABQ is self-condensated during heating in PPA above 60°C.

More consistent with the expected chemical structure, experimental values of percentage content of polymers **IIc–e** compared to those of **IIa, b** indicate a higher cyclization degree of the former polymers which must be due to the greater flexibility of the main chain, due to the presence of "flex points" such as —CH_2—, —O—, or —SO_2— groups. Absorptions characteristic of substituted imidazole ring were clearly shown in IR spectra of the polymers but these could not be used as proof of the absence of some uncyclized amides linkages, because of the common absorption band of carbonyl quinone and amide I at 1650 cm^{-1} and of —NH— of imidazole ring and amide II at 1500 cm^{-1}. The slight bathochromic shift in the λ_{max} of polymers **IIb, d, e** must be due to the more dipolar excited stages possible for these polymers.

For the study of the solubility behavior of the polymers, the solubility parameters (*p*) were calculated by Fedors' method,[9] which requires knowing only the structural formula and not the density of the polymers. A representative sample calculation of solubility parameter is given below for polymer **IIb**.
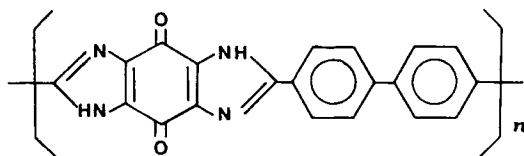
(II b)

Considering Fedors' table of atomic and group contribution to the energy of evaporation (ΔEv) and molar volume (V) Tables I and II for both ΔEv and V of trisubstituted imidazole ring and polymer **IIb** have been set up.

Hence, the solubility parameter of polymer **IIb** is:

$$p = (41.690/199.6)^{1/2} = 14.45(cal/cm^3)^{1/2}$$

TABLE I
Estimation of ΔEv and V of Trisubstituted Imidazole Ring

Group	$\Delta e_i{}^a$ (cal/mole)	$\Delta v_i{}^a$ (cm^3/mole)
NH	2000	4.5
—N=	2800	5.0
3C=	$3 \times 1030 = 3090$	$3 \times (-5.5) = -16.5$
2 Conjugated double bonds	$2 \times \ \ 400 = \ \ 800$	$2 \times (-2.2) = \ \ -4.4$
Ring closure 5 atoms	250	16
Trisubstituted imidazole ring	8940	4.6

^{a} Where Δe_i and Δv_i are the additive atomic and group contribution for the energy of evaporation and molar volume.

TABLE II
Estimation of ΔEv and V of Polymer IIb

Group[a]	Δe_i (cal/mole)	Δv_i (cm³/mole)
2 imidazole ring (trisubst.)	$2 \times 8940 = 17,880$	$2 \times 4.6 = \quad 9.2$
2 C=O	$2 \times 4150 = \quad 8300$	$2 \times 10.8 = \quad 21.6$
Ring closure 6 atoms	250	16
2 Phenylene (p)	$2 \times 7630 = 15,260$	$2 \times 52.4 = 104.8$
		repeat unit = 48[b]
Polymer IIb	41690	199.6

[a] The contribution of the conjugation in the quinone ring to the ΔEv and V of polymer, was not taken into account, but the deviation from the estimated value of p caused by this ommission should be low because of the low resonance energy (5 kcal)[10] of p-benzoquinone ring.

[b] This is the correction factor for molar volume of polymer which is equal to the double number of main chain skeletal atoms in the smallest repeating unit of the polymer.

In Table III are listed the calculated values of solubility parameters of polymers IIa–e. The contribution of —SO$_2$— group to energy evaporation and molar volume of polymer IIe was taken[11] equal to $\Delta e_i = 2200$ cal/mole and $\Delta v_i = 23.6$ cm³/mole.

Polymers IIa–e were completely insoluble in DMAc, DMF, and DMSO, which are known solvents for polybenzimidazoles and also in ethylene glycol, although it is a solvent for which the solubility parameter, calculated by Fedors' method (14.83) and the corresponding experimental value (14.6) is close to those of polymers. This indicates that other factors such as rigidity of main chain, symmetry, and hydrogen bonding are very important for the solubility of the polymers. However the high values of solubility parameters of polymers must be mainly responsible for their insolubility. The prepared polymers showed some solubility in strong acids such as formic acid, methanesulfonic acid, and concentrated sulfuric acid (Table III), because of the formation of the corresponding imidazole salts.

