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. XVII. Azomethine Copolymers

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To cite this Article D'alelio, G. F. , Strazik, W. F. , Feigl, D. M. and Schoenig, R. K.(1968) 'Polymeric Schiff Bases. XVII. Azomethine Copolymers', Journal of Macromolecular Science, Part A, 2: 8, 1457 — 1492

To link to this Article: DOI: 10.1080/10601326808051911

URL: http://dx.doi.org/10.1080/10601326808051911

J. MACROMOL. SCI.—CHEM., A2(8), pp. 1457-1492, December, 1968

Polymeric Schiff Bases. XVII. Azomethine Copolymers

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SUMMARY

Tractable azomethine copolymers are difficult to prepare by solution processes. Melt-polymerization techniques have been used to synthesize random, block, and graft azomethine copolymers in which the repeating units correspond to units derived from either A-B monomers or a pair of A-A and B-B monomers. Not all systems yielded tractable copolymers, and these limitations are discussed. The block copolymers are prepared readily by the reaction of appropriate insoluble oligomers with monomers or by the reaction of two different fusible oligomers. The thermal stabilities of the copolymers are high and comparable to azomethine homopolymers.

INTRODUCTION

Various syntheses of monomeric and polymeric azomethines have been reported in a series of recent papers [1-20].

The direct condensation of aryldicarbonyl compounds with aryldiamines, or the self-condensation of aminoarylcarbonyl compounds, in solution and as melts, yielded, in most cases, low molecular weight, insoluble, infusible brick-dust polymeric azomethines. It was also shown [1, 3-6, 8, 9] that propagation of these brick-dust

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products to higher molecular weight, tractable, black polymers could be accomplished in monomeric azomethines such as benzylideneaniline, which "dissolved" the products as a result of exchange reactions with the termini of the polymer chains:

$$O{=}\!\left[HCAr'CH{=}NAr''N{=}\right]_n H_2 \xrightarrow{C_6H_5CH=NC_6H_5} C_6H_5N{=}\!\left[HCAr'CH{=}NAr''N{=}\right]_n HCC_6H_5 \qquad (1)$$

Alternatively, black, tractable polymers could be synthesized by performing the condensation of the initial reagents in benzylideneaniline, or in the benzaldehyde and aniline components from which the benzylideneaniline was derived:

$$nOHCAr'CHO + nH_2NAr''NH_2 \xrightarrow[\text{or} \atop C_6H_5CHO + C_6H_5NH_2]{C_6H_5CH=NC_6H_5} C_6H_5N{=}\!\left[HCAr'CH{=}NAr''N{=}\right]_n HCC_6H_5 \qquad (2)$$

The reactions of Eq. (2) were shown to be equivalent to the bis exchange reaction:

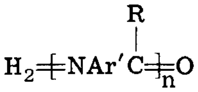
$$nC_6H_5N{=}HCAr'CH{=}NC_6H_5 + nC_6H_5CH{=}NAr''N{=}HCC_6H_5 \longrightarrow C_6H_5N{=}\!\left[HCAr'CH{=}NAr''N{=}\right]_n HCC_6H_5 + (n-1)C_6H_5CH{=}NC_6H_5 \qquad (3)$$

In all cases, propagation was the result of chain-end coupling with the regeneration of benzylideneaniline:

$$2C_6H_5N{=}\!\left[HCAr'CH{=}NAr''N{=}\right]_n HCC_6H_5 \longrightarrow C_6H_5N{=}\!\left[HCAr'CH{=}NAr''N{=}\right]_{2n} HCC_6H_5 + C_6H_5CH{=}NC_6H_5 \qquad (4)$$

Elimination of the benzylideneaniline was complicated by its retention, apparently as a complex, with the polymer in a solid polymer medium, and it could be removed more completely at high temperatures, at which it appeared, also to coreact with the polymer [13-16].

The synthesis of high molecular weight polymeric azomethines would be simplified if the by-product of the condensation was a simple, small, volatile molecule such as water, as would be formed by the interaction of $-NH_2$ and $-CO$ moieties located appropriately in the reactant molecules. Many attempts [1-3] to produce black polymeric azomethines by condensation reactions which eliminated water were not successful. However, it was observed that a number of high molecular weight, black polyketanils [10],


$$H_2\left[NAr'\overset{R}{\overset{|}{C}}\right]_n O$$

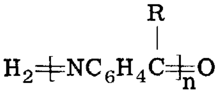
could be prepared in melt systems directly from the A-B type of aminoaryl ketone monomers, $H_2NAr'COR$, without the expedient of adding benzylideneaniline to the reaction mixture. Of the corresponding aminoarylaldehydes, $H_2NAr'CHO$, only the o-aminobenzaldehyde produced [10] homogeneous black polymeric melts, whereas infusible, intractable brick-dust trimers of melting points above 300°C were obtained from the condensations involving m- and p-aminobenzaldehyde, respectively. It was similarly noted that a number of black, high molecular weight polyketanils [8] could also be prepared directly in melt systems by the reaction of aryldiketones, $RCOArCOR$, with aryldiamines, H_2NArNH_2.

These observations led to this related study. First, consideration was given to the use of monomeric aminocarbonyl compounds as "solvents" for the readily prepared low molecular weight yellow-to orange-colored intractable, brick-dust polymeric azomethines. Since "solvents" of this type have reactive moieties which can react with the functional terminal groups of the brick-dust polymer chains without terminating the chains, chain propagation to higher molecular weight, tractable polymers could occur by the simultaneous elimination of water and block copolymer formation. Data on copolymeric azomethines, whether block or random, appear to be absent in the literature. Accordingly, it was of secondary interest to attempt the syntheses of tractable, random azomethine copolymers by using aminoarylcarbonyl monomers and aryl diketones as reactant "solvents," particularly in those polymerization systems whose reactants normally produce intractable, brick-dust polymeric azomethines. In these systems, "solvents" of this type would react statistically, without causing termination of the propagating chains, to yield random copolymers.

These studies were undertaken with the expectation that they would permit the syntheses of a wide variety of high molecular weight, block-, and random-copolymeric azomethines which would pass through a fusible, or at least a tractable, stage. The three block and two random copolymer systems investigated are classified as follows.

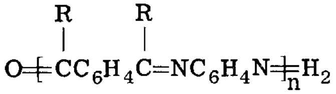
Type I Block Copolymers

This class of block copolymers involves the reaction of oligomeric brick-dust polyazomethines with aminoarylcarbonyl monomers. Typical oligomeric brick dusts were selected from a large variety of A-B oligomers, such as



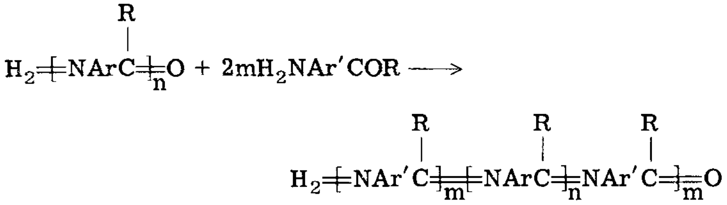
$$H_2\big[NC_6H_4\overset{R}{\overset{|}{C}}\big]_nO$$

or of the A-A: B-B type, such as

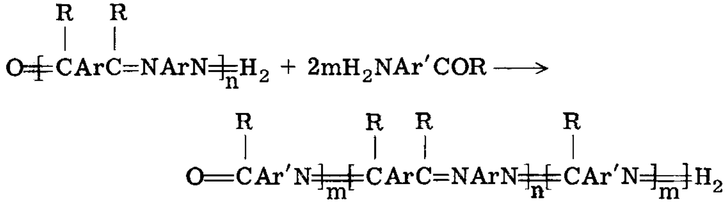


$$O\big[\overset{R}{\overset{|}{C}}C_6H_4\overset{R}{\overset{|}{C}}{=}NC_6H_4N\big]_nH_2$$

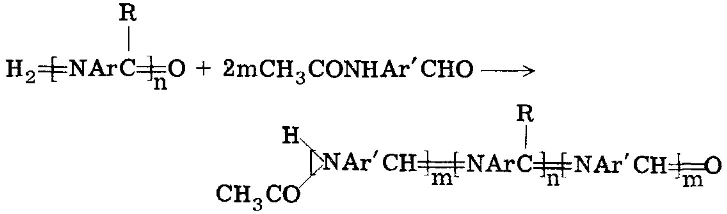
which have been previously reported [1, 8, 9-11]. Some typical reactions for type I block formation can be generalized as



$$H_2\big[NAr\overset{R}{\overset{|}{C}}\big]_nO + 2mH_2NAr'COR \longrightarrow H_2\big[NAr'\overset{R}{\overset{|}{C}}\big]_m\big[NAr\overset{R}{\overset{|}{C}}\big]_n\big[NAr'\overset{R}{\overset{|}{C}}\big]_mO \qquad (5)$$

