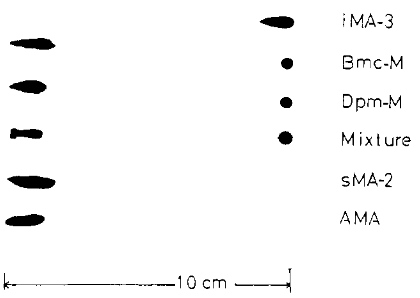

Figure 4. Tlc chromatogram obtained by development of different stereoisomeric types of PMMA with ethyl acetate, *viz.*, isotactic (iMA-3), stereoblock (Bmc-M and Dpm-M), the 1:2 mixture, syndiotactic (sMA-2), and atactic (AMA) PMMA, in order from top to bottom.

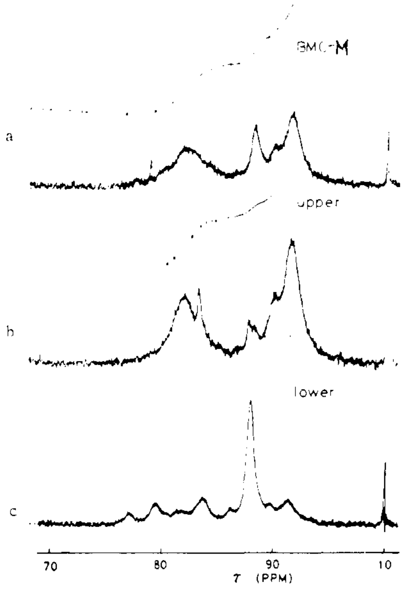

Figure 5. Nmr spectra, obtained in 10% $CDCl_3$ solutions at 60 MHz and at 30°, of original stereoblock polymer Bmc-M, the species contained in the upper and the lower portion separated from Bmc-M with ethyl acetate as developer.

chromatogram thus obtained, in which the two species, the 1:2 mixture, and an atactic PMMA (AMA) prepared with an anionic polymerization technique[11] were developed simultaneously for comparison. This result indicates that the samples Bmc-M and Dpm-M are distinctly separated into an upper and a lower spot.

By using the same procedure employed for the stereoisomeric mixtures the polymer species involved in each spot were recovered and subjected to the nmr analysis. In connection with the extraction of polymer from the thin layer it should be noted that the species thus separated were no longer insoluble in acetone in contrast to the original solubility of the samples in this solvent. Figure 5a shows the nmr spectrum for Bmc-M; Figures 5b and 5c show those for the species contained in the upper and the lower spot, respectively. The spectrum for the upper spot indicates the dominant α-methyl peak at τ 9.13 and the single β-hydrogen peak;[12] for the lower spot the dominant α-methyl peak at τ 8.80 is accompanied by four peaks for the β-hydrogens. In addition, a peak appears in both species at τ 8.98, which may be assigned to heterotactic sequences. On the basis of the nmr data we may conclude that the main components involved in the upper and the lower spot are syndiotactic and the isotactic PMMA, respectively, although these polymers contain considerable amounts of heterotactic sequences.

The relative amount of the two components separated from Dpm-M was determined by a photometric procedure established previously.[2] The chromatogram was developed with a solution of iodine in methanol. The area and blackness of each spot were measured using a photographic negative of the chromatogram. The total blackness was then converted to the amount of polymer by using a factor 1.32 to correct for the difference in the blackness of the isotactic and syndiotactic PMMA spots; iodine molecules have an affinity for the isotactic polymer which is higher by a factor of 1.32 than that for the syndiotactic polymer. The final estimation of the relative amount yielded 0.71 and 0.29 for the syndiotactic and the isotactic portion, respectively, and this is fairly in good agreement with that reported by Liquori, *et al.*[10]

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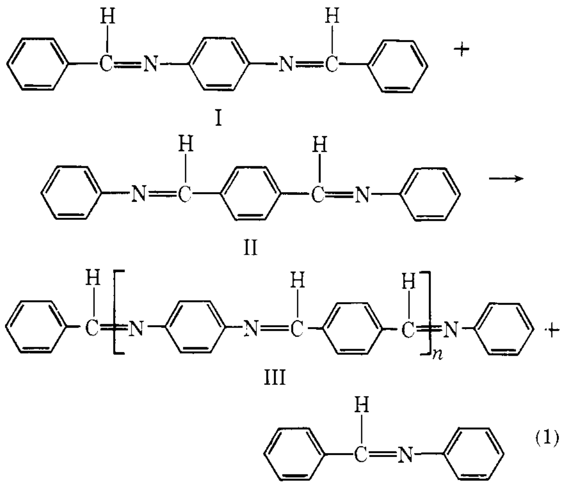
[11] A. Roig, J. E. Fiqueruelo, and E. Llano, *J. Polym. Sci., Part B*, 3, 171 (1965).

