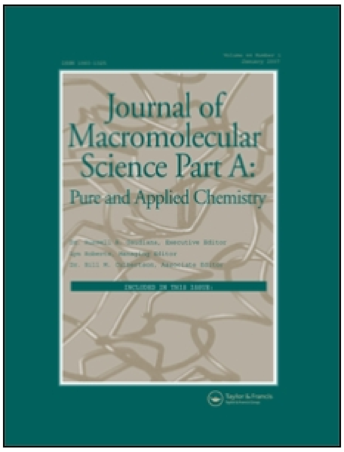

Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Polymeric Schiff Bases. VI. The Direct Syntheses of Poly-Schiff Bases

G. F. D'alelio[a]; J. V. Crivello[a]; R. K. Schoenig[a]; T. F. Huemmer[a]
[a] DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME, NOTRE DAME, INDIANA

To cite this Article D'alelio, G. F. , Crivello, J. V. , Schoenig, R. K. and Huemmer, T. F.(1967) 'Polymeric Schiff Bases. VI. The Direct Syntheses of Poly-Schiff Bases', Journal of Macromolecular Science, Part A, 1: 7, 1321 — 1330

To link to this Article: DOI: 10.1080/10601326708053771

URL: http://dx.doi.org/10.1080/10601326708053771

J. MACROMOL. SCI.—CHEM., A1(7), pp. 1321–1330, Nov., 1967

Polymeric Schiff Bases. VI.
The Direct Syntheses of Poly-Schiff Bases

G. F. D'ALELIO, J, V. CRIVELLO, R. K. SCHOENIG, and
T. F. HUEMMER
DEPARTMENT OF CHEMISTRY
UNIVERSITY OF NOTRE DAME
NOTRE DAME, INDIANA

Summary

The synthesis of black, high molecular weight polymeric Schiff bases directly from aryldiamines and aryldialdehydes by two methods is described. The first method utilizes benzylideneaniline as the reaction medium. The second method is a direct one-step synthesis involving the reaction of the aryldiamine, aryldialdehyde, aniline, and benzaldehyde. The thermogravimetric analyses of the polymers thus prepared compared favorably with similar polymers prepared by the bis-Schiff base exchange method.

It has been shown in previous reports (*1,2*) that black polymeric Schiff base could be prepared most satisfactorily by the bis-Schiff base exchange method (3). The bis-Schiff base exchange reaction can be expressed (*1*) as

$$n\underset{\text{(I)}}{\mathrm{ArCH{=}NAr'N{=}HCAr}} + n\underset{\text{(II)}}{\mathrm{ArN{=}HCAr''CH{=}NAr}} \rightarrow \underset{\text{(III)}}{\mathrm{ArCH{=}[NArN{=}HCAr''CH]_{\mathit{n}}{=}NAr}} + (2n-1)\underset{\text{(IV)}}{\mathrm{ArCH{=}NAr}} \tag{1}$$

wherein Ar is aryl and Ar′ and Ar″ are arylene moieties.

Three steps are involved in this method:

1. The preparation of monomer (I) from an aryl diamine and an aryl monoaldehyde.

2. The preparation of monomer (II) from an aryl dialdehyde and an aryl monoamine.

3. The reaction of (I) with (II) to eliminate the by-product Schiff base (IV) with the formation of polymer (III).

Preliminary studies undertaken to simplify this multistep synthesis were not successful. When the aryl diamines and aryl dicarbonyl compounds were reacted (*1*) in solution, in a large variety of solvents under various conditions, only intractable, yellow, brick-dust polymers were obtained. It was also observed that black poly-Schiff bases could not be obtained by slow heating of the mixture of *p*-phenylenediamine and terephthaldehyde but they could be synthesized by a rapid melting of the reagents. Under such drastic conditions the reaction was difficult to control, particularly if tractable polymers were desired. The amine and aldehyde exchange methods were less satisfactory than the bis exchange technique for the preparation of the poly-Schiff bases. However, satisfactory black polymers were obtained when the amine and aldehyde exchanges were performed in the presence of benzylideneaniline; these reactions were shown (*1*) to be equivalent to the bis exchange reaction.

