Polymers with Anthrazoline Units in the Main Chain

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ABSTRACT: The Friedländer quinoline synthesis was applied to 4,6-diaminoisophthalaldehyde. This compound was condensed with acetophenone, 2-acetylpyridine, 4-acetyldiphenyl ether, and phenylacetaldehyde, yielding the corresponding substituted anthrazolines. These model reactions were then applied to the polycondensation of 4,6-diaminoisophthalaldehyde with *p*-diacetylbenzene, 2,6-diacetylpyridine, and bis(*p*-acetylphenyl) ether. The resulting polymers have a high thermal stability as revealed by thermogravimetric analyses (620° break under nitrogen).

Quinoline derivatives can be conveniently prepared by reaction of *o*-aminoaldehydes with ketomethylenes. The reaction was first carried out by Friedländer with *o*-aminobenzaldehyde and acetaldehyde.[1] Later on, other ketones and aldehydes were reported to react in the same way.[2-4] The reactions are base catalyzed and the yields are high. No intermediates have been isolated, indicating that the first step in the condensation is not slower than the following ones. The reaction can be conveniently visualized as a Claisen condensation followed by a fast ring closure with the amino group.

More recently the Friedländer quinoline synthesis was applied to 4,6-diaminoisophthalaldehyde[5] and 2,5-diaminoterephthalaldehyde derivatives.[6] In analogy with the phenanthrene–phenanthroline nomenclature, the new heterocycles were called *anthrazolines*.[6]

Model Compounds. The reaction of 4,6-diaminoisophthalaldehyde with acetophenone (I), 2-acetylpyridine (II), and 4-acetyldiphenylether (III) yielded the desired condensation products in high yield. Similar reactions were performed with phenylacetaldehyde (IV). In this case, however, the yield was too low and this discouraged later polymerization attempts. The properties of the reaction products are listed in Table I. The obtained anthrazolines are easily crystallized and stable at their melting point.

Polymerizations. Following the synthesis of model compounds, polymers were prepared from 4,6-diaminoisophthalaldehyde and *p*-diacetylbenzene (V), 2,6-diacetylpyridine (VI), and bis(*p*-acetylphenyl) ether (VII), respectively (Figure 1). Pyridine, N,N-dimethylformamide, hexamethylphosphoramide (HMPA), and HMPA containing 10% LiCl were tested as solvents. In every case the condensation products precipitate and this limited the molecular weight of the resulting polymers. For example, low molecular weight products were obtained in the first two solvents. In condensation systems with HMPA the polymers have a better solubility and accordingly longer chains are obtained. However, also in these cases, the polymers precipitate completely toward the end of the reaction. The properties of the polymers obtained with HMPA are listed in Table II. In HMPA the reaction is fast at room temperature, whereas in HMPA with 10% LiCl heating to about 80° is necessary to effectuate a reasonable reaction rate.

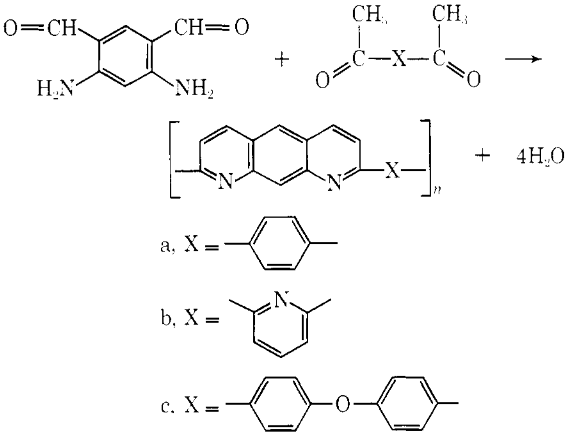

Figure. 1 Polycondensations.

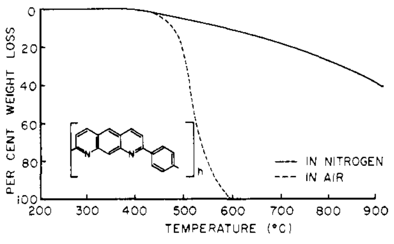

Figure 2. TGA of polymer V.

The yellow materials obtained are completely soluble in sulfuric acid. The Friedländer quinoline synthesis, however, cannot be conducted in acidic solvents, thus excluding sulfuric acid or polyphosphoric acid as solvents for the reaction. Under the basic polymerization conditions, 4,6-diaminoisophthalaldehyde is perfectly stable. It resists the Cannizzarro reaction completely.[6]

Thermal Stability. The results of thermogravimetric analyses are shown in Figures 2–4. Polymer VI has a weight loss of 5% at 650° (under nitrogen). It compares favorably to the best single-strand polyquinoxalines.[7] In air the polymers start decomposing at 450°.

