

# Synthesis and Study of Poly(8-hydroxyquinoline-7,5-diylethylene)

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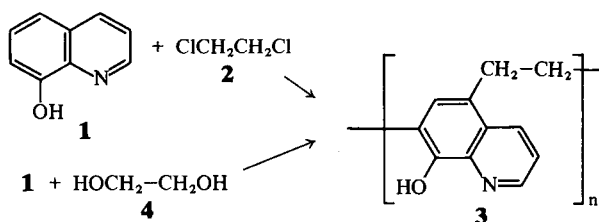
## SUMMARY:

Poly(8-hydroxyquinoline-7,5-diylethylene) (**3**) was prepared both by Friedel-Craft's condensation of 8-hydroxyquinoline (**1**) with 1,2-dichloroethane (**2**) in the presence of anhydrous aluminium chloride and by condensation of **1** with ethylene glycol in the presence of an acid catalyst. The polymer samples were found to be insoluble in acetic acid, sulfuric acid, conc. hydrochloric acid, or formic acid. They were characterized by IR and UV spectra. Their molecular weights were determined by conductometric titration in pyridine. Viscometric studies were carried out in formic acid and in glacial acetic acid at 35 °C. Solutions of the polymer samples in formic acid showed normal behaviour, whereas those in glacial acetic acid showed an abnormal behaviour. Various empirical relations were applied to correlate the viscosity data of solutions in glacial acetic acid with the appropriate concentration function. Aqueous acetic acid and simple electrolytes were used as solvents to suppress the abnormal behaviour.

## Introduction

Condensation polymers from aromatic compounds and dihaloalkanes in the presence of a Lewis acid like anhydrous aluminium chloride, are commonly known as A×F polymers. The condensation of benzene and substituted benzene with 1,2-dichloroethane in presence of anhydrous aluminium chloride has been studied by many workers with the intention to examine the effect of the mole ratio of the two reactants and of the catalyst on the molecular weight of the polymer<sup>1-4</sup>. These studies have shown that the molecular weight of the A×F polymer decreases with increasing amount of the catalyst and with increasing difference of the mole ratio of the two monomers from unity<sup>1-4</sup>. The molecular weights of these polymers have been reported to range from 2000 to 6000<sup>5</sup>. The polymers obtained from benzene and 1,2-dichloroethane have been reported to contain *ortho-para* or *para-para* linkages, as the polymers are reported to yield, on oxidation, isophthalic acid or terephthalic acid, respectively<sup>6-8</sup>.

The present communication describes the synthesis of poly(8-hydroxyquinoline-7,5-diylethylene) (**3**) by Friedel-Craft's reaction of 8-hydroxyquinoline (**1**) with 1,2-dichloroethane (**2**), applying various mole ratios of the two monomers and also different amounts of the catalyst at 90 °C. This type of polymer was also prepared by condensation of **1** with ethylene glycol in the



presence of either conc. sulfuric acid or polyphosphoric acid. The properties of the resulting polymer samples were compared. The probable structure assigned to the polymer is based on analogy. Electrophilic substitution reaction of 8-hydroxyquinoline yields 5,7-disubstituted-8-hydroxyquinolines<sup>9,10</sup>, and 8-hydroxyquinoline-formaldehyde polycondensation is reported to afford a polymer in which the methylen groups are linked at the 5- and 7-positions of 8-hydroxyquinoline residue<sup>11</sup>.

### Experimental Part

*Condensation of 8-hydroxyquinoline (1) with 1,2-dichloroethane (2) in the presence of anhydrous aluminium chloride:* To a well stirred and ice-cooled mixture of 1 and 2 (amounts are indicated in Tab. 1), finely powdered aluminium chloride was added portionwise. The reaction mixture was allowed to come to room temperature and then was heated at 90 °C for 4 h. It was poured in ice-cooled aqueous hydrochloric acid (volume ratio 1 : 10) and left overnight. The solid was filtered, washed with water, and then with dilute alkali. It was repeatedly treated with boiling water and dried. Then, the product was repeatedly treated with boiling ethanol to remove unreacted 1.