In the bis exchange method, the benzylideneaniline functioned (*1*) to maintain homogeneity in the reaction mixture; the homogeneity appeared to be influenced (*1*) by the presence of related end groups in the polymer. In addition, the dissolution of the intractable yellow brick-dust polymers in benzylideneaniline (*1*) allowed the condensation to proceed to the more highly conjugated black polymers. These observations led to considering the use of monomeric Schiff bases, ArCH═NAr, as solvents for the direct condensation of aryldiamines and aryldialdehydes:

$$n\mathrm{H_2NAr'NH_2} + n\mathrm{OHCAr''CHO} \xrightarrow{n\mathrm{ArCH{=}NAr\ (IV)}} \mathrm{H_2{=}\!\!\left[NAr'N{=}HCAr''CH\right]_{\!n}\!{=}O} + (2n-1)\mathrm{H_2O} \quad (2)$$

This method would involve a two-step synthesis:

1. The preparation of ArCH═NAr (IV) from the amine and the aldehyde.

2. The condensation of the diamine and dialdehyde in the presence of adequate amounts of Schiff base (IV) to form the polymer with the elimination of water and the recovery of Schiff base (IV).

Since aldehydes and amines undergo exchange reaction with

Schiff base, the end groups in the polymer will correspond to those in the solvent (IV):

$$\begin{aligned}&H_2\!=\!\!\left[NAr'N{=}HCAr''CH\right]_{\overline{n}}\!O + m\,ArCH{=}NAr \rightarrow \\ &ArCH\!=\!\!\left[NAr'N{=}HCAr''CH\right]_{\overline{n}}\!NAr + (m-2)ArCH{=}NAr + ArCHO + ArNH_2 \qquad (3)\end{aligned}$$

To simplify the two-step synthesis even further, it was speculated that the separate preparation of ArCH=NAr (IV) could be avoided by using appropriate quantities of $ArNH_2$ and ArCHO as the reaction medium for $Ar'(NH_2)_2$ and $Ar''(CHO)_2$.

This paper reports the direct synthesis of Schiff bases by reaction of (1) aromatic dialdehyde with aromatic diamine in benzylideneaniline and (2) dialdehydes with diamines in a mixture of benzaldehyde and aniline.

POLYMERIZATIONS

Freshly purified diamines, dialdehydes, aniline, benzaldehyde, and benzylideneaniline were used in the polymerization (*4*).

Melt Polymerizations of Diamines and Dialdehydes

The arylenediamine (0.005 mole) and the arylenedialdehyde (0.005 mole) were ground together in a mortar and pestle in a dry box in a dry nitrogen atmosphere (*1*). The mixture was then transferred to a 1-in.-diameter, 50-ml Pyrex glass reaction tube (*1*) equipped with a nitrogen capillary inlet supported by a Teflon adapter, a side arm to which was attached a condenser with an adapter for evacuation, and a receiver. After the nitrogen inlet tube was inserted into the top of the reaction tube, a very slow stream of nitrogen was passed over the reaction mixture and the tube assembly inserted into an aluminum block preheated to and controlled at 300°C by a Cole-Parmer Model 1422-071 ProportioNull electronic controller as previously described (*1*). The reaction mixture was maintained at 300°C at atmospheric pressure for 4 hr; then the pressure was reduced to 1.5 mm Hg and heating continued for an additional 2 hr at 399°C. Table 1 lists the pairs of aldehydes and amines evaluated as well as the yield and colors of the polymers obtained.

None of the polymers obtained by the direct reaction of any of the pairs of isomeric diamines with the isomeric dialdehydes were homogeneous throughout. Only the *m*-diamine-*m*-dialdehyde

TABLE 1

Melt Reaction of Selected Dialdehydes and Diamines at 300°C

Reactants		Polymer % yield	Color of product	Fluidity of reactants
Terephthaldehyde	*p*-Phenylenediamine	86.1	Brown	No melt
Terephthaldehyde	*m*-Phenylenediamine	85.0	Black-brown	No melt
Isophthaldehyde	*p*-Phenylenediamine	91.0	Green-brown	No melt
Isophthaldehyde	*m*-Phenylenediamine	96.7	Shiny black	No melt

reactant pair softened perceptibly when heated at 300°C and even in this case a clear melt was not obtained, although fusion was most obvious. As a result, the *m*-dialdehyde-*m*-diamine reaction pair afforded the most uniform polymer. The most inhomogeneous polymer was obtained from the *p*-dialdehyde-*p*-diamine reaction pair, and the inhomogeneity of the polymers obtained from the *p*-dialdehyde-*m*-diamine and the *m*-dialdehyde-*p*-diamine pairs were intermediate to the products obtained from the para-para and the meta-meta pairs.