[12] F. A. Bovey and G. V. D. Tiers, *ibid.* 44, 173 (1960).

Polymeric Schiff Bases

A considerable amount of work has been carried out in recent years in an effort to obtain high molecular weight conjugated Schiff base polymers.[1,2] However, the insolubility of the growing polymer chains in any inert solvent has precluded this. Recently D'Alelio and coworkers[3] claimed to have produced high molecular weight, highly conjugated Schiff base polymers by a bis-Schiff base exchange reaction, using molten reagents at high temperatures. The exchange reaction is shown in eq 1. The reported infrared spectra of the black



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[1] E. Dyer and C. C. Anderson, *J. Polym. Sci., Part A-1*, **5**, 1659 (1967).

[2] E. W. Neuse, H. Rosenberg, and R. R. Carlen, *Macromolecules*, **1**, 424 (1968). This paper also gives a comprehensive list of the recent papers in this field.

[3] G. F. D'Alelio, J. V. Crivello, R. K. Schoenig, and T. F. Kuemmer, *J. Macromol. Sci.*, **A1**, 1161 (1967).

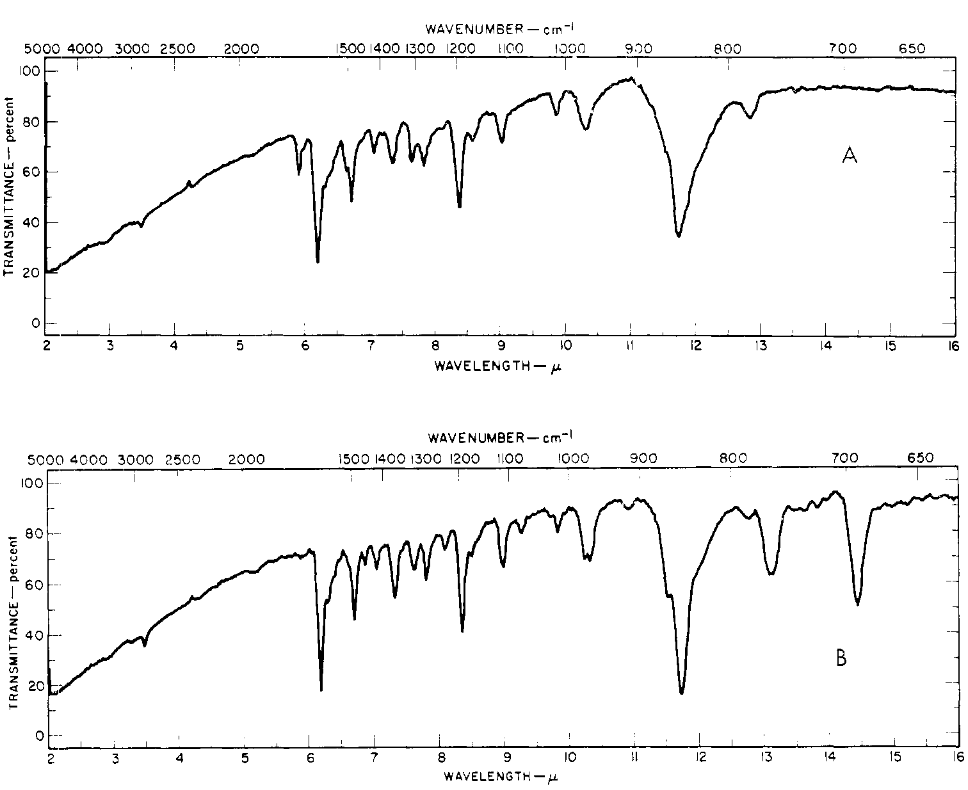

Figure 1. Infrared spectra (KBr): A, solution polymer from *p*-phenylenediamine and terephthalaldehyde; B, solution bis exchange polymer from monomers I and II.

