virtually no peaks at the lower wave numbers and would have a large *para*-substitution peak.

The black bis exchange "polymer" produced by D'Alelio and coworkers had three, almost-equal peaks in these regions, indicating a DP considerably less than 3. In fact, the spectrum, in the low wave number region, was almost identical with that of a mixture of the two monomers (I and II). Heating this material to 600° under nitrogen not only increased the peak at 750 cm^{-1} but decreased the *para*-substitution peak at 850 cm^{-1} which is not consistent with the claim that further linear polymerization took place.

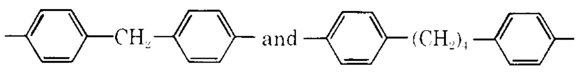
D'Alelio and coworkers[3] used nitrogen analyses as proof of structure for many of their black polymers. Aside from errors in calculated analyses (for example, polymer 5B H-400)[3] difficulties in obtaining complete combustion make this evidence alone very weak. The uncertainty is compounded by yields which are as high as 110% indicating contamination by low molecular weight compounds such as benzylideneaniline. The only complete and consistent analysis reported by D'Alelio and coworkers was for a sample of polymer III, which, as shown in Table I, was much closer to that of the starting materials than to any polymer. Elemental analyses shown for our exchange polymer indicate that it was a trimer, which agrees with the infrared analysis results.

TABLE I
ELEMENTAL ANALYSIS FOR BIS EXCHANGE SCHIFF BASE POLYMERS

	C, %	H, %	N, %
Calcd for $C_{20}H_{16}N_2$ (I or II)	84.51	5.63	9.86
Found: polymer by melt-polymerization[a]	85.59	5.17	9.76
Calcd for $C_{14}H_{10}N_2$ (III, $n = \infty$)	81.53	4.88	13.59
Found: polymer by solution-polymerization	82.50	5.24	12.29
Calcd for trimer ($C_{55}H_{41}N_7$)	82.57	5.17	12.26

[a] See ref 3.

Of further importance is the fact that calculated and experimental electronic spectra of I and II and related compounds indicate that there was very little conjugation between the aromatic rings, unless polar end groups were included in the molecule.[4] The fact that the solution bis exchange products, which have eight or more connected aromatic rings, were only a slightly darker yellow than the starting materials also indicates weak conjugation. Thus the production of simple bis exchange Schiff base polymers that are black tends to be proof against this structure rather than for it. This is especially so where structures such as



are part of the polymer chain.

In a continuing series of papers these workers[5] have reported preparing many black materials by heating molten Schiff base monomers at high temperatures. In these papers the infrared spectra of the products were invariably completely different from the spectra of normal products prepared by these workers using solution-polymerization methods, which again is strong evidence against their postulated structure.

Detailed study of the infrared spectra show that the black materials are complex mixtures, and in many cases prove that there was very little, if any, of the correct type of aromatic substitution for the polymer structure expected. Since no real evidence for the Schiff base structure was presented, we believe that the black materials obtained by the Schiff base exchange in the melt are neither linear polymers nor Schiff bases and are probably cross-linked, condensed, heteroaromatic compounds of very uncertain structure.

Thermal stability studies indicate that these black products are very stable. However, many organic compounds which have been charred at 400–700° for some hours will show very high stability during subsequent thermogravimetric analyses at these temperatures. This stability is due to changes in chemical structure, and unless some effort is made to determine the structural changes, these thermal stability studies can be misleading.

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[5] G. F. D'Alelio, W. F. Strazik, D. M. Feigl, and R. K. Schoenig, *J. Macromol. Sci.*, **A2**, 1457 (1968). This reference lists most of the papers on Schiff base polymers published by these workers to date.

Polyaromatic Pyrazines. I. The Synthesis and a New Method for Increasing Solubility and Modification of Heteropolymer Structures

The condensation of α-amino ketones at moderate temperatures in the presence of air produces excellent yields of 2,5-disubstituted pyrazines. For example, when α-aminoacetophenone hydrochloride is neutralized with ammonium hydroxide in ethanol, it gives a quantitative yield of 2,5-diphenylpyrazine (**2**),[1] demonstrating that the oxidation reaction to afford the aromatic ring proceeds under mild conditions. Because of the high yields from this reaction, we have found it useful in the preparation of polyaromatic pyrazines.

Monomer **3a** was prepared by the bromination of *p*-diacetylbenzene in acetic acid.[2] Monomers **3b** and **3c** were prepared by the Friedel–Crafts acetylation reaction with α-chloroacetyl chloride.[3] Monomers **3a** and **3c** were purified by recrystallization from chloroform, and monomer **3b** was purified by recrystallization from N,N-dimethylformamide. The model compound (**2**) and the polymers were prepared directly from the α-bromoacetophenone and the bis-α-haloaromatic ketones with ammonia in N,N-dimethylacetamide in the presence of air or peroxides (Scheme I).

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[1] G. Nomine, L. Penasse, and V. Delaroff, *Amer. Pharm. Fr.*, **16**, 436 (1958).