Polymerization of Diamines and Dialdehydes in Benzylideneaniline

Equimolar quantities (0.01 mole) of the aryldiamine and the aryldialdehyde together with the desired amount of benzylideneaniline were mixed, ground, and transferred to the reaction tube, and reacted by the procedure given above for the melt polymeriza-

TABLE 2

Polymerization of the Isomeric Xylylidenedialdehydes with Xylylidenediamines in Benzylideneaniline

Polymer number	Mole ratio of reactants			Yield, %	Fluidity of reactants	Polymer appearance
	$OHCC_6H_4CHO$	$H_2NC_6H_4NH_2$	$C_6H_5CH{=}NC_6H_5$			
1	1-para	1-para	0.33	88.8	No melt	Brown powder
2	1-para	1-para	0.66	101.2	Melt	Shiny black
3	1-para	1-meta	0.33	84.2	No melt	Black powder
4	1-para	1-meta	0.66	90.6	Melt	Shiny black
5	1-meta	1-para	0.33	86.4	No melt	Black powder
6	1-meta	1-para	0.66	89.8	Melt	Shiny black
7	1-meta	1-meta	0.33	95.5	Partial melt	Shiny black
8	1-meta	1-meta	0.66	105.0	Melt	Shiny black

TABLE 3

Polymerization of 1 Mole of Aryldiamines and 1 Mole of Aryldialdehydes in 0.5 Mole of Benzylideneaniline

Polymer number	Dialdehyde	Diamine	Color	Yield at 400°C, %
9	$p\text{-}\mathrm{OHCC_6H_4CHO}$	$p\text{-}\mathrm{H_2NC_6H_4SC_6H_4NH_2}$	Black	109.1
10	$p\text{-}\mathrm{OHCC_6H_4CHO}$	$p\text{-}\mathrm{H_2NC_6H_4OC_6H_4NH_2}\text{-}p$	Black	110.6
11	$p\text{-}\mathrm{OHCC_6H_4CHO}$	$p\text{-}\mathrm{H_2NC_6H_4SO_2C_6H_4NH_2}\text{-}p$	Black	105.3
12	$p\text{-}\mathrm{OHCC_6H_4CHO}$	$p\text{-}\mathrm{H_2NC_6H_4CH_2C_6H_4NH_2}\text{-}p$	Black	104.8
13	$p\text{-}\mathrm{OHCC_6H_4CHO}$	$p\text{-}\mathrm{H_2NC_6H_4CH{=}CHC_6H_4NH_2}\text{-}p$	Black	106.4

tion of diamines and dialdehydes. Following heating at 300°C, the temperature was raised over a period of 3 hr to 400°C at 1.5 mm Hg and heating continued under these conditions for 18 hr. The data for the reactions of the isomeric xylylidenedialdehydes with the xylylidenediamines in the presence of various amounts of benzylideneaniline is given in Table 2. In those cases in which the concentration of benzylideneaniline was 0.66 mole per each mole of dialdehyde and diamine, complete or partial liquification of the mixture occurred either on mixing or on heating of the reagents. In those mixtures in which 0.33 mole of benzylideneaniline was used none of the mixtures liquefied on mixing; on heating, partial melting was observed only in the case of the meta-meta mixture. However, the remaining three mixtures softened on heating and the color of the mixtures darkened rapidly.

Table 3 summarizes the reaction to 400°C of other equimolar pairs of diamines (1 mole) and dialdehydes (1 mole) in the presence of 0.5 mole of benzylideneaniline by the same procedure used for the synthesis of the isomeric xylylidenephenylenediamine polymers given above. All mixtures yielded melts when heated.

Polymerization of Diamines and Dialdehydes

In a mixture of benzaldehyde and aniline the general procedure described above was used to mix and to charge the reaction tube with equimolar quantities of the diamine and dialdehyde and the flow of nitrogen started. The selected amounts of benzaldehyde and aniline were then introduced into the reaction tube by means of a calibrated 0-2 ml graduated pipet. The tube was then inserted into the aluminum block already preheated to 120°C and the mixture heated at this temperature for 2 hr, during which time water condensed and refluxed from the walls of the reaction tube. Then the apparatus was converted to a distillation system and the water of the reaction distilled slowly from the reaction mixture. When the distillation of the water at this temperature was completed, the reaction was continued under the conditions of time, temperature, and pressure given in Table 4. Portions of the polymers were condensed to 600°C for 20 min using the procedures described previously (*1*).