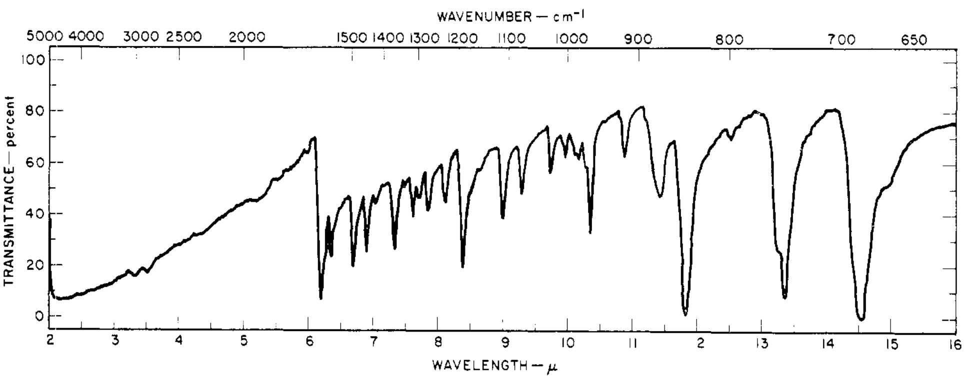

Figure 2. N,N′-Bisbenzylidene-*p*-phenylenediamine (I). KBr disk.

compounds obtained by the above method were totally different from those of polymers prepared by reacting a diamine with a dialdehyde. While some difference could have been due to the presence of different end groups in the two types of polymer, the spectra should have considerable similarities but they did not.

In connection with a program dealing with the synthesis and characterization of a certain type of conjugated Schiff-base polymer,[4] we have also investigated the bis exchange reaction with the same monomers (I and II) using refluxing toluene as solvent, and iodine or zinc chloride as catalyst. We have found that this method gives a controlled reaction at moderate temperatures, and the product precipitates as a clean, yellow solid, which was then extracted with both xylene and alcohol to remove any catalyst or low molecular weight materials. Contrary to D'Alelio's findings, the infrared spectrum of this product was very similar to that of the polymer prepared by normal solution-polymerization of *p*-phenylenediamine and terephthalaldehyde (Figure 1).

A completely *para*-substituted polymer is well suited to infrared analysis, since *para*-disubstituted aromatic compounds have a large absorption peak at about 850 cm^{-1}, whereas monosubstituted aromatic rings have absorption peaks at approximately 750 and 690 cm^{-1}. Both of the starting materials (I, Figure 2, and II) for the bis exchange polymerization have three strong peaks of almost equal intensity at these three positions. Our bis exchange polymer had comparatively small peaks at 750 and 690 cm^{-1} and a large peak at 850 cm^{-1}. The ratios of the peaks indicate a degree of polymerization (DP) between 3 and 4. Thus, high molecular weight exchange polymers would be expected to have

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(4) J. H. Hodgkin, J. Heller, and W. A. Little, ARPA Contract No. DAHC15-68-C-0307 (1969).

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.

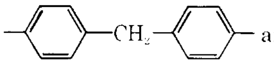
D'Alelio and coworkers[3] used nitrogen analyses as proof of structure for many of their black polymers. Aside from errors in calculated analyses (for example, polymer 5B H-400)[3] difficulties in obtaining complete combustion make this evidence alone very weak. The uncertainty is compounded by yields 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

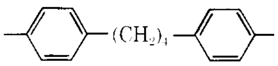
	C, %	H, %	N, %
Calcd for $C_{20}H_{16}N_2$ (I or II)	84.51	5.63	9.86
Found: polymer by melt–polymerization[a]	85.59	5.17	9.76
Calcd for $C_{14}H_{10}N_2$ (III, $n = \infty$)	81.53	4.88	13.59
Found: polymer by solution–polymerization	82.50	5.24	12.29
Calcd for trimer ($C_{55}H_{41}N_7$)	82.57	5.17	12.26

[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



and



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. Nominé, L. Penasse, and V. Deloroff, *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).