Polycondensation of N-Chlorobenzoquinonimines

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Summary

Self-condensations of 4-chloroimino-2,5-cyclohexadiene-1-one 1 (benzoquinone N-chloroimine), 2-tert-butyl-4-chloroimino-2,5-cyclohexa-diene-1-one 2, and 3-tert-butyl-4-chloroimino-2,5-cyclohexadiene-1-one 3 in N-methylpyrrolidinone containing inorganic bases have been investigated. Monomer 1 gave polymers having inherent viscosities of 0.27-0.33 dLg^{-1}. Monomers 2 and 3 only gave oligomers. ^{1}H NMR spectra suggest that poly-merization of 1 mainly occurs at C-2 and C-6 positions. A Michael-type addition mechanism, based on the high α-effect nucleophilicity of =NCl, is proposed.

Introduction

We have been interested in the synthesis of aromatic polyquinonimines as analogues of Aniline Black. Our previous article showed that polyaro-matic anthraquinonimines could be prepared by polycondensation of anthra-quinone with aromatic diamines in polyphosphoric acid (1):
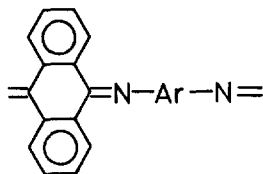

p-Benzoquinone could not be used in this reaction, contrary to a literature report (2), because it underwent Michael addition instead. Our attention was drawn to literature reports (3-4) on the thermal polycondensation of N,N'-dichloro-p-benzoquinonimine resulting in another polyaminoquinone structure:
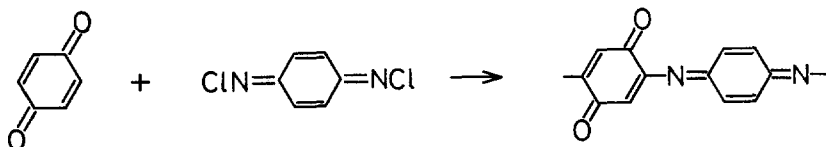
In order to simplify this process, we propose to use monofunctional monochloroimines (AB monomers). In this paper we describe the synthesis and polymerization studies of three p-benzoquinone mono-chloroimines,

4-chloroimino-2,5-cyclohexadiene-1-one <u>1</u>, 2-tert-butyl-4-chloroimino-2,5-cyclohexadiene-1-one <u>2</u>, and 3-tert-butyl-4-chloroimino-2,5-cyclohexadiene-1-one <u>3</u>.
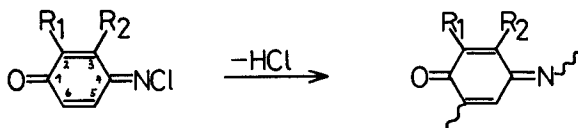
<u>1</u> R_1 = H, R_2 = H
<u>2</u> R_1 = t-C_4H_9, R_2 = H
<u>3</u> R_1 = H, R_2 = t-C_4H_9

Experimental

Materials - All solvents used for polymerizations were purified by conventional methods. Lithium carbonate (Aldrich, 99%), barium oxide (MCB Reagents) and sodium acetate (MCB Reagents) were used as received. 2-tert-Butylphenol (Aldrich) and 3-tert-butylphenol (Aldrich) were also used without purification.

Methods - Elemental analyses were performed by Desert Analytics of Tucson, Arizona. ^{1}H NMR Spectra were recorded on a Bruker WM-250 spectrometer. Viscosities were determined on 0.5% (w/v) polymer solutions in N-methylpyrrolidinone (NMP) at 30°C using a modified Ubbelohde viscometer.

Syntheses of Monomers - 2-tert-Butyl-4-aminophenol hydrochloride and 3-tert-butyl-4-aminophenol hydrochloride were prepared according to the literature procedures from 2-tert-butylphenol (5) and 3-tert-butylphenol (6), respectively. 1,4-Benzoquinone monoxime p-toluenesulfonate, m.p. 132°C, (lit. m.p. 132°C) was prepared according to the literature (7).

The N-chloroimines were synthesized by hypochlorite oxidation of the appropriate aminophenols.

3-tert-Butyl-4-chloroimino-2,5-cyclohexadiene-1-one <u>3</u>: Commercial bleach (sodium hypochlorite solution 5%, 650 mL) was placed into a three-necked flask (1L) equipped with a mechanical stirrer and a dropping funnel, and the flask was cooled in an ice-bath. 3-tert-Butyl-4-aminophenol hydrochloride (10.0g) was dissolved in 100 mL of 1N hydrochloric acid. This solution was added to the bleach with stirring. After addition, the yellow precipitate was filtered and washed with water. Recrystallization from benzenehexane (1:1) yielded yellow needles, 8.0g (82%), m.p. 71°C; ^{1}H NMR - (CDCl$_3$): $\delta 1.37$ (s, 9H), 6.43 (d, H_2), 7.88 (d, H_5), 6.54 (dd, H_6) ppm, $J_{2,6}$ = 1.93Hz, $J_{5,6}$ = 10.18 Hz.