Tab. 1. Mole ratios of 8-hydroxyquinoline (1) and 1,2-dichloroethane (2) in the synthesis of polymer samples no. 1 to 7; UV spectroscopic data and intrinsic viscosities of poly(8-hydroxyquinoline-7,5-diethylene)

Sample No.	Mole ratios of reactants			UV-Data <sup>a)</sup>		[ $\eta$ ] · 10 <sup>2</sup> /(dl · g <sup>-1</sup> ) <sup>b)</sup>
	1	2	AlCl <sub>3</sub>	OD · 10 <sup>2</sup> at 215 ± 1 nm	OD · 10 <sup>2</sup> at 255 ± 5 nm	
1	1	1	4	2,1	1,9	5,5
2	1	3	4	5,6	7,5	4,8
3	1	3,5	4	6,0	11,6	4,3
4	1	4,5	4	5,4	14,0	3,8
5	1	5	4	5,0	15,0	4,6
6	1	1	2	5,2	32,0	5,6
7	1	1	6	2,4	26,0	3,9
8 <sup>c)</sup>	—	—	—	5,6	12,4	4,9
9 <sup>d)</sup>	—	—	—	3,2	20,4	5,7

<sup>a)</sup> OD: Optical density (absorbance).

<sup>b)</sup> In formic acid at 35 °C.

<sup>c)</sup> 8-HQEG/PPA copolymer: (8-HQEG: 8-hydroxyquinoline-ethylene glycol; PPA: polyphosphoric acid).

<sup>d)</sup> 8-HQEG/SA copolymer: (SA: sulfuric acid).

Seven polymer samples were prepared following this procedure and using the reactants and catalyst in different mole ratios. Details about the experimental conditions are presented in Tab. 1.

*Condensation of 1 with ethylene glycol in the presence of poly(phosphoric acid) (PPA):* To a well stirred and ice-cooled mixture of 1 (7.25 g, 0.05 mol) and ethylene glycol (3.4 ml, 0.06 mol) poly(phosphoric acid) (25 g) was added. The reaction mixture was left at room temperature for 0.5 h and was heated at 215 °C for 12 h. Then, it was cooled and poured into ice/water (100 g) and left overnight. The black particles suspended in the clear solution were filtered off. The filtrate was neutralized by an alkali solution and then rendered acidic by adding an acid, whereby a reddish brown solid separated. It was filtered, washed with hot water, and dried. It was repeatedly extracted with boiling ethanol to remove unreacted 1. This polymer sample has been labelled as sample no. 8. It melts at 260 °C with decomposition.

*Condensation of 1 with ethylene glycol in the presence of conc. sulfuric acid (SA):* To a well stirred and ice-cooled mixture of 1 (7.25 g, 0.05 mol) and ethylene glycol (3.4 ml, 0.06 mol) conc. sulfuric acid (2 drops) were

added dropwise. The yellow reaction mixture was allowed to come to room temperature and then it was heated at 140 °C for 6 h. The contents were cooled and poured into ice/water (100 g) and left overnight. The solution was neutralized by adding a dilute alkali solution and then it was rendered acidic by adding an acid. The solid product was filtered, washed with boiling water, and dried. It was powdered and repeatedly extracted with boiling ethanol to remove unreacted 1. This polymer sample was labelled as sample no. 9; m. p. > 360 °C.

### Measurements

**IR Spectra:** IR spectra of all the polymer samples were taken in KBr with a IR 5 Spectrophotometer.

**UV Spectra:** UV spectra of the polymer samples were studied in 4.8 M aqueous hydrochloric acid containing 8 mg of the polymer sample per liter.

**Conductometric titration:** Conductometric titration of a solution of the sample containing 50 mg of polymer in 50 ml of pyridine was carried out against 0.01154 M solution of sodium methoxide in the same solvent beyond the stage of neutralization. After addition of each lot of sodium methoxide, conductance was read. The values of the product of conductance with cell constant — the so called specific conductance — were plotted against milli-equivalent of sodium methoxide added per 100 g of polymer sample. Each plot comprising several peaks terminated in a step beyond which there was a continuous increase in specific conductance with the progress of titration. Relevant information about these titrations is furnished in Tab. 2.

**Viscometric measurements:** The measurements were carried out with Ubbelohde suspended level type viscometer at five concentrations. Plots of specific viscosity vs. concentration were made. They were found to be linear. Method of least square was applied to the data to evaluate the intrinsic viscosity.

### Characterization of the Polymers

All the polymer samples are insoluble in dioxane, dimethylformamide, or dimethyl sulfoxide. They are soluble in conc. hydrochloric acid, in sulfuric acid, in formic acid, or in glacial acetic acid.