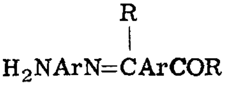


$$O\big[\overset{R}{\overset{|}{C}}Ar\overset{R}{\overset{|}{C}}{=}NArN\big]_nH_2 + 2mH_2NAr'COR \longrightarrow O{=}\overset{R}{\overset{|}{C}}Ar'N\big]_m\big[\overset{R}{\overset{|}{C}}Ar\overset{R}{\overset{|}{C}}{=}NArN\big]_n\big[\overset{R}{\overset{|}{C}}Ar'N\big]_m\big\}H_2 \qquad (6)$$



$$H_2\big[NAr\overset{R}{\overset{|}{C}}\big]_nO + 2mCH_3CONHAr'CHO \longrightarrow \genfrac{}{}{0pt}{}{H}{CH_3CO}\!\!>\!NAr'CH\big]_m\big[NAr\overset{R}{\overset{|}{C}}\big]_n\big[NAr'CH\big]_mO \qquad (7)$$

Equimolar amounts of a dicarbonyl compound, $Ar(CRO)_2$, and a diamino compound, $Ar(NH_2)_2$, can be considered as equivalent to the aminocarbonyl monomers, $H_2NArCOR$, of Eq. (5), since on reaction they yield

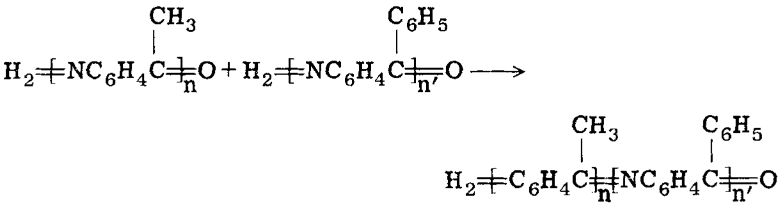


$$H_2NArN{=}\overset{R}{\overset{|}{C}}ArCOR$$

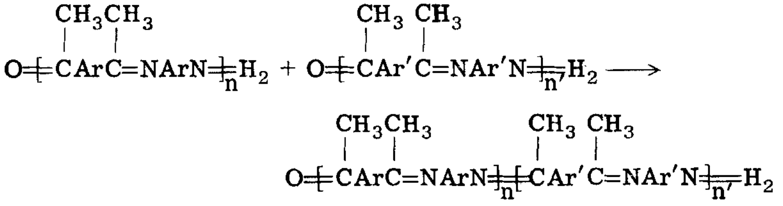
intermediates, and so these systems were also evaluated in this study.

Type II Block Copolymers

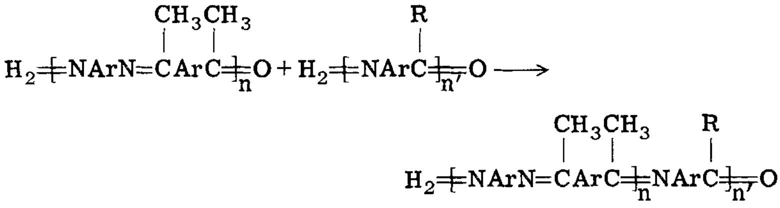
This class of block copolymers is synthesized from pairs of fusible, tractable oligomers; some typical reactions can be generalized as



$$H_2{=}\left[NC_6H_4\overset{CH_3}{\overset{|}{C}}\right]_n{=}O + H_2{=}\left[NC_6H_4\overset{C_6H_5}{\overset{|}{C}}\right]_{n'}{=}O \longrightarrow H_2{=}\left[C_6H_4\overset{CH_3}{\overset{|}{C}}\right]_n\left[NC_6H_4\overset{C_6H_5}{\overset{|}{C}}\right]_{n'}{=}O \quad (8)$$

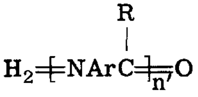


$$O{=}\left[\overset{CH_3}{\overset{|}{C}}Ar\overset{CH_3}{\overset{|}{C}}{=}NArN\right]_n{=}H_2 + O{=}\left[\overset{CH_3}{\overset{|}{C}}Ar'\overset{CH_3}{\overset{|}{C}}{=}NAr'N\right]_{n'}{=}H_2 \longrightarrow O{=}\left[\overset{CH_3}{\overset{|}{C}}Ar\overset{CH_3}{\overset{|}{C}}{=}NArN\right]_n\left[\overset{CH_3}{\overset{|}{C}}Ar'\overset{CH_3}{\overset{|}{C}}{=}NAr'N\right]_{n'}{=}H_2 \quad (9)$$



$$H_2{=}\left[NArN{=}\overset{CH_3}{\overset{|}{C}}Ar\overset{CH_3}{\overset{|}{C}}\right]_n{=}O + H_2{=}\left[NAr\overset{R}{\overset{|}{C}}\right]_{n'}{=}O \longrightarrow H_2{=}\left[NArN{=}\overset{CH_3}{\overset{|}{C}}Ar\overset{CH_3}{\overset{|}{C}}\right]_n\left[NAr\overset{R}{\overset{|}{C}}\right]_{n'}{=}O \quad (10)$$

As a modification of Eq. (10), similar to that mentioned for the type I block copolymers, the fusible oligomer,



$$H_2{=}\left[NAr\overset{R}{\overset{|}{C}}\right]_{n'}{=}O$$

can be reacted with equimolar portions of $Ar(COR)_2$ and $Ar(NH_2)_2$ instead of with the fusible A-A plus B-B type of oligomer.

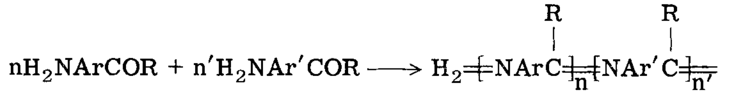
Type III Block Copolymers

The synthesis of this class would involve reacting an infusible, high molecular weight, black polymeric azine with aminoarylcarbonyl monomers, which normally homopolymerized to tractable, fusible polymers, to determine whether or not they would become grafted to the infusible, polymeric azines. Conceivably, in such cases, grafting would occur by the reaction of the terminal $-NH_2$ or C=O groups in the polymers with the complimentary H_2N- or C=O group in the $H_2NArCOR$ monomers, or in their equivalent, equal molar quantities of $Ar(COR)_2$ with $Ar(NH_2)_2$. Accordingly, such copolymers are classified as graft-block copolymers.

Graft copolymerization of this type would permit the fabrication of infusible polyazomethines by the simple expedient of dispersing the infusible polymer in a monomer or tractable polymer, which would act as a temporary plasticizer, and, then, forming the mass under heat and pressure to achieve graft copolymerization simultaneously with the formation of a structure of the desired shape.

Random Copolymers

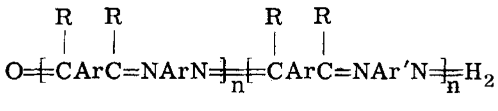
The polymers of this system would contain two different types of repeating units and would be prepared directly from unpolymerized monomers. The simplest polymer would be one derived from two A-B monomers (class I) as given by



$$nH_2NArCOR + n'H_2NAr'COR \longrightarrow H_2{=}\left[NAr\overset{R}{\overset{|}{C}}{=}\right]_n\left[NAr'\overset{R}{\overset{|}{C}}{=}\right]_{n'} \quad (11)$$

Random copolymer should also result from the reaction of a multiplicity of A-A with B-B monomers (class II), such as

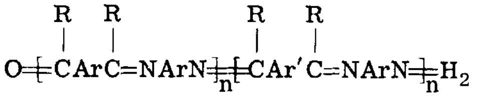
$$2nRCOArCOR + nH_2NArNH_2 + nH_2NAr'NH_2 \longrightarrow$$



$$O{=}\left[\overset{R}{\overset{|}{C}}Ar\overset{R}{\overset{|}{C}}{=}NArN{=}\right]_n\left[\overset{R}{\overset{|}{C}}Ar\overset{R}{\overset{|}{C}}{=}NAr'N{=}\right]_n H_2 \quad (12)$$

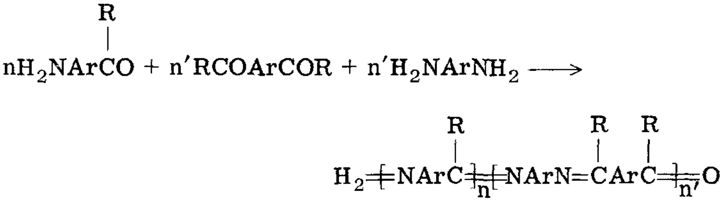
and

$$2nH_2NArNH_2 + nRCOArCOR + nRCOAr'COR \longrightarrow$$



$$O{=}\left[\overset{R}{\overset{|}{C}}Ar\overset{R}{\overset{|}{C}}{=}NArN{=}\right]_n\left[\overset{R}{\overset{|}{C}}Ar'\overset{R}{\overset{|}{C}}{=}NArN{=}\right]_n H_2 \quad (13)$$

as well as by a combination of A-B monomers with A-A plus A-B monomers, thus,



$$nH_2NAr\overset{\overset{R}{|}}{C}O + n'RCOArCOR + n'H_2NArNH_2 \longrightarrow H_2{=}\!\left[NAr\overset{\overset{R}{|}}{C}{=}\right]_n\!\left[NArN{=}\overset{\overset{R}{|}}{C}Ar\overset{\overset{R}{|}}{C}{=}\right]_{n'}O \quad (14)$$

In Eq. (11)-(14), the segmers represented by n and n′ are located statistically in the chain and are shown in brackets only as a matter of convenience.