2-tert-Butyl-4-chloroimino-2,5-cyclohexadiene-1-one 2: Using the same
method, 2 was prepared by oxidation of 2-t-butyl-4-aminophenol hydro-
chloride. Yellow needles from hexane, m.p. 83°C, yield 33%. ^{1}H NMR
(CDCl$_3$): δ1.33 (s, 9H), 7.11 (d, H$_3$), 7.65 (dd, H$_5$), 6.54 (d, H$_6$) ppm, J$_{3,5}$
= 2.74 Hz, J$_{5,6}$ = 9.82 Hz.

4-Chloroimino-2,5-cyclohexadiene-1-one 1: 1 was prepared by oxidation of
p-aminophenol by the same method. Recrystallization from benzene-hexane
(1:1). Yield 40%, yellow needles, m.p. 84°C (lit. (8) 85°C). ^{1}H NMR
(CDCl$_3$): δ6.66 (dd, H$_2$), 7.78 (dd, H$_3$, syn), 7.29 (dd, H$_5$, anti), 6.57
(dd,H$_6$); J$_{2,3}$ = 10.30Hz, J$_{2,6}$ = 2.06Hz, J$_{3,5}$ = 2.87Hz, J$_{5,6}$ = 10.27 Hz.

Self-Polycondensation - In a typical polymerization (Table 1, No. 3), the
monomer, 1 (1.00 g, 7.1 mmol), lithium carbonate (0.5272 g, 100 mol% of
monomer), and NMP (4.0 mL) were placed in a three-necked round-bottom
flask. The mixture was heated under nitrogen at 80°C for 7 h, at 140° for
15 h, and at 165°C for 6 h. After heating, the mixture was poured into
water, and the polymer was filtered. The polymer was extracted with
refluxing water and methanol until the extract was colorless. Yield,
0.49g (66%), black powder. When excess barium oxide was used as a base,
remaining barium oxide was removed by washing the polymer with 10% (v/v)
aqueous acetic acid. Polymerization of 2 and 3 proceeded similarly.
Workup was the same as described above except that hexane was used for
extraction instead of methanol.

Attempted Polymerization of 1,4-Benzoquinone Monoxime p-Toluenesulfonate -
1,4-Benzoquinone monoxime p-toluenesulfonate (1.00 g, 3.6 mmol), lithium
carbonate (0.269 g, 3.6 mmol), and NMP (4.0 mL) were heated at 95°C for
18 h under nitrogen. After workup, no polymer was obtained.

Electrical Conductivity Measurement - The conductivities of pressed pellets
of poly-1, with or without treatment with hydrochloric acid, were less than
10^{-8} ohm^{-1}cm^{-1}.

Results

Polymerizations - The reactions were carried out by heating monomers 1, 2,
and 3 under nitrogen in various solvents and bases (Table I). Since
hydrogen chloride is eliminated during the course of polymerization,
heating monomers without base results in protonated polymers. Without
adding any base, polymer having a chlorine content of 12.45% (No. 2) was
obtained. To remove hydrogen chloride, excess of lithium carbonate or
barium oxide were used. Under our conditions, these were more effective
than sodium acetate used previously.

The yield of polymer depends on the heating conditions. Longer
heating times and higher temperatures gave better yields (Table I,
No. 1,3). The solvent is also important. Good yields were obtained in NMP