All polymer samples prepared by different methods showed identical IR spectra. The IR spectrum of sample 1 is shown in Fig. 1. It comprises a broad band in the region from 3555 to 3410

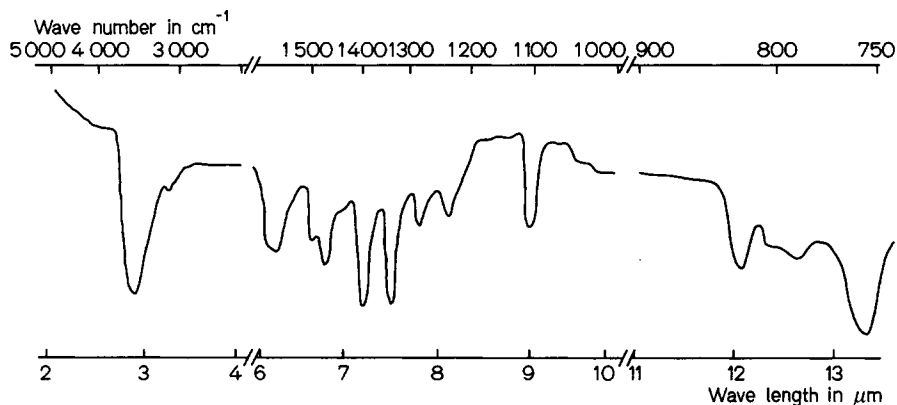


Fig. 1. IR spectrum of polymer sample 1

cm<sup>-1</sup> which has been assigned to the hydroxy group of 8-hydroxyquinoline bonded to the ring nitrogen by a hydrogen bridge<sup>12,13</sup>) and a band at about 3030 cm<sup>-1</sup> to the aromatic C—H stretching vibration<sup>12,13</sup>). The bands around 2960, 2890, and 2835 cm<sup>-1</sup> have been assigned to C—H stretching of —CH<sub>2</sub>CH<sub>2</sub>— acting as bridges between the heterocyclic units, and the bands at 2955

Tab. 2. Conductometric titration in pyridine of poly(8-hydroxyquinoline-7,5-diethylene) (3). Milli-equivalents (meq) of sodium methoxide per 100 g of polymer at completion of each break in the plot of specific conductance against meq of titrant. Weight of polymer: 50 mg in 50 ml of pyridine. Titrant base: 0.01154 M sodium methoxide in pyridine. Temp.: 35 °C

	Sample No.								
	1	2	3	4	5	6	7	8	9
meq. of NaOMe at break-	108	99	175	242	246	92	196	112	90
sequence	216	296	350	484	494	484	761	350	272
	647	593	525	715	705	831	1223	525	449
	1150	2182	1225	1419	1237	1615	1915	830	726
	1617	—	3843	3664	3637	2261	3530	1401	1798
	2041	—	—	—	—	3784	—	2559	3861
	3969	—	—	—	—	—	—	—	—
$\bar{P}_n \pm 0.2^{a)}$	37	22	21	15	14	41	18	23	43
Average Molecular weight $\pm 35$	6300	3800	3600	2600	2400	8000	3100	4000	7400

<sup>a)</sup>  $\bar{P}_n$  = meq of titrant added up to the final break/meq added up to the first break.

and  $2885\text{ cm}^{-1}$  in the IR spectrum of 8-hydroxyquinoline-formaldehyde polymer to CH-stretching of the  $-\text{CH}_2-$ bridges between the two heterocyclic nuclei<sup>11</sup>). Besides a series of bands in the region from  $1390$  to  $1035\text{ cm}^{-1}$ , bands at  $1510$  and  $1480\text{ cm}^{-1}$  were observed. Some of them have also been observed in the IR spectrum of **1**<sup>12,13</sup>). A series of bands around  $900$ ,  $830$  and  $790\text{ cm}^{-1}$  may be assigned to the out of plane bending vibration of an isolated hydrogen atom<sup>12</sup>), a system of two adjacent hydrogen atoms<sup>13</sup>) and a system of three adjacent hydrogen atoms<sup>12,14</sup>), respectively. These IR spectral characteristics are compatible with the structure assigned to the polymer.

The UV spectrum of each polymer sample in dil. aq. HCl comprises two bands; a weak band around  $215\text{ nm}$  and a strong band around  $255\text{ nm}$ , respectively. The values of optical densities at these two positions are shown in Tab. 1. The corresponding bands in the UV spectrum of **1** were observed at  $216$  and  $267\text{ nm}$ .

Since the polymer samples are insoluble in common organic solvents, it was not possible to apply osmometric or light scattering methods for the determination of the molecular weight of the polymer samples. Therefore, like other polymeric compounds containing phenolic OH groups in the repeating units, e. g. cresol/formaldehyde or *p*-hydroxybenzoic acid/formaldehyde polymer, the molecular weights were estimated by the conductometric method<sup>15-23</sup>), which involves conductometric titration of the polymer solution in pyridine against a standard solution of sodium methoxide in the same solvent. Information about this method and the resulting molecular weights of the polymer samples are presented in Tab. 2. Examination of these data revealed that the molecular weight decreases as the mole ratio of the two monomers in the reaction mixture increases ( $>1$ ), it also decreases with increasing amounts of aluminium chloride. The molecular weight of the polymer sample obtained by condensation of **1** with ethylene glycol in the presence of sulfuric acid is higher than those prepared by other methods.