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(1) P. Friedländer, *Chem. Ber.*, **15**, 2574 (1882)

(2) P. Friedländer and C. F. Gohring, *ibid.*, **16**, 1833 (1883).

(3) O. Stark, *ibid.*, **42**, 715 (1909).

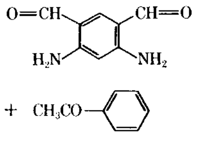
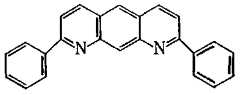
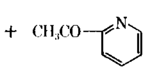
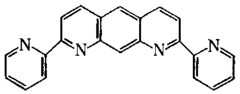
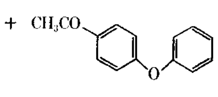
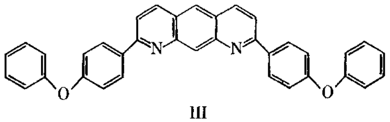
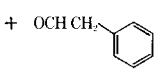
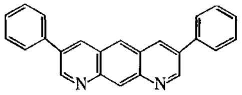
(4) C. Schöpf and G. Lehman, *Ann.*, **497**, 7 (1932).

(5) P. Ruggli and P. Hindermann, *Helv. Chim. Acta*, **20**, 272 (1937).

(6) P. Ruggli and F. Brandt, *ibid.*, **27**, 274 (1944).

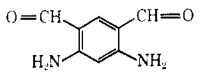
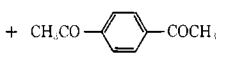
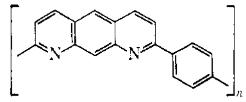
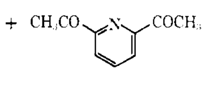
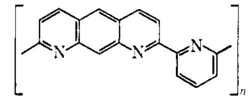
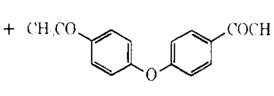
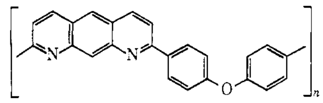
(7) J. K. Stille and E. L. Mainen, *Macromolecules*, **1**, 36 (1968).

TABLE I
PROPERTIES OF MODEL COMPOUNDS

Reaction	Reaction product	Yield, %	Mp, °C	Fluorescence[a] in H_2SO_4	λ_{max} in H_2SO_4, mμ	Formula	Elemental Analysis Calcd, % C	Calcd, % H	Calcd, % N	Found, % C	Found, % H	Found, % N
	 I	80	217 (5)	Blue white, ++++	409 297 255							
	 II	90	250	Yellow green, +++	385 290 256	$C_{22}H_{14}N_4$[c]	79.02	4.23	16.75	79.17	4.20	16.82
	 III	91	277	Yellow, +	458 383 (weak) 288 259	$C_{36}H_{24}N_2O_2$[b]	83.70	4.68	5.42	83.84	4.88	5.38
	 IV	30	279	0	417 327 282	$C_{24}H_{16}N_2$[b]	86.72	4.85	8.43	86.33	4.95	8.34

[a] +, moderate fluorescence; +++, strong fluorescence; ++++, very strong fluorescence. [b] Recrystallized from *m*-xylene. [c] Recrystallized from *m*-xylene + EtOH.

Table II
Properties of Polyanthrazolines

Reaction	Reaction products	$[\eta]_{inh}$[a] Product obtained in HMPA	$[\eta]_{inh}$[a] Product obtained in HMPA + 10% LiCl	λ_{max} in H_2SO_4, mμ	Fluorescence[b] in H_2SO_4
 + 	 V	0.14	0.24	430 297 255	Yellow green, +++
+ 	 VI	0.12	0.24	384 267	Orange, ++
+ 	 VII	0.26	0.23	478 380 (weak) 294 259	Yellow, ++

[a] $[\eta]_{inh}$ is measured in H_2SO_4 at 25° with 0.5 g/100 ml of solutions. [b] ++, moderately strong fluorescence; +++, strong fluorescence.

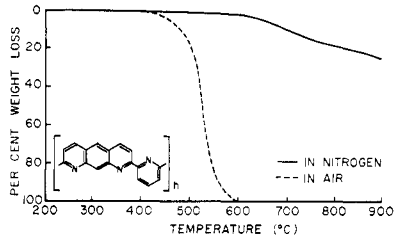


Figure 3. TGA of polymer VI.

