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Polycondensation of Glyoxal with Aromatic Diamines

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SUMMARY

New diamines containing alkaneoxy linkages have been prepared by hydrolysis of the corresponding diamides which were obtained by reaction of p-hydroxyacetanilide with different dibromo alkanes. These diamines were copolymerized with glyoxal to yield insoluble copolymers in solvents such as DMSO, CH_3OH, CH_3COCH_3, $CHCl_3$. The diamides and diamines were characterized by IR, ^1H NMR spectroscopy and elemental analyses and the copolymers were characterized by IR spectroscopy and elemental analyses.

INTRODUCTION

Is known that glyoxal sulphate reacts with ethylamine(1) whereas aqueous glyoxal reacts with cyclohexylamine (2) or with n-butyl-amine and isopropylamine. Earlier it has been found that p-aminophenol (3), 3-hydroxy-5-nitroaniline (4) react with glyoxal to give N-substituted aromatic 1,2-diimines.

In this paper is reported the synthesis of aromatic diimines with an alkaneoxy bridge and its polycondensation with aqueous glyoxal.

EXPERIMENTAL PART

Materials: Aqueous glyoxal 30% (Merck). All the chemicals were the best available commercial products and were used without further purification.

Synthesis of Diamines: Amine derivatives, were obtained by reaction of p-hydroxyacetanilide with dihalogen derivatives in basic media, and subsequent basic hydrolysis. A typical example for the synthesis of the amide and amine derivatives is as follows:

Synthesis of 1,3-propylene-bis-(phenoxy-4-acetylamide). Thirty g (0.2 mole) of p-hydroxyacetanilide were dissolved in 100 ml DMF. To this solution an aqueous solution of KOH (0.25 mole) were added slowly under vigorous stirring. Then 12.3 ml (0.12 mol) of 1,3-dibromopropane were added drop by drop. The reaction was refluxed for 8 hrs. The product was precipitated in water, filtered and dried under vacuum at 50°C till constant weight.

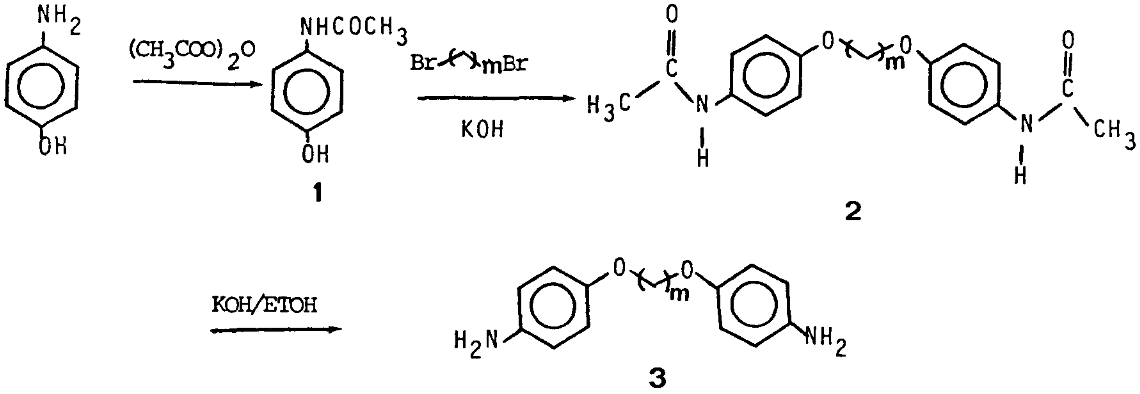
Synthesis of 1,3-propylene-bis(phenoxy-4-amine). Basic hydrolysis was carried out by dissolving in isobutanol 10.3g (0.03 mole) of amide. To this solution an aqueous solution of KOH (7.5 ml, 20 N) was slowly added. The reaction mixture was refluxed for 7 hrs. This solution was washed with water until neutral. The crude product was purified by crystallization from a mixture of methanol/water (90/10) and dried under vacuum.

Polycondensation: A general procedure is as follows : To a flask that contains 0.020 mole of diamine in 70 ml ethanol, 0.020 mole glyoxal was slowly added. It was stirred for 1 h and a polymer precipitated. It was filtered, washed with ethanol and dried under vacuum.