Table I

No.	Monomer	Concent.[1] (%)	Solvent	Base	Heating Conditions (°C/h)	Yield (%)	Found (%)[2] C	H	N	Cl	Inherent Viscosity (dLg^{-1})
1.	1	26	NMP	Li$_2$CO$_3$ (20 mol%)	75/6	26	59.63	2.54	11.13	9.97	--
2.	1	25	Sulfolane	None	75/6 100/15 125/21	16	58.45	2.26	9.45	12.45	--
3.	1	25	NMP	Li$_2$CO$_3$ (100%)	80/7 140/15 165/6	66	65.13	3.06	12.47	1.16	0.27
4.	1	25	NMP	BaO (180%)	80/6 160/20	61	64.87	3.92	11.55	0	0.33
5.	1	25	1,2-dichloro-benzene	NaOAc (200%)	85/1 170/21	47	59.65	2.42	10.83	11.38	--
6.	1	30	DMSO	Li$_2$CO$_3$ (100%)	9/13 140/21	86	59.70	3.16	10.19	--	--
7.	1	30	DMSO	BaO (130%)	80/1 130/24	76	62.01	3.28	10.78	--	--
8.	2	40	NMP	None	70/18	75	68.46	6.31	6.85	--	--
9.	2	25	NMP	Li$_2$CO$_3$ (50%)	75/15 110/77	91	71.47	7.02	8.39	--	--
10.	2	25	NMP	Li$_2$CO$_3$ (100%)	90/7 140/15	66	71.54	6.52	8.82	--	0.10
11.	2	25	NMP	BaO (130%)	90/6 165/22	81	70.39	6.71	9.06	--	--
12.	3	25	NMP	Li$_2$CO$_3$ (100%)	70/1,90/25	88	68.48	6.58	8.58	--	--
13.	3	25	NMP	BaO (130%)	80/15,95/16 115/7	55	--	--	--	--	--

[1]Concentration (%) = (wt. of monomers (g)/vol. of solvent (ml)) x 100
[2]Calc. for Nos. 1-7, C, 68.57; H, 2.88; N, 13.33
 Calc. for Nos. 8-13, C, 74.51; H, 6.88; N, 8.69

(No. 3,4) or in DMSO (No. 6,7). The yield is not satisfactory when sul-
folane (No. 2) or 1,2-dichlorobenzene (No. 5) were used.

Polymer from $\underline{1}$ is insoluble in acetone, methanol, or chloroform, but
is soluble in NMP, DMF and DMSO. This polymer has an inherent viscosity of
0.33 dLg^{-1} indicating it has a reasonable molecular weight.

The polymerization of $\underline{2}$ yields a low polymer having a molecular weight
of ca. 1000 (D.P. ca 5-6) measured by SEC. The low polymer has an inherent
viscosity of 0.10 dLg^{-1}. It is soluble in most organic solvents, such as
acetone, methanol, or chloroform.

Polymerization of $\underline{3}$ yields oligomer (No. 12, 13).

Polymer Structure - The positions of the linkages in the polymer can be
elucidated by ^{1}H NMR spectroscopy. Surprisingly, no ^{1}H NMR data of monomer
$\underline{1}$ have been reported to date. We assigned the downfield signal in CDCl$_3$ to
the proton (H$_3$) at C-3 which is syn to chlorine, and the upfield signal to
the anti proton (H$_5$) at C-5, in accordance with literature data (9). By
decoupling studies, the four protons can be completely assigned (see
Experimental). When $\underline{1}$ is dissolved in DMSO-d$_6$, the solution immediately
becomes blue in color, and the ratio of integration of peaks changes; the
H$_2$ and H$_6$ signals become less intense (Fig. 1A). After heating at 90° for
ca. 30 min, the solution becomes viscous, and peaks due to H$_2$ and H$_6$
disappear (Fig. 1B). The peaks due to H$_3$ and H$_5$ become broad and lose
their splitting. This suggests that the polymerization mainly occurs at
C-2 and C-6 positions. However, we still cannot completely exclude the
possibility of attack on the C-3 and C-5 positions. A broad peak is
observed at $\delta 7.0$ ppm in the ^{1}H NMR spectra of the polymers. For monomers $\underline{2}$
and $\underline{3}$, only oligomers can be obtained. Steric hindrance by a tert-butyl
group at either of C-2 or C-3 positions retards the polymerization.

Discussion

We have shown that benzoquinone monochloroimines $\underline{1}$ - $\underline{3}$ smoothly
polymerize with varying sizes of molecular weight. The structures are
regular and are not complicated by the self-polycondensation of dichloro-
imine encountered by earlier investigations.

The polymers exhibit no definite melting point, but are soluble in
available solvents. Their electrical conductivities, with or without added
acids, are very low.

The previous investigators proposed the following mechanism, following
the suggestion of L'Ecuyer (10) who proposed a chloride anion-carried chain
reaction:

I.