The viscosities of the polymer samples were studied in formic acid at  $55^\circ\text{C}$ . The values are reported in Tab. 1. The trend in the value of intrinsic viscosities follows that in the values of molecular weights. It was found that the Mark-Kuhn-Sakurada-Houwink relation<sup>24</sup>) between intrinsic viscosity and molecular weight is not applicable to the present data.

The viscosities of the polymer samples were also studied in glacial acetic acid at  $35^\circ\text{C}$ . The plot of reduced viscosity against concentration indicated an abnormal behaviour. Such a plot based on the viscosity data of sample **1** (Tab. 3) is shown in Fig. 2. For each polymer sample the value of reduced viscosity increases with decrease in the concentration of the polymer solution. Such an abnormal behaviour is known as a polyelectrolyte behaviour.

The literature survey reveals that the behaviour of solutions of polyamides in such experiments depends upon the nature of the solvent<sup>25</sup>). In the present cases an abnormal behaviour is observed in the viscometric study of a solution in acetic acid and not with a solution in formic acid. This dif-

Tab. 3. Viscosity data of solutions of polymer sample **1** in acetic acid at  $35^\circ\text{C}$

Concentration (C) in g/dl	Specific viscosity $\eta_{sp}$	Reduced viscosity $\eta_{sp}/C$ in $\text{dl} \cdot \text{g}^{-1}$	$\frac{C^{1/2}}{\text{g}^{1/2} \cdot \text{dl}^{-1/2}}$	$\frac{C}{\eta_{sp}}/(\text{g} \cdot \text{dl}^{-1})$	$\frac{\eta_{sp}}{C^{1/2}}/(\text{dl}^{1/2} \cdot \text{g}^{-1/2})$
2,000	0,1936	0,0968	1,415	10,3306	0,1369
1,429	0,1574	0,1103	1,195	9,0788	0,1317
1,111	0,1173	0,1056	1,054	9,4714	0,1113
0,909	0,0996	0,1095	0,953	9,1265	0,1045
0,769	0,0931	0,1211	0,877	8,2601	0,1062

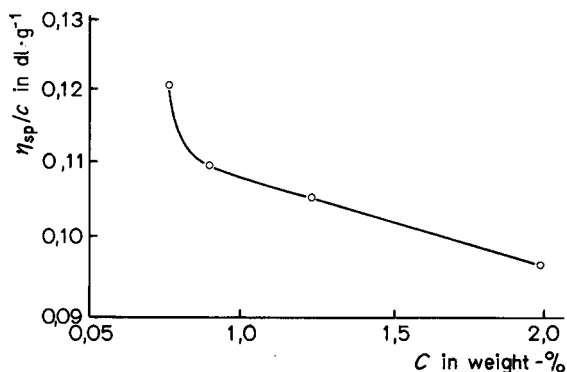


Fig. 2. Plot of reduced viscosity vs. concentration of the solution of polymer sample 1 in glacial acetic acid

ference may be attributed to the much higher dielectric constant and the smaller size of formic acid in comparison with acetic acid.

The polyelectrolyte behaviour of certain polymers in solution is reported to be suppressed partly or completely either by increasing the polarity of the solvent<sup>26-29)</sup> or by adding salts to the polymer solution<sup>30-34)</sup>. In view of this, the viscometric study of the solution of polymer sample 1 was carried out in acetic acid/water mixture (volume ratios 60:40 and 40:60) and in acetic acid saturated with KCl, KNO<sub>3</sub>, KBr, or KOCOCH<sub>3</sub>. The reduced viscosities of solutions of polymer sample 1 in all the above mentioned media are shown in Tab. 4. Examination of these data reveals that the polyelectrolyte behaviour is not removed even in these solvents. Hence, a study of viscosity in acetic acid/water in the presence of an electrolyte was undertaken. The results of the viscometric study of the solutions of polymer sample 1 in acetic acid/water (volume ratio 60:40) containing 2 and 4 weight-% of KBr, respectively, at 35 °C are presented in Tab. 4. Examination of these data reveals that the polyelectrolyte behaviour is suppressed partially in the medium containing 2 weight-% of KBr and completely in the medium containing 4 weight-% of KBr. The value of the