The copolymers of this study were prepared by melt procedures previously published [1, 4, 6, 8-10]. To contrast with the melt procedures, the syntheses of a number of copolymers were attempted using solution methods to determine whether or not the disorder, resulting in the polymer from the use of a plurality of monomers, would contribute some measure of solubility.

EXPERIMENTAL

Reactants

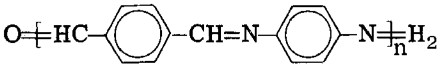
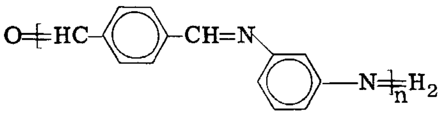
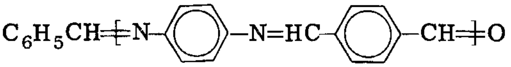
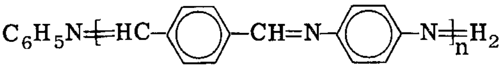
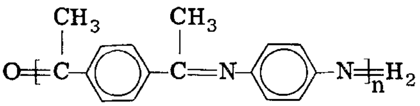
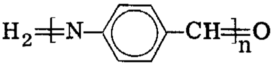
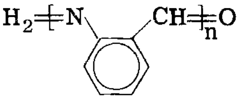
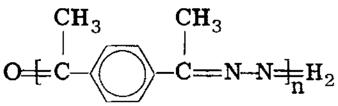
Monomers. The purification or synthesis of the aryldiamines, aryldicarbonyl, and the aminoarylcarbonyl compounds used in this study have been reported previously [2, 8, 10].

Brick-Dust Polyazomethines. The synthesis of the intractable, brick-dust oligomeric azomethines used as reactants in this study have been reported previously or prepared by procedures previously published [1, 8-11] and are given in Table 1.

Fusible, Low Molecular Weight Polyazomethines. Melt condensation procedures, previously published [1, 8, 10], were used to synthesize the fusible, tractable, low molecular weight polymers used in this study. The condensations were performed to the stage where the softening point of the polymers was at least 100°C, and the data are given in Table 2.

Infusible, Black Polyazomethines. Previously published melt-polymerization procedures [1, 8, 10] were used to prepare the insoluble, infusible, high molecular weight polymers used in this study, and all of them were substantially insoluble in concentrated sulfuric acid at room temperature. The maximum temperature used in synthesis of the polymer is designated according to previous codings [1] by the suffix H followed by the maximum temperature used. The data on the polymers used are given in Table 3.

Table 1. Data on Infusible Oligomeric Azomethines Used as Reactants

Oligomer	Structure	Color	Value[a] of n	Ref.
I-Y		Yellow	4.0	[1]
II-Y		Yellow	4.8	[1]
III-Y		Orange	5.1	[1]
IV-Y		Yellow	3.2	[1]
V-Y		Yellow	3.4	[8]
VI-Y		Yellow	3.0	[10]
VII-Y		Yellow-brown	6.0	[10]
VIII-Y		Yellow	2.0	[11]

[a]Value estimated from analytical data.

Table 2. Data on Fusible Oligomeric Azomethines Used as Reactants

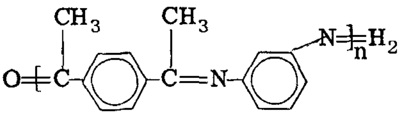
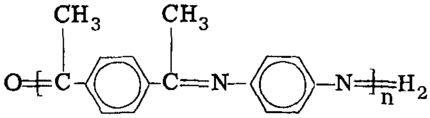
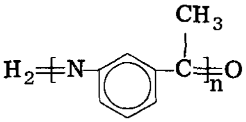
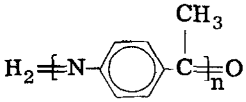
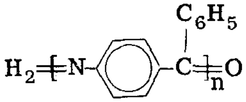
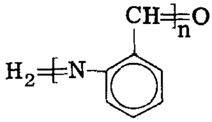
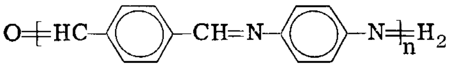
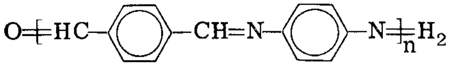
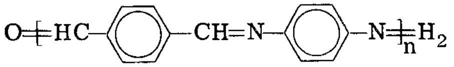
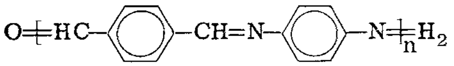
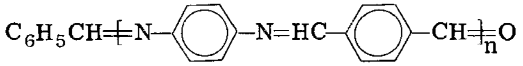
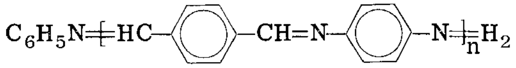
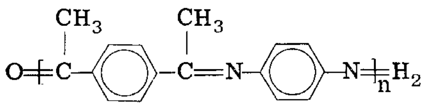
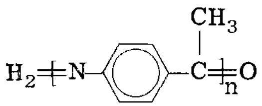
Oligomer	Structure	Color	Softening temp., °C	Ref.
I-F		Brown	111	[8]
II-F		Brown	133	[8]
III-F		Brown	98	[10]
IV-F		Dark brown	107	[10]
V-F		Black	110	[10]
VI-F		Black	158	[10]

Table 3. Data on Infusible Black Polyazomethines Used as Reactants

Polymer	Maximum temp., °C	Structure[a]	Ref.
I-B	H260		[1]
II-B	H400		[1]
III-B	H600		[1]
IV-B	H1176		[1]
V-B	H380		[1]
VI-B	H400		[1]
VII-B	H400		[8]
VIII-B	H400		[10]

[a] These structures are idealized structures and the polymers which have been heated at 400°C or higher contain other structures resulting from inter- and intramolecular reactions [1, 14-16].

Copolymerizations

In Solution. The copolymerizations were performed using 0.02 mole as the total weight of monomer in 150 ml of solvent and 0.02 g of zinc chloride as a catalyst, when used. When benzene was used as the inactive solvent, the continuous azeotropic method was used [1]. Dimethylacetamide (DMAC) was evaluated also, as an active solvent [1]. Insoluble polymers were separated from DMAC by filtration; the soluble polymers were isolated by distillation of the DMAC from the reaction mass at 15 mm Hg pressure. Table 4 summarizes the data on the random copolymers prepared in solution.

Melt Copolymerizations. The melt procedure and the thermostatically controlled apparatus previously reported were used [1, 4, 6, 8-10]. An intimate mixture of the reactants was placed in the polymerization tube at room temperature and a nitrogen atmosphere established in the apparatus. The reaction tube was then inserted in the aluminum heat sink at 180°C and the reaction allowed to proceed according to the following schedule:

Temp., °C	Time, hr
180	4
225	2
325	17
400	1

In a number of cases, samples were isolated during or at the end of the time periods at 225, 325, and 400°C for evaluation, and they are designated in accordance with previous coding [1], as the H225, H325, and H400 polymers.

The polymerizations were attempted first as uncatalyzed reactions; when polymerization, as evidenced by an increase in melt viscosity, did not occur readily within 1 hr at 180°C, or was very sluggish, the reactions were repeated using 0.5 wt.% of zinc chloride as the catalyst.

Thermogravimetric Analyses

Thermogravimetric procedures previously published were used [1] and performed on a du Pont 900 differential thermal analyzer in conjunction with a du Pont 950 thermogravimetric analyzer. The sample size was 10 mg ground to a powder of approximately 500 pieces; the rate of heating was 15°C/min in a dry nitrogen or