The presence of the flexible —CH$_2$—, —O—, and —SO$_2$— groups into the main chain caused only a slight increase of the solubility of the polymer

TABLE III
Calculated Solubility Parameter and Solubility of Polymers

Polymer	Solubility parameter (p)[a]	Solubility[b]							Reducing mixture
		DMF	DMAc	DMSO	Ethylene glycol	HCOOH	Methane sulf. acid	Concd. H$_2$SO$_4$	
IIa	15.87	—	—	—	—	0.08%	+	+	52%
IIa[c]	15.87	—	—	—	—	—	—	—	55%
IIb	14.47	—	—	—	—	0.07%	+	+	60%
IIc	14.03	—	—	—	—	0.16%	+	+	65%
IId	14.38	—	—	—	—	0.2%	+	+	63%
IIe	13.96	—	—	—	—	0.2%	+ +	+ +	70%

[a] The dimensions of p are (cal/cm³)$^{1/2}$.

[b] Solubility: (+ +) soluble; (+) partially soluble; (—) no dissolution, no swelling.

[c] Polymer prepared[1] by thermal polycyclodehydration of the precursor poly(amino-p-benzoquinone)amide.

TABLE IV
Estimation of ΔEv and V of Polymer IIIb

Group	Δe_i (cal/mole)	Δv_i (cm³/mole)
2 Imidazole ring (trisubst.)	$2 \times 8940 = 17{,}880$	$2 \times \quad 4.6 = \quad 9.2$
2 C=	$2 \times 1030 = \quad 2060$	$2 \times (-5.5) = -\ 11$
Ring closure 6 atoms	250	16
3 Conjugated double bonds	$3 \times \quad 400 = \quad 1200$	$3 \times (-2.2) = -\ 6.6$
2 OH	$2 \times 7120 = 14{,}240$	$2 \times \quad 10 \ = \quad 20$
2 Phenylene (p)	$2 \times 7630 = 15{,}260$	$2 \times \quad 52.5 = \quad 104.8$
		repeat unit = $\quad 48$
Polymer IIIb	50890	180.4

into strong acids. The lower temperature (200°C) of preparation of polymer IIa by one-stage polycondensation than that (300°C) of two-stage preparation must be responsible for the solubility of the former polymer in strong acids. Solutions of polymers in formic acid were used in the determination of inherent viscosity, because of the greater solubility of the polymers in this solvent, although its solubility parameter calculated by Fedors' method is only 11.5. No films could be prepared from solutions of polymers in formic acid, because of the very low concentration of them. All polymers were soluble (in extent referred to in Table III) in a reducing mixture consisting of potassium hydroxide and sodium dithionite in aqueous DMAc. These were soluble in the form of potassium hydroquinone salts, as in the case of vat dyes. However, the corresponding free poly(p-hydroquinono)diimidazoles (IIIa–e), obtained from such solutions after neutralization were practically insoluble in organic solvents. It was interesting to calculate by Fedors' method and the solubility parameter of these reduced polymers. The estimation of the energy evaporation and molar volume of polymer IIIb is shown in Table IV and its solubility parameter p was found equal to 16.79 (cal/cm³)^{1/2}. The solubility parameter of polymers IIIa, IIIc–e, analogously calculated were found equal to 19.31, 16.20, 16.66, and 16.05, correspondingly. These values are 1.15–1.2 times higher than those of the corresponding oxidized polymers IIa–e and must be mainly responsible as well for the insolubility of polymers IIIa–e in organic solvents.

No marked change in inherent viscosity and IR and UV spectra of polymers IIa–e was obtained after reduction into the above referred mixture and oxidation by passing through the solution a stream of air, which indicates that no chain scission occurred on reductive solubilization.

Comparative data obtained by dynamic thermogravimetric analysis in nitrogen and air for IIa–e are shown in Figure 1 and Tables V and VI.