The four isomeric xylylidenephenylenediamines were prepared from the corresponding dialdehydes and diamines at various molar ratios of benzaldehyde and aniline, and the yield data at 400 and 600°C are summarized in Table 5. Black polymers were obtained from all the reactions given in Table 5; however, when the 1:1:1:1 ratio of reactants was used, only the meta-meta system yielded a satisfactory fluid melt during the condensation. Partial or incomplete melting was found in the para-meta, meta-para, and para-para pairs of reactants. The least satisfactory was the para-para system. All systems yielded satisfactory melts and shiny black polymers when the ratio of reactants was at least 1:1:2:2. The appearance of the melt of the meta-meta system at a ratio of dialdehyde to amine to benzaldehyde to aniline of 1:1:1:1 indicated that the amounts of benzaldehyde and aniline could be reduced. The lowest ratio studied which yielded satisfactory melts for the meta-meta systems was 1:1:0.5:0.5; unsatisfactory melts were obtained at a ratio of 1:1:0.25:0.25.

TABLE 4

Reaction Conditions

Time, hr	Temp., °C	Pressure, mm Hg
1	120	760
1	200	760
4	300	760
4	300	1.5
18	400	1.5

TABLE 5

Direct Synthesis of the Four Isomeric Xylylidenephenylenediamines in Benzaldehyde and Aniline

Polymer number	Mole ratio of reactants				Yield, %		Fluidity of reactants
	$OHCC_6H_4CHO$	$H_2NC_6H_4NH_2$	C_6H_5CHO	$C_6H_5NH_2$	400°C	600°C	
14	1-para	1-para	1.0	1.0	127.0	101.1	No melt
15	1-para	1-para	2.0	2.0	129.6	104.2	Melt
16	1-para	1-para	3.0	3.0	131.4	108.3	Melt
17	1-para	1-meta	1.0	1.0	132.0	117.1	No melt
18	1-para	1-meta	2.0	2.0	153.0	130.0	Melt
19	1-para	1-meta	3.0	3.0	181.1	155.0	Melt
20	1-meta	1-para	1.0	1.0	129.4	112.6	No melt
21	1-meta	1-para	2.0	2.0	136.2	118.8	Melt
22	1-meta	1-para	3.0	3.0	136.9	121.3	Melt
23	1-meta	1-meta	0.5	0.5	111.0	97.3	Melt
24	1-meta	1-meta	0.5	0.5	111.0	96.9	Melt
25	1-meta	1-meta	1.0	1.0	131.0	109.0	Melt
26	1-meta	1-meta	1.0	1.0	133.0	107.0	Melt
27	1-meta	1-meta	2.0	2.0	164.1	118.0	Melt
28	1-meta	1-meta	3.0	3.0	182.2	124.6	Melt

THERMOGRAVIMETRIC ANALYSES

The thermogravimetric analyses were performed on a du Pont Model 900 differential thermal analyzer in conjunction with a du Pont Model 950 thermogravimetric analyzer using the technique and conditions previously reported (*1*,*2*). The weight of sample used was 10 mg ground to a fine powder of about 50 pieces per milligram. The heating rate was 15°C/min in a stream of dry nitrogen or air at a gas flow rate of 1 standard liter/min.

The thermogravimetric data in nitrogen of a number of polymers prepared by the two direct methods to a condensation temperature of 400°C are given in Table 6.

CONCLUSIONS

Previous conclusions (*1*) have been confirmed; the melt polymerization of aryldiamines with aryldialdehydes is not a promising direct method of synthesis for Schiff base even though a favorable isomer effect was evident when *m*-phenylenediamine was reacted with isophthaldehyde. By appropriate modification of the reaction medium, the direct synthesis of polymeric Schiff bases from aryldiamines and aryldialdehydes was achieved by two methods. The

TABLE 6

Thermogravimetric Data of Some Schiff Base Polymers
Prepared by the Direct Methods