Table 4. Data on Random Copolymerizations in Solution

Poly-mer	Reactants A	B	C	Mole ratio A : B : C	Solvent[a]	Cata-lyst	% Yield	Characteristic of polymer
S-1	p-$C_6H_4(CHO)_2$	m-$C_6H_4(CHO)_2$	m-$C_6H_4(NH_2)_2$	1 : 1 : 2	B	No	100	Yellow, brick dust
S-2	m-$C_6H_4(CHO)_2$	p-$C_6H_4(CHO)_2$	m-$C_6H_4(NH_2)_2$	1 : 1 : 2	B	No	98	Yellow, brick dust
S-3	p-$C_6H_4(CHO)_2$	m-$C_6H_4(NH_2)_2$	p-$C_6H_4(NH_2)_2$	2 : 1 : 1	B	No	94	Yellow, brick dust
S-4	m-$C_6H_4(CHO)_2$	m-$C_6H_4(NH_2)_2$	p-$C_6H_4(NH_2)_2$	2 : 1 : 1	B	No	93	Yellow, brick dust
S-5	p-$C_6H_4(CHO)_2$	p-$C_6H_4(COCH_3)_2$	m-$C_6H_4(NH_2)_2$	1 : 1 : 2	B	No	89	Yellow, brick dust
S-6	p-$C_6H_4(CHO)_2$	p-$C_6H_4(NH_2)_2$	o-$H_2NC_6H_4CHO$	1 : 1 : 1	B	No	86	Yellow, brick dust
S-7	p-$H_2NC_6H_4CHO$	o-$H_2NC_6H_4CHO$	—	1 : 1 : 0	B	Yes	79	Yellow, brick dust
S-8	p-$H_2NC_6H_4COCH_3$	p-$H_2NC_6H_4CHO$	—	1 : 1 : 0	B	Yes	90	Yellow, brick dust
S-9	m-$C_6H_4(CHO)_2$	p-$C_6H_4(CHO)_2$	m-$C_6H_4(NH_2)_2$	1 : 1 : 2	DMAC	No	93	Yellow, brick dust
S-10	m-$C_6H_4(CHO)_2$	p-$C_6H_4(NH_2)_2$	p-$H_2NC_6H_4COCH_3$	1 : 1 : 1	DMAC	Yes	88	Yellow, brick dust
S-11	p-$C_6H_4(COCH_3)_2$	m-$C_6H_4(NH_2)_2$	p-$C_6H_4(NH_2)_2$	2 : 1 : 1	DMAC	Yes	91	Yellow, brick dust
S-12	p-$H_2NC_6H_4COCH_3$	m-$H_2NC_6H_4COCH_3$	—	1 : 1 : 0	DMAC	Yes	95	Brown, soluble, fusible
S-13	p-$C_6H_4(COCH_3)_2$	m-$C_6H_4(NH_2)_2$	p-$H_2NC_6H_4COCH_3$	1 : 1 : 1	DMAC	Yes	93	Brown, soluble, fusible

[a] B, benzene; DMAC, dimethylacetamide.

Table 5. Type I Block Copolymers from Infusible Oligomers and A-B Monomers

Polymer	Oligomer used	Monomer used[a]	Zinc chloride	%[b] Yield	Analyses per cent H325 C	Analyses per cent H325 H	Analyses per cent H325 N	Analyses per cent H400 N
COP-1A	I-Y	o-$H_2NC_6H_4COCH_3$	No	96	80.29	5.63	12.52	12.64
COP-2A	II-Y	o-$H_2NC_6H_4COCH_3$	No	98	80.31	5.58	12.49	12.68
COP-3A	III-Y	o-$H_2NC_6H_4COCH_3$	Yes	94	81.21	5.56	12.63	12.70
COP-4A	IV-Y	o-$H_2NC_6H_4COCH_3$	Yes	91	81.20	5.52	12.07	12.26
COP-5A	V-Y	o-$H_2NC_6H_4COCH_3$	No	89	80.71	6.01	11.81	11.84
COP-6A	VI-Y	o-$H_2NC_6H_4COCH_3$	No	97	79.02	5.63	12.30	12.44
COP-7A	VII-Y	o-$H_2NC_6H_4COCH_3$	No	97	79.10	5.66	12.34	12.43
COP-8A	VIII-Y	o-$H_2NC_6H_4COCH_3$	No	93	76.56	6.35	14.31	14.52
COP-9A	I-Y	m-$H_2NC_6H_4COCH_3$	Yes	100	80.43	5.52	12.50	12.67
COP-10A	II-Y	m-$H_2NC_6H_4COCH_3$	No	99	80.36	5.61	12.53	12.69
COP-11A	I-Y	p-$H_2NC_6H_4COCH_3$	No	98	80.33	5.53	12.48	12.59
COP-12A	I-Y	p-$CH_3CONHC_6H_4CHO$	Yes	96	80.80	4.98	13.43	13.49

[a] The molar amounts of monomer used corresponded to the value of n of the oligomer so that feed was that of a 1 : 1 copolymer.

[b] All reactions yielded clear, homogeneous melts or solutions at 180°C.

air stream at a gas flow rate of 1 standard liter per minute to a recorded 1200°C temperature, which corresponds to 1176°C when corrected for the nonlinearity of the Chromel-Alumel thermocouple.

Spectral Analyses

A Perkin-Elmer 421 grating spectrophotometer was used to examine the samples prepared as potassium bromide disks.

Postheating of the Polymers

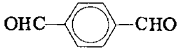
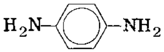
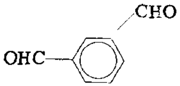
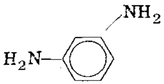
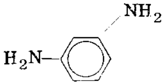
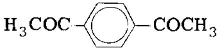
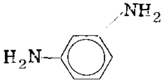
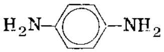
A few samples of the copolymers were postheated to 600 and 1176°C by procedures previously published [1].

The formulations, elemental analyses, and thermogravimetric analyses of the copolymers prepared are given in Tables 5 to 12.

Table 6. Thermogravimetric Analyses in Nitrogen on Some Type I Block Copolymers from Infusible Oligomers and Monomers

Polymer	Atmosphere	Per cent weight loss at °C							
		400	500	600	700	800	900	1000	1176
COP-1A-H400	Nitrogen	0.0	0.0	2.8	8.9	11.9	13.7	14.8	17.9
COP-1A-H600	Nitrogen	0.0	0.0	0.0	2.6	6.5	10.1	11.2	13.9
COP-2A-H400	Nitrogen	0.0	0.0	2.4	4.6	8.0	13.5	14.5	17.6
COP-2A-H600	Nitrogen	0.0	0.0	0.0	1.8	6.2	8.7	10.8	13.2
COP-4A-H400	Nitrogen	0.0	0.0	2.9	9.3	12.2	14.1	15.2	18.3
COP-4A-H600	Nitrogen	0.0	0.0	0.0	2.8	7.3	9.4	11.7	14.6
COP-6A-H400	Nitrogen	0.0	0.0	3.2	9.5	12.5	14.5	15.6	18.8
COP-6A-H600	Nitrogen	0.0	0.0	0.0	3.0	7.2	9.3	11.4	16.2
COP-8A-H400	Nitrogen	0.0	0.0	1.9	3.9	7.6	12.9	13.9	17.5
COP-8A-H600	Nitrogen	0.0	0.0	0.0	2.5	7.0	9.1	12.0	15.3
COP-9A-H400	Nitrogen	0.0	0.0	3.0	9.6	12.7	14.8	15.7	18.7
COP-9A-H600	Nitrogen	0.0	0.0	0.0	2.6	6.2	8.2	11.5	14.9
COP-10A-H400	Nitrogen	0.0	0.0	2.3	4.2	7.7	13.3	14.4	17.6
COP-10A-H600	Nitrogen	0.0	0.0	0.0	3.0	7.2	9.2	11.2	16.0
COP-11A-H400	Nitrogen	0.0	0.0	2.5	4.8	8.2	13.8	14.8	17.8
COP-11A-H600	Nitrogen	0.0	0.0	0.0	1.9	6.5	8.9	10.9	14.3
COP-12A-H400	Nitrogen	0.0	0.0	2.6	5.0	8.3	14.0	15.1	18.1
COP-12A-H600	Nitrogen	0.0	0.0	0.0	2.1	5.7	7.9	11.9	14.8

Table 7. Type I Block Copolymers from Infusible Oligomers with A-A plus B-B Monomers

						Analyses, %			
		Reactants[a]				H325			
Polymer	Oligomer	A-A monomer	B-B monomer	% Yield	Observations at 180°C	C	H	N	H400 N
COP-1B	VI-Y			95	Clear initially, then brick dust	—	—	—	—
COP-2B	VI-Y			97	Partly in solution initially, then more heterogeneous, then brick dust	—	—	—	—
COP-3B	VI-Y			94	Clear solution and melt	81.19	5.76	12.42	12.44
COP-4B	VII-Y			92	Clear solution and melt	80.97	5.72	12.39	12.46
COP-5B	VII-Y			98	Clear solution and melt	81.20	5.70	12.43	12.43

[a] The reactants were used in a 1:1 ratio in amounts which corresponded to the n value of the oligomer, so that the feed would correspond to a 1:1 block copolymer.

Table 8. Thermogravimetric Analyses of Type I Block Copolymers from Infusible Oligomers with A-A plus B-B Monomers

Polymer	Atmosphere	Per cent weight loss at °C						
		500	600	700	800	900	1000	1176
COP-3B-H400	Nitrogen	0.0	2.6	4.9	8.2	13.8	14.7	17.8
COP-3B-H600	Nitrogen	0.0	0.0	0.0	1.4	6.6	10.3	14.0
COP-4B-H400	Nitrogen	0.0	3.2	9.3	12.1	14.3	15.2	18.4
COP-4B-H600	Nitrogen	0.0	0.0	0.0	1.2	5.8	10.7	15.0
COP-5B-H400	Nitrogen	0.0	3.0	9.0	12.0	13.9	14.9	18.1
COP-5B-H600	Nitrogen	0.0	0.0	0.0	2.0	7.7	10.3	15.4

Table 9. Block Copolymers from Mixtures of Fusible Oligomers

Copolymer	Reactants[a]		Melt at 180°C	Analyses, %			
				H325			H400
	Oligomer	Oligomer		C	H	N	N
COP-1C	I-Y	VI-Y	No	—	—	—	—
COP-2C	I-F	III-F	Clear	81.43	6.01	11.41	11.78
COP-3C	I-F	IV-F	Clear	81.37	6.00	11.70	11.84
COP-4C	I-F	V-F	Clear	81.41	5.97	11.78	11.85
COP-5C	II-F	IV-F	Clear	80.81	5.51	12.59	12.67
COP-6C	II-F	VI-F	Clear	83.64	5.53	9.82	9.93
COP-7C	I-Y	IV-F	No	—	—	—	—
COP-8C	III-F	IV-F	Clear	81.04	6.11	11.77	11.88
COP-9C	III-F	V-F	Clear	83.30	5.61	9.79	9.86
COP-10C	I-F	VIII-F	Clear	81.79	5.96	11.90	11.94

[a] Reactants were used in amounts equivalent to a 1 : 1 copolymer.