II.
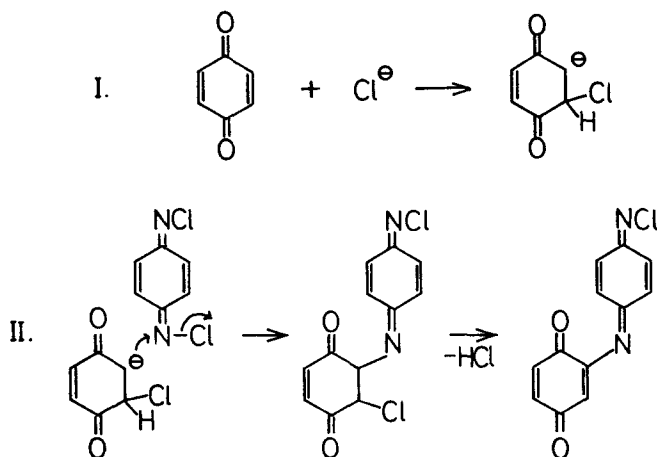
This is very reasonable. However, p-benzoquinones and p-benzoquinon-imines are well known acceptors in Michael addition reactions. Moreover, the nucleophilic character of nitrogen is enhanced by the adjacent chlorine through the α-effect:
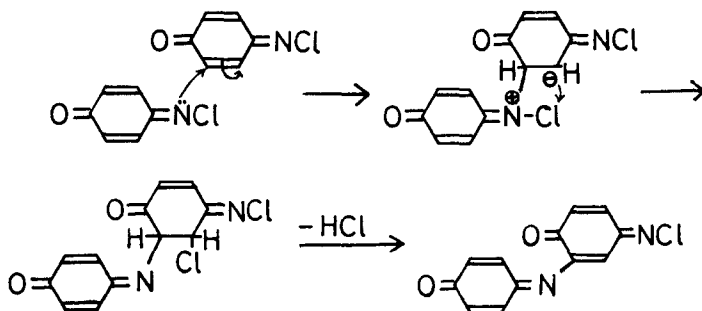
Hence, we may also propose a Michael-type addition mechanism. In the zwitterionic adduct, the positive chlorine is transferred to the carbanion center, followed by loss of hydrogen chloride. This mechanism is supported by the failure of the mono tosylate to react, because the α-effect of adjacent tosyloxy would be very weak. The direction of addition indicates that =NCl can stabilize negative charge better than =O.

This mechanism can also apply to the self-polycondensation products from p-benzoquinone-N,N'-dichloroimine reported previously (3). We propose that their observed largely linear structures result from selective reactions because of the push-pull stabilization in the intermediate:
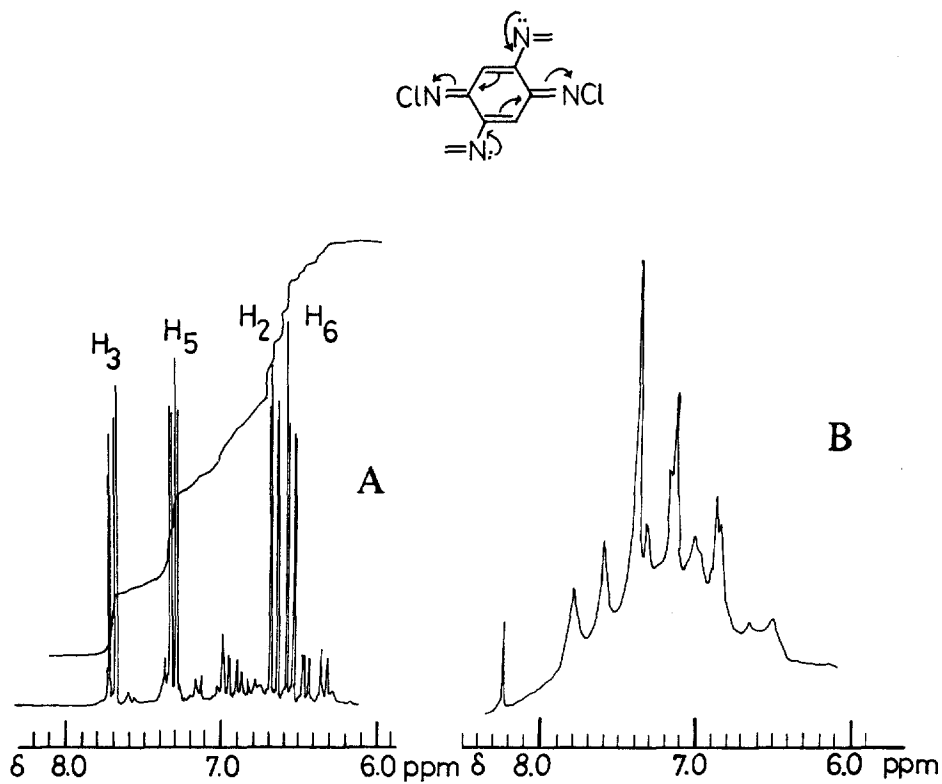
Figure 1. (A) ^{1}H-NMR spectra of monomer $\underline{1}$ after ca. 10 min in DMSO-d$_6$ at room temp., (B) monomer $\underline{1}$ after heating at 90°C for ca. 30 min in DMSO-d$_6$.

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