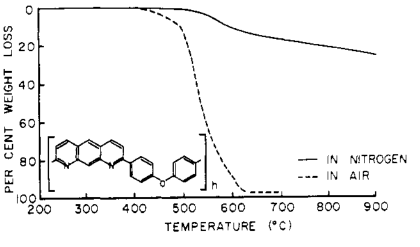


Figure 4. TGA of polymer VII.

Experimental Section

1. Starting Materials. Acetophenone, *p*-diacetylbenzene, 2-acetylpyridine, 2,6-diacetylpyridine, and phenylacetaldehyde were acquired commercially.

p-Diacetylbenzene was purified by crystallization from ethanol and subsequent sublimation at 90° (0.1 mm), mp 114°.[8] 2,6-Diacetylpyridine was recrystallized from isooctane (cooled to −20°) under addition of some Al_2O_3, mp 44–46°.[9] 4-Acetyldiphenyl ether was prepared by acetylation of diphenyl ether, mp 45°.[10] Bis(*p*-acetylphenyl) ether was prepared by acetylation of diphenyl ether, mp 101°.[11]

4,6-Diaminoisophthalaldehyde was prepared from *m*-xylene. The nitration of *m*-xylene gives 30% 4,6-dinitro-1,3-xylene.[12] This product reacts with *p*-nitrosodimethylaniline to $N^1,N^{1'}$-(4,6-dinitroisophthalylidene)bis[N^4,N^4-dimethyl-*p*-phenylenediamine].

The hydrolysis gives 4,6-dinitroisophthalaldehyde which after reduction yields 4,6-diaminoisophthalaldehyde, mp 208°.[5] The product was purified by sublimation at 180° (0.1 mm).

2. Model Compounds. Model products were prepared by the following procedure. 4,6-Diaminoisophthalaldehyde (100 mg) and 0.3 g of acetyl compound (excess) were dissolved in 4 ml of ethanol. After addition of four drops of a 25% methanolic potassium hydroxide solution the mixture was heated to 80° until no more crystals separated (2–8 hr). The mixture was cooled and the yellow reaction product was filtered and recrystallized.

3. Polymerizations. A. In HMPA. 4,6-Diaminoisophthalaldehyde (1 g) dissolved in 15 ml of HMPA was mixed with an equimolar amount of diacetyl compound and then 10 drops of a 10% methanolic potassium hydroxide solution was added. The reaction mixture was gradually heated from room temperature to 120° (in 4 hr) and kept at this temperature for 2 hr. After completion of the polymerization the mixture was cooled and diluted with 200 ml of water. The polymer was filtered, washed, and dried. Final drying was done at 250° (0.1 mm) (for viscosity determination) but the materials were heated for 1 hr at 350° (0.1 mm) to obtain samples suitable for elemental and thermogravimetric analyses. Under these conditions slight cross-linking occurred with yields of V 91%, VI 99%, VII 98%.

B. In HMPA and Lithium Chloride. Lithium chloride

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(8) L. Berend and P. Herms, *J. Prakt. Chem.*, **74**, 134 (1906).

(9) A. P. Terent'ev, E. G. Rukhadze, I. G. Mochalina, and V. V. Rode, *Zh. Vses. Khim. Obshch. im. D. I. Mendeleeva*, **6**, 116 (1961); *Chem. Abstr.*, **55**, 14450 (1961).

(10) H. Kipper, *Chem. Ber.*, **38**, 2491 (1905).

(11) W. Dilthey, E. Bach, H. Grütering, and E. Hausdörfer, *J. Prakt. Chem.*, **117**, 350 (1927).

(12) P. Ruggli, A. Zimmermann, and R. Thouvay, *Helv. Chim. Acta*, **14**, 1250 (1931).

(1.5 g) was dissolved in 15 ml of HMPA. 4,6-Diaminoisophthalaldehyde (1 g) and an equimolar amount of diacetyl compound were then added. To the solution, 0.5 ml of a 10% aqueous lithium hydroxide mixture was added. The mixture was heated for 1 hr at 80°, 2 hr at 100°, 2 hr at 120°, and 2 hr at 140°. The materials were isolated as under A: yields V 94%, VI 93%, VII 95%.

Anal. Calcd for $C_{18}H_{10}N_2$ (V, prepared in HMPA + 10% LiCl): C, 85.02; H, 3.6; N, 11.02. Found: C, 82.83; H, 4.71; N, 9.25.