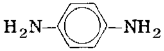
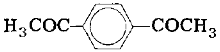
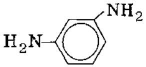
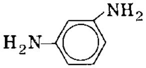
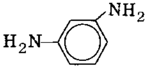
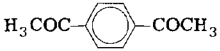
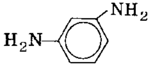
Table 10. Thermogravimetric Analyses of Block Copolymers Prepared from Mixtures of Oligomer

Copolymer	Atmosphere	Per cent weight loss at °C 500	600	700	800	900	1000	1176
COP-2C-H400	Nitrogen	0.0	2.7	5.1	8.4	13.7	14.7	16.9
	Air	2.5	69.3	100.0	—	—	—	—
COP-3C-H400	Nitrogen	0.0	2.1	4.5	9.8	13.8	15.1	17.1
	Air	3.4	71.8	100.0	—	—	—	—
COP-4C-H400	Nitrogen	0.0	3.1	5.7	11.6	14.4	15.2	18.3
	Air	3.7	72.6	100.0	—	—	—	—
COP-5C-H400	Nitrogen	0.0	2.4	4.7	8.1	13.6	14.7	17.5
	Air	3.3	69.7	100.0	—	—	—	—
COP-6C-H400	Nitrogen	0.0	2.3	4.8	10.1	14.2	15.8	17.4
	Air	2.7	71.3	100.0	—	—	—	—
COP-8C-H400	Nitrogen	0.0	2.6	8.3	11.6	13.5	14.4	17.6
COP-8C-H600	Nitrogen	0.0	0.0	1.9	5.8	7.8	10.7	14.8
COP-8C-H1176	Nitrogen	0.0	0.0	0.0	0.0	0.0	0.0	2.0
COP-9C-H400	Nitrogen	0.0	2.9	8.0	9.8	14.8	15.9	21.1
COP-9C-H600	Nitrogen	0.0	0.0	3.3	7.5	9.5	11.1	16.0
COP-9C-H1176	Nitrogen	0.0	0.0	0.0	0.0	0.0	0.0	3.3
COP-10C-H400	Nitrogen	0.0	2.9	8.2	9.7	14.0	15.1	18.5
	Air	3.6	69.9	100.0	—	—	—	—

Graft-Block Copolymerizations. The general procedure consisted in grinding the infusible, black polyazomethines to a very fine powder, to which was added the monomer, and zinc chloride, if used. The mixture was then blended to uniformity, in a Spex-Mixer-Mill, introduced into the polymerization tube, and a nitrogen atmosphere was established in the tube, which was then inserted into the metal heat sink preheated to and controlled at 180°C. The polymerization schedule used was

Temp., °C	Time, hr
180	1
225	1
300	2
400	8

Table 11. Type II Block Copolymers from Fusible Oligomers with A-A Plus B-B Monomers

		Reactants[a]				Elemental analyses			
						H325			H400
Polymer	Oligomer	A-A monomer	B-B monomer	% Yield	Observation at 180°C	C	H	N	N
COP-1D	III-F			91	Heterogeneous, then brick dust	—	—	—	—
COP-2D	III-F			96	Clear solution and melt	81.26	6.04	11.85	11.90
COP-3D	V-F			94	Clear solution and melt	81.31	6.01	11.87	11.93
COP-4D	VI-F			93	Clear solution and melt	82.99	5.70	10.51	10.58
COP-5D	VII-F			97	Clear solution and melt	81.26	5.74	12.40	12.45

[a] A-A and B-B monomers were used in a 1 : 1 molar ratio in amounts with the oligomer to give a 1 : 1 copolymer.

Table 12. Thermogravimetric Analyses of Type II Block Copolymers from Fusible Oligomers with A-A Plus B-B Monomers

Polymer	Atmosphere	Per cent weight loss at °C 500	600	700	800	900	1000	1176
COP-2D-H400	Nitrogen	0.0	3.2	9.6	12.4	14.5	15.7	18.8
COP-2D-H600	Nitrogen	0.0	0.0	0.0	6.5	8.9	11.4	15.3
COP-3D-H400	Nitrogen	0.0	2.9	9.7	12.7	14.4	15.9	18.0
COP-3D-H600	Nitrogen	0.0	0.0	0.0	5.7	8.1	10.7	14.5
COP-4D-H400	Nitrogen	0.0	2.1	4.4	9.7	13.4	14.4	17.4
COP-4D-H600	Nitrogen	0.0	0.0	0.0	6.3	8.3	11.1	14.9
COP-5D-H400	Nitrogen	0.0	1.1	3.8	7.5	13.0	14.2	16.3
COP-5D-H600	Nitrogen	0.0	0.0	0.0	1.0	5.3	10.1	13.8

Duplicate experiments were performed for a number of these copolymerizations so that samples could be withdrawn at the end of the 300°C heating period and extracted with dimethylacetamide and acetone. The infusible polymer and monomer were used in a ratio of 1 g of polymer to 4 g of monomer. None of the mixtures melted during the course of the reaction; at the end of the reaction, the product was isolated as a compact integral button. The data for these polymerizations are summarized in Tables 13 and 14.

DISCUSSION

The reactants for the syntheses of the copolymers of this study were selected so that, in all cases, the by-product of condensation would be a simple molecule such as water, the only exception being the use of formyl acetanilide, which eliminated acetic acid readily. Preliminary studies indicated that they could be prepared relatively easier by the exchange reactions, particularly by the bis-Schiff base exchange reactions [1], but this method was not used, primarily to avoid the complications of inter- and intramolecular reactions that occur in polymer systems containing benzylideneaniline [1, 9, 14-16].

The statistically large number of copolymer compositions possible from the large number of monomers available [1, 6, 8, 10] for this study required first that a choice be made of the monomers to be used. Accordingly, the relatively simple, available monomeric

Table 13. Data on Graft Copolymers from Infusible Polyazomethines and Aminoarylcarbonyl Monomers

Graft copolymer	Reactants used		$ZnCl_2$	%[a] Yield at 300°C	% Yield at 400°C	Analyses of H400 polymers, %		
	Polymer(*)	Monomer				C	H	N
GC-1	I-B-H260	m-$H_2NC_6H_4COCH_3$	No	205	363	81.01	5.98	12.28
GC-2	II-B-H400	m-$H_2NC_6H_4COCH_3$	Yes	238	429	80.93	6.01	12.06
GC-3	III-B-H600	m-$H_2NC_6H_4COCH_3$	Yes	262	408	81.21	6.10	12.43
GC-4	IV-B-H1176	m-$H_2NC_6H_4COCH_3$	Yes	248	437	80.68	5.88	12.19
GC-5	V-B-H380	o-$H_2NC_6H_4CHO$	Yes	226	438	80.66	5.25	12.98
GC-6	VI-B-H400	o-$H_2NC_6H_4CHO$	Yes	243	421	81.11	6.07	12.01
GC-7	VII-B-H400	p-$H_2NC_6H_4COCH_3$	Yes	222	427	81.10	6.33	11.91
GC-8	VIII-B-H400	o-$H_2NC_6H_4CHO$	No	197	378	80.68	6.07	12.23
GC-9	VII-B-H400	o-$H_2NC_6H_4COCH_3$	Yes	228	414	81.09	6.28	12.01
GC-10	VII-B-H400	o-$H_2NC_6H_4COC_6H_5$	Yes	239	432	84.66	5.27	8.82

[a] Based on weight of infusible polymer(*) used as 100%

Table 14. Thermogravimetric Analyses of Some Graft H400-Copolymers

		Per cent weight loss at °C							
Copolymer	Atmosphere	400	500	600	700	800	900	1000	1176
GC-1-H400	Nitrogen	0.0	0.0	2.7	8.8	12.0	13.9	15.0	18.1
	Air	0.0	2.6	70.1	100.0	—	—	—	—
GC-3-H400	Nitrogen	0.0	0.0	3.0	9.2	12.1	14.2	15.2	18.4
	Air	0.0	3.5	72.8	100.0	—	—	—	—
GC-4-H400	Nitrogen	0.0	0.0	2.8	4.7	8.1	13.5	15.4	18.8
	Air	0.0	3.9	72.7	100.0	—	—	—	—
GC-5-H400	Nitrogen	0.0	0.0	2.3	4.7	7.9	13.6	14.6	17.7
	Air	0.0	3.0	71.7	100.0	—	—	—	—
GC-6-H400	Nitrogen	0.0	0.0	2.4	4.9	8.3	13.9	14.9	18.0
	Air	0.0	3.3	71.0	100.0	—	—	—	—
GC-7-H400	Nitrogen	0.0	0.0	2.9	8.6	11.6	14.1	15.0	18.3
	Air	0.0	2.9	68.5	100.0	—	—	—	—
GC-8-H400	Nitrogen	0.0	0.0	2.6	5.0	8.3	13.9	14.8	17.9
	Air	0.0	3.1	69.1	100.0	—	—	—	—
GC-10-H400	Nitrogen	0.0	0.0	1.4	4.1	7.9	13.3	14.5	16.9
	Air	0.0	2.4	70.2	100.0	—	—	—	—

reactants shown in Table 4 were selected. Even with a small number of monomers, the possible number of copolymers is large, since the number of copolymer compositions, from reactants which can produce two different repeating units, is very high between the range of 100 molar per cent of one repeating unit to 100 molar per cent of the second repeating unit. Thus it was decided that those copolymers which contained only two types of repeating units in a 1 : 1 molar ratio would permit ready comparison between the various copolymers, so the monomer feed corresponding to this 1 : 1 composition was used in the syntheses.