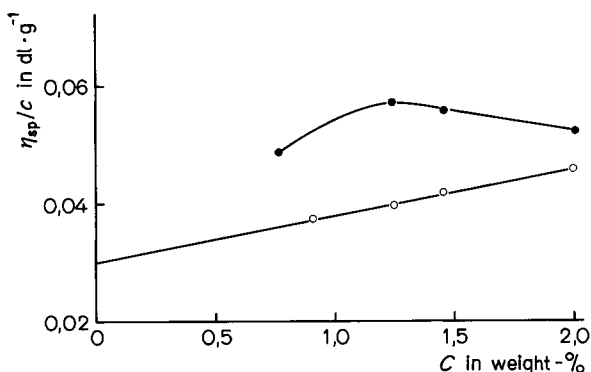
Tab. 4. Reduced viscosity data of solutions of polymer sample 1 in various media

Composition of the medium			Reduced viscosity <sup>a)</sup> in $\text{dl} \cdot \text{g}^{-1}$ at concentrations (in weight-%)				
vol. of acetic acid in ml	vol. of water in ml	salt	2,000	1,429	1,111	0,909	0,769
60	40	—	0,0425	0,0444	0,0465	0,0478	0,0484
40	60	—	0,0499	0,0503	0,0512	0,0520	0,0525
100	—	KBr	0,0938	0,1046	0,1089	0,1165	0,1289
100	—	KCl	0,1120	0,1150	0,1250	0,1370	0,1440
100	—	KNO <sub>3</sub>	0,1088	0,1152	0,1157	0,1200	0,1339
100	—	KOAc	0,1025	0,1107	0,1282	0,1311	0,1430
60	40	2% KBr <sup>b)</sup>	0,051	0,055	0,057	0,050	0,049
60	40	4% KBr <sup>b)</sup>	0,045	0,041	0,039	0,037	—
80	20	2% KOAc <sup>b)</sup>	0,058	0,055	0,051	0,050	—

<sup>a)</sup> At 35 °C.

<sup>b)</sup> Weight-%.

Fig. 3. Plot of reduced viscosity vs. concentration of the solution of polymer sample 1 in acetic acid/water (volume ratio 60:40) containing 2 weight-% of KBr (●), and 4 weight-% of KBr (○)



intrinsic viscosity was determined from the plot of reduced viscosity vs. concentration (Fig. 3) to be 0,031 dl · g<sup>-1</sup>. The polyelectrolyte behaviour was also suppressed completely in acetic acid/water (volume ratio 80:20) containing 2 weight-% of KOCOCH<sub>3</sub>. The value of intrinsic viscosity, estimated from the plot of reduced viscosity vs. concentration, was found to be 0,043 dl · g<sup>-1</sup>.

#### Empirical Treatment of Abnormal Viscosity Data

Empirical equations have been applied to correlate the reduced viscosity with certain concentration functions linearly, in the case of polymer solutions exhibiting polyelectrolyte behaviour. The proposed equations<sup>35-37)</sup> correlating the reduced viscosity with some functions of concentration  $C^{-1/2}$  or  $C^{1/2}$  (Tab. 3) involves more than one constant. The empirical relation proposed by Jones and Dole<sup>35)</sup> and that proposed by Yuan, Dougherty, and Stivala<sup>37)</sup> were applied to the present set of data indicating abnormal behaviour. Both these relations were found to apply almost equally to the present viscosity data about the solution of the polymer sample in acetic acid.

$$\frac{\eta_{sp}}{C^{1/2}} = A + B \cdot C^{1/2} \quad (1)$$

$$\frac{\eta_{sp}}{C} = [\eta]_{\alpha} + \frac{K \cdot [\eta]_{\alpha}}{C^{1/2}} \quad (2)$$

where  $A$ ,  $B$ , and  $[\eta]$  are constant.

The values of the constants are shown in Tab. 5. These were evaluated graphically by dotting the viscosity function with the required concentration functions.

Tab. 5. Application of the empirical equation to the viscosity data of solution of sample 1 in acetic acid

Sample No.	$\eta_{sp}/C^{1/2} = A + B \cdot C^{1/2}$ (Eq. (1))		$\eta_{sp}/C = [\eta]_{\alpha} + K[\eta]_{\alpha}/C^{1/2}$ (Eq. (2))	
	$A$	$B$	$[\eta]_{\alpha}$	$K$
1	0,031	0,071	0,047	1,362
2	0,078	0,105	0,010	0,790
3	0,038	0,057	0,031	1,613
4	0,064	0,018	0,027	2,074
5	0,053	0,016	0,012	4,917

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