Characterization: IR, ^{1}H-NMR spectra were recorded on a Perkin Elmer 577 and Varian T-60A spectrometer respectively.

RESULTS AND DISCUSSION

The exothermic reaction between aqueous solutions of glyoxal and primary aromatic diamines give hydrolitically stable Schiff bases (5).



m:3,4,5,6,8

All the compounds give a IR and ^{1}H NMR spectra corresponding to the expected structures. In addition the compounds were characterized by elemental analyses summarized in Table 1.

Table 1.- Yields reaction and elemental analyses for amide <u>2</u> and amine <u>3</u> derivatives.

	AMIDE					AMINE			
	Yield		C	H	N	Yield	C	H	N
m	(%)		(%)	(%)	(%)	(%)	(%)	(%)	(%)
3	51	Calc	66.70	6.43	8.19	55	69.77	6.98	10.80
		Found	66.50	6.41	8.46		69.72	6.62	10.37
4	73	Calc	67.42	6.74	7.86	80	70.59	7.35	10.29
		Found	67.76	6.42	7.83		70.15	7.40	10.27
5	76	Calc	68.11	7.03	7.57	76	71.33	7.69	9.79
		Found	67.76	7.16	7.91		70.80	7.52	9.79
6	73	Calc	68.75	7.29	7.29	93	72.00	8.00	9.33
		Found	68.94	7.93	7.25		71.93	7.92	9.14
8	43	Calc	69.90	7.77	6.79	75	73.17	8.54	8.54
		Found	69.35	7.65	6.48		73.10	7.99	8.50

The infrared spectra of the amides 2 show absorption bands at 3300 cm^{-1} and 1670 cm^{-1} corresponding to the ν_{N-H} and $\nu_{C=O}$ vibration respectively. For the amines the absorption band at $\nu_{C=O}$ dissapears (see Fig. 1).

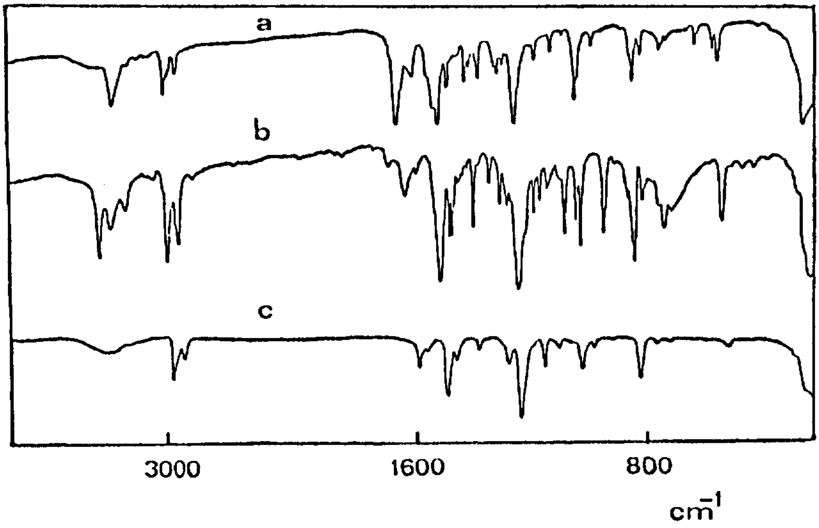


Figure 1.- Infrared spectra (KBr) of a) Amide with m=8; b) Amine with m=8 and c) copolymer 4e.

The ^{1}H NMR spectrum of the compounds shows the signals expected. Figure 2 shows as an example the ^{1}H NMR spectra of one amide and amine. The ^{1}H NMR of 1,3-propylene-bis(phenoxy-4-acetylamine) shows a singlet and a multiplet at 2.2 ppm ($C\underline{H_3}CO$ and $C\underline{H_2}$-C); a triplet at 4.3-4.0 ppm ($C\underline{H_2}$-O) and at 6.9-7.3 ppm (aromatic protons). On the other hand, the ^{1}H NMR spectrum of 1,3-propylene-bis(phenoxy-4-amine) shows the following signals:multiplet at 2.4-2.0 ppm ($C\underline{H_2}$-C);triplet at 4.3-3.9 ppm ($C\underline{H_2}$-O) and at 6.7-7.0 ppm (aromatic protons).