Copolymerizations in Solutions

Copolymerizations in solution were undertaken first using a relatively inactive solvent such as benzene, and an active solvent such as dimethylacetamide (DMAC), to determine if soluble or fusible copolymers could be thus prepared. These copolymers are designated as the S series, shown in Table 4.

As a rule, the random copolymerizations in solution of the A-A plus B-B monomers yielded intractable brick-dust polymers whether the solvent was benzene or DMAC, or whether a pair of isomeric A-A aldehyde monomers were reacted with 2 moles of B-B diamine monomer, or a pair of B-B diamine monomers were reacted with 2 moles of A-A aldehyde monomers, as evident in polymers S-1 to S-4 and S-9. In general, it appeared that if the individual pairs of the A-A plus B-B reactants yielded intractable, brick-dust polymers, the copolymers were obtained also as brick dusts, since the disorder in the chain was insufficient to contribute solubility even in DMAC. Similarly, brick-dust copolymers were obtained when even greater linear disorder was introduced in the polymer chain by substituting half the molar quantity of A-A dialdehyde monomer by an A-A diketone monomer in the reaction with a B-B diamine, as in polymer S-5. Similarly, complete substitution of the dialdehyde in polymer S-3 by a diketone in the reaction with a pair of diamines as in polymer S-11 yielded an intractable brick-dust polymer. Modification of the A-A dialdehyde plus B-B diamine reaction by an aminoaryl carbonyl monomer as in polymers S-6 and S-10 also failed to yield tractable polymers. Also the reaction pairs of aminoaldehydes in benzene, as in S-7, or the reaction of an aminoaldehyde with an aminoketone in benzene, as in S-8, yielded intractable polymers. In contrast, the copolymerizations in DMAC of two aminoketones in S-12, or the coreaction of an A-A diketone plus a B-B diamine with an aminoketone as in S-13, yielded soluble, fusible polymers. These results were not unexpected, since (1) the individual low molecular weight polymers of the p- and m-aminoacetophenones, respectively, are very soluble in DMAC [10], and (2) the low molecular weight polymers from p-diacetylbenzene and m-phenylenediamine are slightly soluble in DMAC [8], which solubility is increased by copolymerization with p-aminoacetophenone. In general, it may be concluded that copolymerization in solution does not yield tractable polymers if the monomeric components normally produce individual intractable homopolymers in that specific solvent.

Preliminary experiments, in solution, of such reactant pairs as (1) infusible oligomers (Table 1) with A-B type monomers and (2) pairs of fusible oligomers (Table 2) also yielded intractable products. In view of the broad inapplicability of solution polymerizations for the syntheses of polyazomethines, the melt process was used to attempt the syntheses of the copolymers.

Melt Copolymerizations

Type I Block Copolymers from infusible Oligomers and A-B Monomers. These were prepared by the melt process and are designated as the COP-A series in Table 5. The feed composition for these copolymers, shown in Table 5, corresponds to that required for a 1 : 1 molar ratio of two different repeating units and thus offers a comparison with the S series of copolymers made in solution. The reaction mixtures in the COP series yielded clear, homogeneous melts by the end of the heating period at 180°C; at the end of the 225°C heating period, the intrinsic viscosities in 98% H_2SO_4 were in the range 0.09-0.11 dl/g and the softening points of the low molecular weight copolymers ranged from 190 to 245°C. The initial intrinsic viscosities of the oligomers used were in the range 0.04-0.05 [1], and under similar thermal treatment, in the absence of zinc chloride, the A-B monomers used do not polymerize, while in the presence of zinc chloride, under the same conditions, the intrinsic viscosities in H_2SO_4 of the homopolymers from the A-B monomers range from 0.02 to 0.04 dl/g. The solubilization of the oligomers and the intrinsic viscosity data indicate that copolymerization had occurred. Since the A-B monomers and their homopolymers formed at 225°C are soluble in acetone [10], whereas the oligomers used are insoluble in acetone [1], samples of the H225 polymers were extracted with acetone and dried at 225°C and the increase in weight as a function of the original weight of the oligomer was in the range 7-16%. As the polymerization proceeded, the melt viscosity of the copolymer increased, the color changed progressively from yellow to brown to dark brown, and water of condensation was eliminated. All the copolymers were hard, black, glassy polymers at the end of the 325°C heating period and were insoluble in concentrated sulfuric acid. Samples withdrawn from the reactions of polymers COP-1A and COP-5A after 2 hr of heating at 325°C had intrinsic viscosities in concentrated sulfuric acid of 0.32 and 0.27 dl/g, respectively. The elemental analyses of the H325 polymers are in good agreement with the calculated values for the 1 : 1 copolymers, which would indicate that the polymers had not undergone inter- and intramolecular reactions to any great extent, as occurs readily when the polymers are prepared by exchange reactions [1], particularly those which eliminated an amine or a Schiff base [15, 16]. The infrared spectrum of H325 polymers showed the presence of bands for —C=N— in the region 1600 cm^{-1} with some evidence for the C=O function in the 1700-cm^{-1} region and NH_2 in the 3380-cm^{-1} region; the spectra for the H400 polymers showed the bands for the C=N linkages but not for the NH_2 and C=O functions. The spectra of these copolymers corresponded to those obtained by superimposing the spectra [1, 8, 10] of the oligomers used on the spectrum of the polymerized A-B monomer; for example, the spectrum of COP-1A appeared to be the spectrum of the polymer [1]

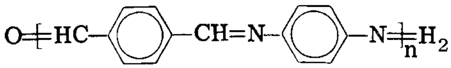
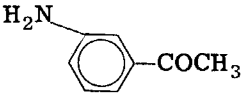
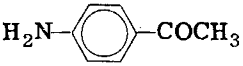
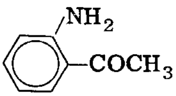
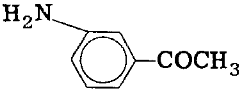
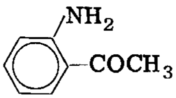
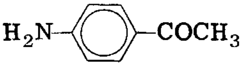
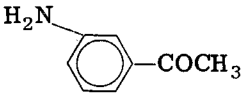
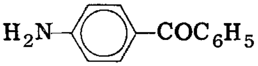
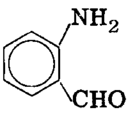
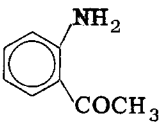
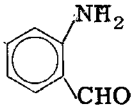
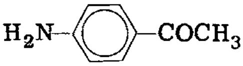
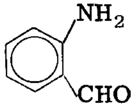
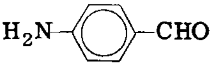


Table 15. Random Copolymers from

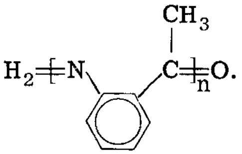
Polymer	Reactants^a			
	Monomer	Mole	Monomer	Mole
RC-1A		1.0		1.0
RC-2A		1.0		1.0
RC-3A		1.0		1.0
RC-4A		1.0		1.0
RC-5A		1.0		1.0
RC-6A		1.0		1.0
RC-7A		1.0		1.0

^{a}All reactions were catalyzed by zinc chloride.

Pairs of A-B Monomers

Observation at 180°C	Analyses, %			
	H325			H400
	C	H	N	N
Melt	80.83	6.07	11.83	11.93
Melt	80.73	6.11	11.81	11.91
Melt	80.91	5.99	11.77	11.89
Melt	83.51	5.66	9.82	9.88
Melt	80.57	5.58	12.60	12.68
Melt	81.01	5.60	12.59	12.66
Brick dust	—	—	—	—

superimposed on the spectrum of the polymer [10]



The thermal stabilities of representative H400 and H600 type I block copolymers are given in Table 6 and, in general, are comparable to the stabilities of typical H400 and H600 polyazomethines previously reported [1, 5-9, 12-16].