These data indicate that one-stage polycondensation in PPA, for preparation of IIa, gave the polymer more stability than that obtained by two-stage polycondensation via the corresponding poly(amino-p-benzoquinone)amide and also that p-biphenylene linking group is more stable than the p-phenylene one. The unexpected increase of thermal stability of the polymer in nitrogen by the incorporation of a methylene group between the benzene rings of the biphenylene group, could be attributed to the higher cyclization degree of polymer obtained by this incorporation. While polymer
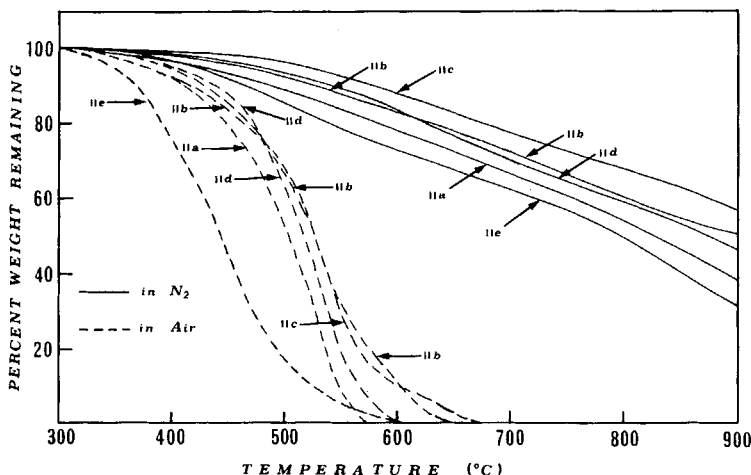
Fig. 1. Thermogravimetric curves of poly(p-benzoquinono)diimidazoles IIa−e.

IId (containing —O— groups) showed only a slightly better initial thermal stability than IIb, yet it showed a lower one at higher temperatures, both in nitrogen and air, and polymer IIe (with —SO₂— groups) showed the lowest thermal and thermo-oxidative stability, although the cyclization degree of both polymers is also higher than that of IIb. Such superior thermal stability of —CH₂— with respect to —SO₂— linking group is also referred in the literature.[12]

During dynamic thermal oxidative treatment of polymers, polymer IIc showed a slightly different behavior than the other polymers. It gained 1% of weight by heating from 250°C up to 350°C, followed then by a weight loss. Such weight gain was not observed on heating in nitrogen. During isothermal oxidative treatment of IIc at 250°C, it gained 1% of weight in 24 min and only 1.2% in about 15 hr. This gain probably could be attributed according to the literature[3] to oxidation of the —CH₂— group to a —CO—

TABLE V
Data of Thermal Stability of Polymers IIa−e in Nitrogen

Polymer	Decomp. temp. of 5% weight loss	Half-volatilization point (°C)	ipdt[a] (°C)	% Total weight loss at 900°C
IIa	420	675	630	60
	405[b]	645[b]	610[b]	65[b]
IIb	438	680	647	51
IIc	485	676	653	42
IId	470	667	651	53
IIe	422	700	632	73

[a] ipdt = Integral procedural decomposition temperature determined for the temperature range 50–900°C.

[b] For IIa prepared[1] by thermal polycyclodehydration of the corresponding poly(amino-p-benzoquinone)amide.

TABLE VI
Data of Thermal Stability of Polymers IIa–e in Air

Polymer	Decomp. temp. of 5% weight loss	Half-volatilization point (°C)	Temp. of max. rate of weight loss (°C)	Temperature of 100% weight loss (°C)
IIa	380	510	522	590
	354[a]	508[a]	520[a]	575[a]
IIb	380	530	540	650
IIc	400	525	532	740
IId	402	518	520	620
IIe	345	423	410	620
			454	

[a] For IIa prepared[1] by thermal polycyclodehydration of the corresponding poly(amino-p-benzoquinone)amide.

group (1% of weight gain corresponds to about 25% oxidation). IR spectra could not be used to prove such oxidation, because the carbonyl absorption band appeared also in the preoxidized polymer (carbonyl quinone). After isothermal oxidative treatment, polymer IIc appeared slightly more stable thermally in nitrogen, which enhances the view that oxidation of some —CH$_2$— group to more thermally stable —CO— group could have occurred.

No detectable T_g of polymers IIa–e was observed in DSC curves recorded on heating up to 400°C.

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