Anal. Calcd for $C_{17}H_9N_3$ (VI, prepared in HMPA + 10% LiCl): C, 79.99; H, 3.55; N, 16.46. Found: C, 77.64; H, 4.87; N, 15.04.

Anal. Calcd for $C_{24}H_{14}N_2O$ (VII, prepared in HMPA): C, 83.22; H, 4.07; N, 8.09. Found: C, 82.98; H, 4.09; N, 7.79.

Thermogravimetric analyses were run with a 10°/min temperature increase.

Acknowledgment. In conclusion, I wish to thank Dr. J. K. Stille and Loren Gotter of the University of Iowa for performing the thermogravimetric analyses of our samples. The financial support of this investigation by the Petroleum Research Fund administered by the American Chemical Society is gratefully acknowledged.

Non-Markoffian Monomer Distributions in Copolymers. The Copolymerization of Ethylene Oxide and Maleic Anhydride

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ABSTRACT: The monomer distribution in ethylene oxide–maleic anhydride copolymers catalyzed by $SnCl_4$ has been determined by a proton nmr analysis of the whole chains and a glpc analysis of the glycol ethers obtained upon hydrolysis of the chains. The analyses have established that while the monomer distribution is probably homogeneous from chain to chain, it has a directly observable, long-range nonrandomness which is non-Markoffian. This result is interpreted in terms of a copolymerization model in which the catalyst can either coordinate different combinations of monomers prior to their addition to the chain or can add them directly to the chain. The model also accounts for the $SnCl_4$-generated monomer distributions in copolymers made from related cyclic ethers and anhydrides.

If the relative probabilities of addition of monomers to a growing copolymer chain can be predicted by the knowledge of a finite number of preceding additions, the resulting monomer distribution can be described by Markoffian statistics. This is the situation for most copolymers generated by free radicals. However, the monomer distributions in some copolymers generated by Freidel–Crafts catalysts have irregularities which cannot be described by Markoffian statistics.[1,2] More information about these copolymerizations is required than just a history of the past few events in order to predict the relative addition probabilities.

The monomer distribution in ethylene oxide–maleic anhydride (EO–MA) copolymers, polymerized using $SnCl_4$ as a homogeneous catalyst, is an example of a distribution which cannot be described by Markoffian statistics. The distribution has been determined by nmr analysis of the whole chains and by glpc analysis of the glycol ethers obtained upon hydrolysis of the chains. It appears to be homogeneous from chain to chain but has a directly observable long-range nonrandomness which is distinctly non-Markoffian. (Thus the nonrandomness is different from that of an alternating copolymer or that of a block copolymer.) Such a distribution is consistent with a propagation model in which one chemically unique type of catalyst can either coordinate different combinations of monomers prior to their addition to the chain or can simply add them directly to the chain. The competition between these two kinds of processes produces the non-Markoffian character of the distribution. Simpler models fail to describe all the details of the observed monomer distribution. The model is sufficiently general to describe the $SnCl_4$-generated monomer distributions in copolymers made from related cyclic ethers and anhydrides.

Experimental Section

1. Copolymerizations of Ethylene Oxide and Maleic Anhydride. Ethylene oxide and maleic anhydride were copolymerized in a 100-ml round-bottomed flask fitted with a magnetic stirrer and a 6-in. neck, the latter to allow for immersion in a constant-temperature bath maintained at 33°. The reactants were added in various molar ratios but with the sum of reactants always equal to 0.4 mol. After the addition of reactants, the flask was sealed with a rubber serum cap. Catalyst solution (100 μl containing 0.83 mmol/ml of $SnCl_4$ in cyclohexane) was injected into the reaction mixture by a syringe gun with a micrometer dial. Reaction times were varied from 1.5 to 48 hr to produce low (2–4%) and high (60–80%) conversion copolymers. The extent of reaction was determined by a combination of nmr and gravimetric techniques.

2. Nuclear Magnetic Resonance Spectroscopic Analysis. Proton nmr spectra at 60 and 100 MHz of 15% (by weight) solutions of the copolymers in $CDCl_3$ were obtained using Varian A-60 and HA-100 spectrometers, respectively, with operating probe temperatures of about 35°. The relative

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[1] J. Schaefer, R. J. Kern, and R. J. Katnik, *Macromolecules*, **1**, 107 (1968).

[2] J. Schaefer, *ibid.*, **1**, 111 (1968).