Polymer number	Per cent weight loss at °C							
	400	500	600	700	800	900	1000	1176
2	0	2.0	11.3	18.3	21.1	23.7	25.0	31.9
4	0	3.0	7.8	13.4	14.6	17.0	18.7	25.1
6	0	3.1	7.2	12.9	14.9	17.1	21.2	27.0
8	0	0.0	10.0	19.1	21.6	22.8	24.7	30.2
9	0	1.2	3.0	13.2	23.8	26.8	29.1	30.7
10	0	2.1	14.9	23.7	24.6	26.7	28.0	34.3
11	0	2.4	11.9	17.8	21.5	23.9	24.9	31.0
12	0	3.8	6.7	21.0	28.2	31.9	32.4	37.7
13	0	1.6	7.4	24.1	32.8	34.2	37.4	41.1
15	0	2.0	8.3	14.9	17.7	20.6	21.8	28.7
18	0	2.1	7.0	12.6	14.8	16.6	18.2	23.9
21	0	2.7	7.2	12.9	14.9	16.9	18.8	24.0
23	0	2.1	6.8	12.4	14.2	16.1	17.7	24.1
25	0	1.0	3.8	9.1	11.2	11.4	12.5	23.2

first method utilized benzylideneaniline as the reaction medium whereby it functions as a solvent and as a reactant (*1–3*). The ease of synthesis and the amount of benzylideneaniline required was related to the structure of the polymer resulting from the isomeric structures of the aryldialdehyde and the aryldiamine used in the reaction. The diminishing order of ease of reaction and amounts of benzylideneaniline required for the various isomeric polyxylylidenephenylenediamine was found to be meta-meta > para-meta > meta-para > para-para.

The second method is a direct one-step synthesis which reacts a mixture of aryldiamine, aryldialdehyde, benzaldehyde, and aniline in which the pairs of aryldiamine-aryldialdehyde and benzaldehyde-aniline are used in molar equivalent quantities. The molar ratios evaluated varied from 1:1:0.5:0.5 to 1:1:3:3. The ease of synthesis of the four isomeric xylylidenephenylenediamine polymers paralleled that found for the related syntheses using the dialdehyde and diamine in benzylideneaniline. The *m*-xylylidene-*m*-phenylenediamine polymer was most easily prepared at a 1:1:1:1 mole ratio of diamine, dialdehyde, benzaldehyde, and aniline, and readily prepared at a mole ratio of reactants of 1:1:0.5:0.5. The related isomeric para-meta, meta-para, and para-para polymers were readily prepared at a mole ratio of reactants of 1:1:2:2 but not at 1:1:1:1.

The thermogravimetric analyses of some of the polymers prepared by these two direct methods show that they compare most favorably with similar polymers previously prepared by the bis-Schiff base exchange method (*1*,*2*).

Acknowledgments

This work was supported by Grant NsG339 of the National Aeronautics and Space Administration. The technical assistance of A. Raghunath in the preparation of some of the polymers is acknowledged.

REFERENCES

1. G. F. D'Alelio, J. V. Crivello, R. K. Schoenig, and T. F. Huemmer, *J. Macromol. Sci.*, **A1**, 1161 (1967).
2. G. F. D'Alelio, R. K. Schoenig, and J. V. Crivello, *J. Macromol. Sci.*, **A1**, 1299 (1967).
3. G. F. D'Alelio, J. V. Crivello, T. Kurosaki, and R. K. Schoenig, *J. Macromol. Sci.*, **A1**, 1259 (1967).
4. G. F. D'Alelio, J. V. Crivello, R. K. Schoenig, and T. F. Huemmer, *J. Macromol. Sci.*, **A1**, 1251 (1967).

Zusammenfassung

Es wird die Synthese von schwarzen, hochmolekularen, polymeren Schiff'schen Basen nach zwei Methoden direkt aus Aryldiaminen und Aryldialdehyden beschrieben. In der ersten Methode wird Benylidenanilin als Reaktionsmedium benutzt. Die zweite Methode ist eine Einstufenreaktion der Komponenten Aryldiamin, Aryldialdehyd, Anilin und Benzaldehyd. Thermogravimetrische Analysen der so dargestellten Polymeren geben vergleichbar günstigere Ergebnisse als die von ähnlichen nach der zweifachen Schiff-Basenaustauschreaktion hergestellten Polymeren.

Résumé

Synthèse directe par deux méthodes des bases de Schiff polymériques, noires, à masse moléculaire elevée, à partir d'aryldiamines et aryldialdehydes. La premiére méthode utilise la benzylidene aniline comme milieu réactionnel. La deuxieme méthode est une synthése directe par réaction d'une aryldiamine, d'aryldialdehyde, d'aniline, et du benzaldehyde. Les analyses thermogravimétriques des polyméres ainsi preparés se comparent favorablement avec des polymères analogues preparés par la reaction d'échange de bis-bases de Schiff.

Received by editor May 12, 1967
Submitted for publication August 22, 1967