Type I Block Copolymers from Infusible Oligomers with A-A plus B-B Monomers. These also were prepared by the melt process and the pertinent data are given in Tables 7 and 8. Homogeneous melts were obtained at 180°C only in those systems in which the A-A plus B-B monomer pairs themselves would homopolymerize to tractable polymers, as evidenced by copolymers COP-3B to COP-5B. This was in contrast with systems COP-1B and COP-2B, which showed some measure of initial homogeneity before becoming heterogeneous and yielded brick-dust polymers. The brick-dust polymers were not characterized further. The analytical values of the copolymers which passed through a clear melt stage are in good agreement with the calculated values, and the thermal properties given in Table 8 are typical values for typical H400 and H600 polyazomethines previously reported [1, 5-9, 12-16].

Type II Block Copolymers from Pairs of Fusible Oligomers. This class of copolymers was synthesized from pairs of fusible oligomers of the type shown in Table 2, and the pertinent data on these copolymers are given in Tables 9 and 10. These copolymers are designated as the COP-C series. Included, for contrast, in the studies of Table 9 are attempts to prepare COP-1C from a pair of infusible oligomers, and COP-7C from a mixture of a fusible and an infusible oligomer; both efforts were unsuccessful. The syntheses of block copolymers from fusible oligomers were more facile, as would be expected, than the synthesis of the type I block copolymers from an infusible oligomer with an A-B or with A-A plus B-B monomers. The elemental analyses of the block copolymers are in good agreement with the calculated values for the 1:1 copolymers, and their infrared spectra corresponded, as in the type I block copolymers, to the superimposition of the spectra of the homopolymers of the two reacting components. The thermal stabilities of this class of block copolymers are summarized in Table 10, and they are comparable to the stabilities of typical polymeric azomethines [1, 5-9, 12-16].

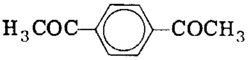
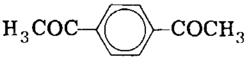
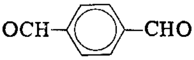
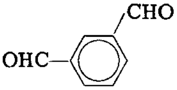
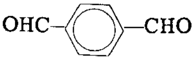
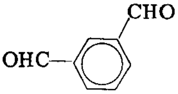
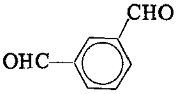
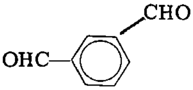
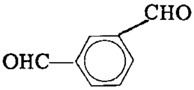
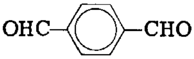
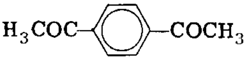
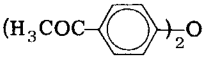
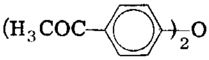
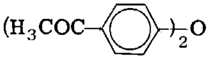
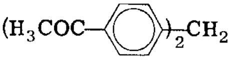
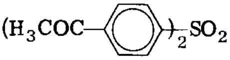
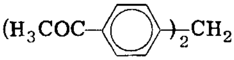
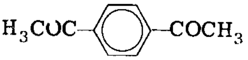
Type II Block Copolymers from Fusible Oligomers with A-A Plus B-B Monomers. The pertinent data are given in Tables 11 and 12, and these copolymers are designated as the COP-D series. As in the case of the type I block copolymer series, only those systems were successful in which the A-A with B-B monomers normally would yield fusible homopolymers, as seen for COP-3D to COP-5D. The system for COP-1D was not successful, although it had been anticipated that a homogeneous melt would be obtained due to the solubilizing effect of the fusible oligomer III-F. Such was not the case, and the result confirmed the similar results obtained for the type I block copolymers, COP-1B and COP-2B. The elemental analyses shown in Table 11 of the copolymers which yielded homogeneous melts and their thermal analytical data, shown in Table 12, are typical of polymeric azomethines.

Type III Block Copolymers from Infusible Polymers with A-B Monomers. The systems evaluated for the synthesis of this class of copolymers and the pertinent data are given in Tables 13 and 14. The per cent yields given in Table 13 have been calculated on the amount of initial infusible polymer as the 100% basis. The yield values of the H300 polymers at 300°C were obtained by extracting samples of the polymers first with DMAC, then with acetone, followed by drying at 200°C. These extractions removed unreacted monomers and low molecular weight homopolymers, if any, of the aminoketones

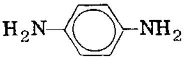
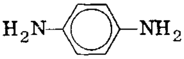
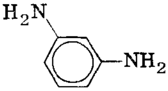
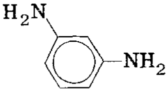
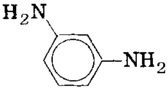
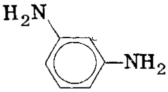
Table 16. Thermogravimetric Analyses of Some Random Copolymers from Pairs of A-B Monomers

Polymer	Atmosphere	Per cent weight loss at °C						
		500	600	700	800	900	1000	1176
RC-1A-H400	Nitrogen	0.0	3.0	8.3	9.8	14.1	15.2	18.3
RC-1A-H600	Nitrogen	0.0	0.0	1.9	6.4	8.8	10.8	13.8
RC-1A-H1176	Nitrogen	0.0	0.0	0.0	0.0	0.0	0.0	1.8
RC-2A-H400	Nitrogen	0.0	2.4	4.6	9.7	13.7	14.9	18.4
RC-2A-H600	Nitrogen	0.0	0.0	2.1	5.6	7.8	11.7	14.9
RC-2A-H1176	Nitrogen	0.0	0.0	0.0	0.0	0.0	0.0	2.1
RC-3A-H400	Nitrogen	0.0	2.7	5.2	9.4	14.3	15.6	17.4
RC-3A-H600	Nitrogen	0.0	0.0	3.0	7.3	9.3	11.3	15.9
RC-3A-H1176	Nitrogen	0.0	0.0	0.0	0.0	0.0	0.0	2.4
RC-5A-H400	Nitrogen	0.0	2.6	8.4	11.7	13.7	14.8	17.9
RC-5A-H600	Nitrogen	0.0	0.0	2.6	5.9	8.5	11.1	15.0
RC-5A-H1176	Nitrogen	0.0	0.0	0.0	0.0	0.0	0.0	2.8

Table 17. Random Copolymers from a Pair of

Polymer	Reactants: Monomer	Mole	Monomer	Mole
RC-1B		0.50		0.50
RC-2B		0.25		0.75
RC-3B		0.50		0.50
RC-4B		0.50		0.50
RC-5B		0.25		0.75
RC-6B		0.25		0.75
RC-7B		0.25		0.75
RC-8B		0.25		0.75
RC-9B		0.50		0.50
RC-10B		0.50		0.50
RC-11B		0.50		0.50
RC-12B		0.50		0.50

A-A Type Monomers with a Single B-B Monomer

		Observations at °C		
Reactant	Mole	180	225	325
	1.0	Melt	Brick dust	—
	1.0	Melt	Brick dust	—
	1.0	Melt	Brick dust	—
	1.0	Melt	Brick dust	—
	1.0	Melt	Brick dust	—
	1.0	Melt	Very viscous	Black, glassy
	1.0	Melt	Very viscous	Black, glassy
	1.0	Melt	Very viscous	Black, glassy
	1.0	Melt	Very viscous	Black, glassy
	1.0	Melt	Very viscous	Black, glassy
	1.0	Melt	Very viscous	Black, glassy
	1.0	Melt	Very viscous	Black, glassy

which may have formed. The theoretical yield for the H400 polymers is in the range 445-447% on the basis of initial infusible polymer. The yields of the uncatalyzed reactions were lower than those which were catalyzed by $ZnCl_2$, and the lower than theoretical yield in all cases is attributable to sublimation losses of the monomer. The thermogravimetric data of Table 14 are representative of typical polymeric azomethines. The interesting observation made in these studies is that integral castings were obtained, in most cases, at a ratio of 4 parts of monomer to 1 part of polymer, and not at lower ratios of monomer to polymer. At the lower ratios the monomer appeared to be absorbed by the polymer and to become unavailable to function as an adhesive.