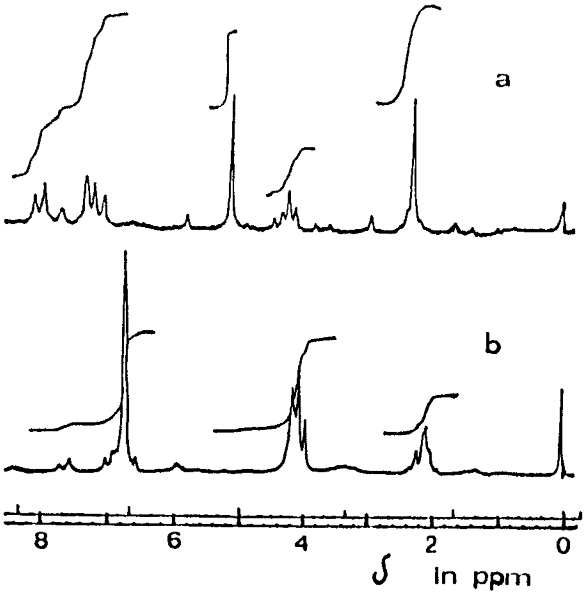
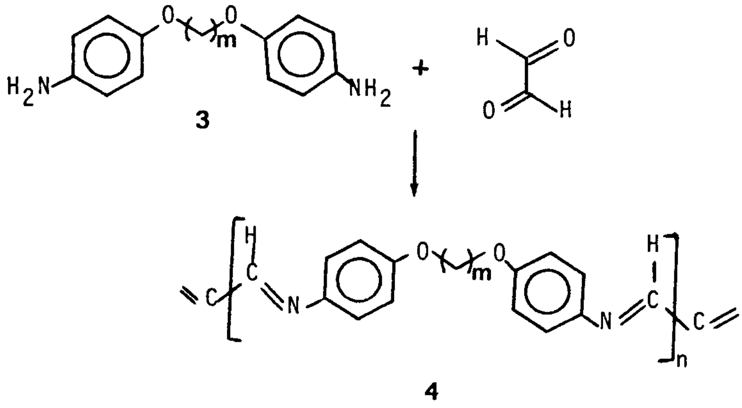


Figure 2.- ^{1}H NMR spectra (60MHz, C_5D_5N, room temperature, TMS as internal standard) of a) 1,3-propylene-bis(phenoxy-4-acetyl-amide and b) 1,3-propylene-bis(phenoxy-4-amine).

The aromatic diamines containg different lengths of alkaneoxy bridges were reacted with aqueous glyoxal.



All the copolymers are insoluble in water and organic solvents such as, ethanol, dimethylsulfoxide, acetone. Copolymers were characterized by elemental analyses and IR spectroscopy. All IR spectra are similar and show among others an absorption band at 1610 cm-1, corresponding to the $\nu_{C=N}$ vibration (see Figure 1).

Table 2. Elemental analyses of copolymers $4_{a\rightarrow e}$

Copolymer	m	Empirical Formula		C (%)	H (%)	N (%)
4a	3	$(C_{17}H_{16}N_2O_2)_n$	Calc	72.86	5.71	10.00
			Found	70.98	5.65	9.85
4b	4	$(C_{18}H_{18}N_2O_2)_n$	Calc	73.47	6.12	9.52
			Found	72.85	5.97	9.29
4c	5	$(C_{19}H_{20}N_2O_2)_n$	Calc	74.03	6.49	9.09
			Found	74.32	6.83	8.93
4d	6	$(C_{20}H_{22}N_2O_2)_n$	Calc	74.53	6.83	8.69
			Found	74.45	6.74	8.48
4e	8	$(C_{22}H_{26}N_2O_2)_n$	Calc	75.43	7.43	8.00
			Found	74.72	6.66	7.81

These polymers now are examined as chelating compounds for copper(II).

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