[2] P. Ruggli and E. Gassenmeier, *Helv. Chim. Acta*, **22**, 503 (1939).

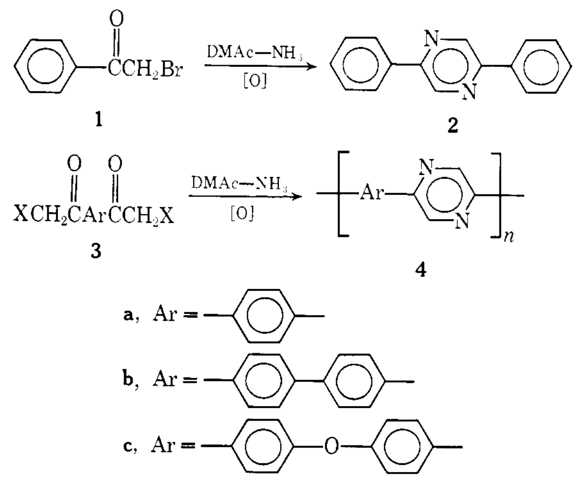
[3] E. Gryszkiewicz-Trachimowski, O. Gryszkiewicz-Trachimowski, and R. S. Levy, *Bull. Soc. Chim. Fr.*, 1156 (1958).

TABLE I
POLYMER PROPERTIES

		Solubility		Viscosity[b] (η_{inh})		Elemental analysis[d]					
						Calcd, %			Found, %		
Polymer	Solvents		H_2O_2[a]		H_2O_2[a]	C	H	N	C	H	N
4a	HCO_2H	Insol.	Sol.		0.40	77.93	3.89	18.18	73.63	4.11	15.75
	H_2SO_4	Insol.	Sol.		1.30						
	H_3PO_4	Insol.	Sol.								
	DMAc	Insol.	P. sol.[c]								
4b	HCO_2H	Insol.	Sol.		0.43	83.47	4.34	12.17	80.76	4.58	9.98
	H_2SO_4	Insol.	Sol.		0.35						
	H_3PO_4	Insol.	Sol.								
	DMAc	Insol.	P. sol.								
4c	HCO_2H	Sol.	Sol.	0.40	0.54	78.04	4.06	11.38	75.79	3.74	9.52
	H_2SO_4	P. sol.	Sol.		0.12						
	H_3PO_4	P. sol.	Sol.								
	DMAc	P. sol.	P. sol.								

[a] 0.25 ml of H_2O_2/15 ml of solvent. [b] 0.25 g of polymer/100 ml of solvent. [c] Partially soluble. [d] Ash content 3–11%.

SCHEME I
PREPARATION OF THE MODEL COMPOUND AND POLYMERS



A thorough study of the preparation of the model compound under similar reaction conditions as those for the polymerization reactions revealed that the model compound could be obtained in quantitative yield. In order to determine the extent to which the polymers had been aromatized in the polymerization reactions, the model compound was prepared under different oxidation conditions. It was found that the model compound could be completely aromatized either by refluxing for several hours while air was passed into the dimethylacetamide solution or by refluxing for a few minutes with a 5% molar excess of 30% hydrogen peroxide or peracid in dimethylacetamide solution. The latter technique did not produce any detectable N→O groups as determined by ir and a mixture melting point with an authentic sample of 2,5-diphenylpyrazine. When the polymers were exposed to the same oxidation procedures as those for the model compound, only a small absorption band was present at 1650 cm^{-1} in the ir spectra for each of the polymers. These small absorption bands are probably due to a small amount of nonaromatized imine linkages, polymer end groups, and/or both.[4]

Polymerizations were carried out in dimethylacetamide–ammonia solution by stirring the monomers for 1 hr at room temperature, 1 hr at 60–70°, and then refluxing for 6–36 hr. Polymer **4c** was soluble in formic acid and partially soluble in concentrated sulfuric acid. Polymers **4a** and **4b** were insoluble in all solvents tried (Table I), but all polymers were quite soluble in formic, phosphoric, and sulfuric acids when 0.25 ml of 30% H_2O_2 was added to the hot solvent–polymer mixtures. The polymers were also partially soluble in dimethylformamide and dimethylacetamide when heated in the presence of peroxides. The increase in solubility is probably due to the introduction of the polar N-oxide group along the polymer chain. Infrared spectra for the modified polymers showed a strong absorption band in the 1220–1270-cm^{-1} region and the oxidized model compound gave a strong band at 1250 cm^{-1} (N→O).[4] These absorption bands were absent in the model compound and polymers **4a** and **4b** before the oxidation reactions were carried out.

Although the polymers are apparently modified by the formation of the polar N-oxide groups, this technique should be very valuable, not only for the modification of the many already existing heteropolymers, but also for studying the solution properties of the insoluble ones. Further studies of the peroxide technique and the modified polymers are in progress. Also the preparation of additional polypyrazines, including a variety of copolymers, is in progress.

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(4) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," 2nd ed, Richard Clay and Co., Ltd., London, 1958, pp 267–271.