Type I Random Copolymers

The unsuitability of the solution method for preparing random copolymers led to the use of melt polymerizations in attempts to prepare these copolymers according to Eqs. (11)-(14). The random copolymerization of the type represented by Eq. (11) was most facile when the A-B monomers were the aminoaryl ketones, each of which homopolymerized to tractable polymers, or when one A-B monomer was an aminoketone and the other A-B monomer was an aminoaldehyde. However, an intractable brick-dust polymer was

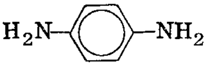
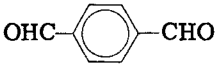
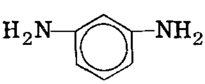
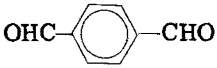
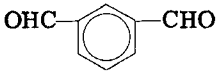
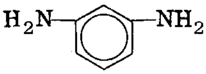
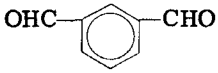
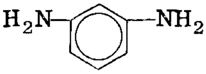
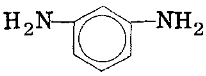
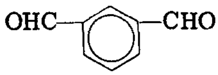
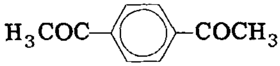
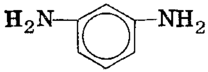
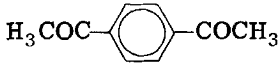
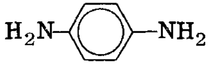
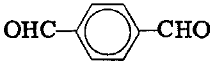
Table 18. Elemental Analyses of the Tractable RC-B Series of Random Copolymers

	Analysis, %			
	H325			H400
Polymer	C	H	N	N
RC-6B	80.88	5.37	12.66	12.71
RC-7B	80.79	5.42	12.63	12.69
RC-8B	80.81	5.51	12.70	12.74
RC-9B	80.77	5.70	10.16	10.20
RC-10B	82.24	5.82	8.52	8.54
RC-11B	77.19	5.33	7.99	8.02
RC-12B	82.94	5.99	10.22	10.27

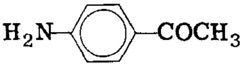
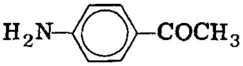
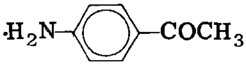
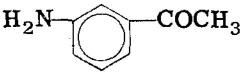
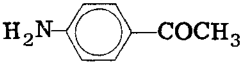
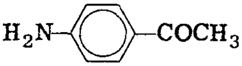
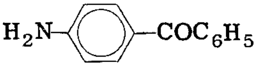
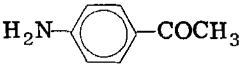
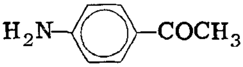
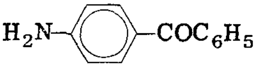
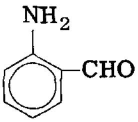
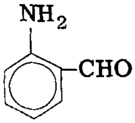
Table 19. Thermogravimetric Analyses of Some of the RC-B Series of Random Copolymers in Nitrogen and in Air

Polymer	Atmos-phere	Per cent weight loss at °C							
		400	500	600	700	800	900	1000	1176
RC-6B-H400	Nitrogen	0.0	0.0	2.5	4.7	8.0	13.6	14.5	17.6
RC-6B-H400	Air	0.0	6.2	100.0	—	—	—	—	—
RC-7B-H400	Nitrogen	0.0	0.0	2.9	9.0	12.0	13.8	14.9	18.0
RC-7B-H400	Air	0.0	6.3	100.0	—	—	—	—	—
RC-8B-H400	Nitrogen	0.0	0.0	3.0	9.3	12.2	14.2	15.2	18.4
RC-8B-H400	Air	0.0	7.4	100.0	—	—	—	—	—
RC-9B-H400	Nitrogen	0.0	0.0	3.3	9.6	12.5	14.6	15.6	18.9
RC-9B-H400	Air	0.0	6.8	100.0	—	—	—	—	—
RC-10B-H400	Nitrogen	0.0	0.0	3.1	9.7	12.7	14.8	15.8	18.8
RC-10B-H400	Air	0.0	8.1	100.0	—	—	—	—	—
RC-11B-H400	Nitrogen	0.0	0.0	1.9	4.0	7.7	13.0	14.0	17.4
RC-11B-H400	Air	0.0	7.7	100.0	—	—	—	—	—
RC-12B-H400	Nitrogen	0.0	0.0	2.3	4.2	7.8	13.4	14.3	17.5
RC-12B-H400	Air	0.0	7.3	100.0	—	—	—	—	—

Table 20. Random Copolymers from

	Reactants			
Polymer	Monomer	Mole	Monomer	Mole
RC-1C		1.0		1.0
RC-2C		1.0		1.0
RC-3C		1.0		1.0
RC-4C		1.0		1.0
RC-5C		1.0		1.0
RC-6C		1.0		1.0
RC-7C		1.0		1.0
RC-8C		1.0		1.0
RC-9C		1.0		1.0
RC-10C		1.0		1.0
RC-11C		1.0		1.0
RC-12C		1.0		1.0

Mixtures of A-A, B-B, and A-B Monomers

		Observations at °C		
Monomer	Mole	180	225	325
	3.0	Paste	Granular	Partly glassy
	3.0	Melt	Granular	Black, granular
	4.0	Melt	Viscous	Black, glassy
	4.0	Melt	Viscous	Black, glassy
	4.0	Melt	Viscous	Black, glassy
	4.0	Melt	Viscous	Black, glassy
	4.0	Melt	Viscous	Black, glassy
	2.0	Melt	Viscous	Black, glassy
	1.0	Melt	Viscous	Black, glassy
	1.0	Melt	Viscous	Black, glassy
	1.0	Melt	Viscous	Black, glassy
	4.0	Brick dust	Granular	Granular

obtained when both A-B monomers were aldehydes. These copolymers are designated as RC-A series and the pertinent data are given in Tables 15 and 16.

The random copolymerizations of the type represented by Eqs. (12) and (13) and designated as the RC-B series were also very facile and tractable melts were obtained when the dicarbonyl compounds, RCOArCOR, were the diketones, as shown by copolymers RC-9B to RC-12B in Table 17. In contrast, only brick-dust polymers were obtained when the dicarbonyl compounds were dialdehydes, as represented by copolymers RC-3B, RC-4B, and RC-5B, in which a 2.5 : 7.5 ratio of repeating units was introduced instead of the 1 : 1 ratio. With an equimolar mixture of a dialdehyde, $Ar(CHO)_2$, and a diketone, $Ar(COCH_3)_2$, as represented by copolymer RC-1A, only brick-dust polymers were obtained and tractable systems were obtained only when the ratio diketone/dialdehyde was 7.5 : 2.5, as in copolymers TC-6B, RC-7B, and RC-2B. In the case of RC-2B, the product was a granular, brick-dust, intractable polymer at the end of the 225°C heating period. The elemental and thermogravimetric analyses of polymers RC-6B to RC-12B, which in the course of synthesis, remained homogeneous, are given in Tables 18 and 19.

Table 21. Elemental Analyses of Some of the RC-C Series of Random Copolymers

	Analyses, %			
	H325			H400:
Polymer	C	H	N	N
RC-3C	80.56	5.70	12.21	12.29
RC-4C	80.50	5.74	12.28	12.31
RC-5C	80.49	5.69	12.24	12.33
RC-6C	80.54	5.71	12.27	12.39
RC-7C	83.97	5.06	9.63	9.71
RC-8C	81.09	6.05	11.82	11.83
RC-9C	81.13	6.02	11.80	11.87
RC-10C	83.61	5.56	9.81	9.84
RC-11C	80.93	5.49	12.63	12.68

The random copolymerizations represented by Eq. (14) were also very facile, and homogeneous, tractable melts were obtained when the dicarbonyl compound was a diketone, $CH_3COArCOCH_3$, in which case the aminocarbonyl compound, $H_2NArCOR$, could be either a ketone or an aldehyde; such products are represented by copolymers RC-8C to RC-11C of Table 20.

When the dicarbonyl compound in Eq. (14) was a dialdehyde, $C_6H_4(CHO)_2$, intractable condensation products were obtained unless 4 or more moles of aminoketone were used, as shown by copolymer numbers RC-1C to RC-7C. However, even when 4 moles of an aminoaldehyde were used instead of the aminoketone, as shown by copolymer RC-12C, a brick-dust product was obtained.

Elemental analyses and the thermogravimetric data of the RC-C series of copolymers are given in Tables 21 and 22 and are typical of the polymeric azomethines.

Table 22. Thermogravimetric Analyses of Some of the RC-C Series of H400 Random Copolymers in Nitrogen

Polymer	Atmosphere	Per cent weight loss at °C							
		400	500	600	700	800	900	1000	1176
RC-3C-H400	Nitrogen	0.0	0.0	2.6	4.8	8.1	13.5	14.7	17.5
RC-4C-H400	Nitrogen	0.0	0.1	2.8	8.9	11.9	13.7	14.8	18.1
RC-5C-H400	Nitrogen	0.0	0.0	3.0	9.4	12.3	14.3	15.7	18.9
RC-6C-H400	Nitrogen	0.0	0.0	3.2	9.5	12.4	14.5	15.5	18.9
RC-7C-H400	Nitrogen	0.0	0.2	2.3	4.3	7.9	13.5	14.4	17.9
RC-8C-H400	Nitrogen	0.0	0.3	1.9	4.1	7.7	13.3	14.7	17.4
RC-9C-H400	Nitrogen	0.0	0.0	2.5	5.0	8.3	13.7	14.9	17.7
RC-10C-H400	Nitrogen	0.0	0.0	2.9	9.1	12.1	14.0	15.2	18.2
RC-11C-H400	Nitrogen	0.0	0.0	2.1	4.1	7.6	13.2	14.1	17.4

ACKNOWLEDGMENTS

This work was performed under NASA Grants NGR-15-004-028 and NsG339. The generous contribution of time and effort by W. F. Strazik and D. M. Feigl is gratefully acknowledged.

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Accepted by editor August 26, 1968
Received for publication August 29, 1968