ABSTRACT OF THE DISCLOSURE

Schiff-base polymers having the formula
\[ \text{HCArCH} = \text{NArN} \]
where Ar is an arylene moiety, exhibit outstanding heat resistant properties. Polymers having this structure can withstand temperatures in excess of 400°C for sustained periods without undergoing significant degradation or phase changes. This high degree of thermal stability is believed to result from the conjugated structure of the polymer, the double bond \(-\text{C=N}-\) linkage characteristics of Schiff bases being alternated with arylene groups. Schiff-base polymers offer an attractive material for applications in the aerospace field as well as for other uses requiring high-temperature stability.

Schiff base polymers have been prepared previously by a condensation reaction of an aromatic dialdehyde with an aromatic diamine in a solution system, for example, by reaction of terephthaldehyde with p-phenylene-diamine in benzene or alcohol. The product of this reaction has been a yellow-to-orange "brick dust" powder having a low molecular weight, approximately that of a dimer. The "brick dust" polymer is an intractable material, infusible and insoluble in most solvents and therefore not amenable to fabrication into useful products. Black polymers should be expected from these reactants if the molecular weight is sufficiently high that conjugation is extensive. It is desired to prepare these polymers in the form of tractable, black high-molecular-weight material suitable for further processing.

Black Schiff-base polymers have now been prepared by reacting the aromatic diamine and aromatic dialdehyde in a melt system, a mixture of the reagents being heated to a temperature above the melting point. Polymerization to a high molecular weight proceeds very rapidly under these conditions, but the reaction is difficult to control, and this process does not permit the ready isolation of a tractable, fusible polymer at an intermediate stage. Better control over this reaction has been achieved by use of a molten monofunctional Schiff base such as benzylideneaniline for the reaction medium, the monofunctional Schiff base serving both as a solvent and moderator for the reaction. This process is the subject matter of applicant's application Ser. No. 593,593, filed Nov. 9, 1966. Further improvement has been obtained by employing Schiff-base exchange reactions wherein difunctional Schiff bases are reacted with an aromatic diamine, an aromatic dialdehyde or another difunctional Schiff base to prepare the Schiff-base polymers. These reactions, and particularly the bis-exchange reaction of a Schiff base having an aromatic diamine moiety with a Schiff base having an aromatic dialdehyde moiety, proceed more slowly than the diamine-dialdehyde condensation reaction so that isolation of a fusible, tractable polymer is facilitated. The Schiff-base exchange processes and polymers formed thereby are the subject matter of applicant's application Ser. No. 593,594, filed Nov. 9, 1966.

Schiff-base exchange reactions present a disadvantage in that they require as starting material a difunctional Schiff base, which reagent is expensive or unavailable so that it must be synthesized. A process retaining the ease of control of Schiff-base exchange reactions, but eliminating the need for a difunctional Schiff base starting material would be highly desirable. It is therefore an object of this invention to provide an improved process for synthesizing Schiff base polymers.

Another object is to provide a process for preparing Schiff-base polymers in a tractable, fusible form suitable for further processing.

In the present invention Schiff-base polymers having the formula
\[ \text{HCArCH} = \text{NArN} \]
are prepared by reacting an aromatic diamine with an aromatic dialdehyde, an aromatic monoamine, and an aromatic monoaldehyde. This reaction proceeds in a controllable manner similar to Schiff-base exchange reactions, but a difunctional Schiff base reagent is not required. The amine and aldehyde reactants required are readily available at relatively low cost so that substantial savings are realized.

Although this invention is not to be understood as limited to a particular theory, it is postulated that polymerization occurs both by a condensation of the dialdehyde with the diamine and by Schiff-base exchange reactions. The latter mechanism occurs in two stages; in the first stage the dialdehyde reacts with the monoaldehyde to produce a Schiff base having an aromatic diamino moiety, and the diamine reacts with the monoaldehyde to produce a Schiff base having an aromatic dialdehyde moiety. These reactions as exemplified for the specific reactants...
p-phenylenediamine, terephthaldehyde, benzaldehyde and aniline, proceed as follows:

\[ \text{OHC} \overset{\text{CHO}}{\text{N}} + 2\text{NH}_2 \rightarrow \text{H}_2\text{NN} \]

The two resulting difunctional Schiff bases can enter into the condensation reaction in the second stage. The two Schiff bases can undergo a bis exchange reaction with each other to produce a Schiff base polymer and a monofunctional Schiff base by-product. The bulk of the polymer is believed to be formed by this means and by the condensation reaction of the dialdehyde with the diamine. The Schiff base having a difunctional amino moiety can react with the dialdehyde to produce the polymer by means of a carbonyl exchange reaction, and the Schiff base having the difunctional aldehyde moiety can react with the diamine to give the polymer by means of amine exchange. The overall reaction is represented by the following equation:

\[ \text{nAr(CH}=\text{CHO}_z + \text{mNH}_2 \rightarrow \text{mAr-N=H}_z \]

where \( \text{Ar} \) is an arylene moiety and \( R \) is an aryl moiety.

The aromatic monoamine reactant is represented by the formula

\[ \text{H}_2\text{NHArNH}_2 \]

where \( \text{Ar} \) is an arylene moiety. The arylene moiety can be a single phenylene ring structure such as \( \text{m-phenylene}, \) p-phenylene or a phenylene ring having one or two hydrogen atoms substituted by methyl groups; a diphenylene group; or a group consisting of two phenylene rings linked by one or more heteroatoms as groups such as \( \text{O}, \text{S}, \text{SO}_2, \text{C}={\text{O}}, \text{NH}_2, \text{N} \sim \text{CH}_3, \text{C}_2\text{H}_5, \) or \( \text{SO}_2 \). Aliphatic chain linkings containing more than one methylene group are excluded from the groups between phenylene rings since the conjugated structure of the polymer backbone, which is critical to the thermal stability, would not be attained. In the latter groups the linkages attached to the phenylene rings can be in the meta-meta, para-para, or para-meta positions. Illustrative examples of specific amine reactants are p-phenylenediamine, m-phenylenediamine and the \( p, p'; p, m' \); and \( m, m' \) forms of biaMine, diaminophenyl methylmine, diaminophenyl oxide, diaminophenyl sulfone, diaminophenyl sulfide, diaminophenyl ketone, diaminophenylamine and m-phenyl methyl amine, diaminodiphenyl ethylene, diaminodiphenyl acetylene, etc. The meta and para phthalaldehydes are preferred because of their availability and lower cost.

The aromatic monoamine reactant is represented by the formula

\[ \text{RNH}_2 \]

where \( R \) is an aryl radical. \( R \) can be \( \text{C}_6\text{H}_5, \text{CH}_2\text{C}_6\text{H}_5, (\text{CH}_2)_2\text{C}_6\text{H}_5, \text{C}_2\text{H}_5\text{C}_6\text{H}_4, \text{C}_6\text{H}_5\text{OC}_6\text{H}_4, \text{C}_6\text{H}_5\text{SC}_6\text{H}_4, \text{CH}_2\text{OC}_6\text{H}_4, \) etc. Illustrative examples of specific amines included are aniline, and \( \omega, \) \( m' \) and \( p-toluidine. \) The simplest and least expensive amine in this class, aniline, is preferred.

The aromatic monodialdehyde is represented by the formula

\[ \text{OCHO} \]

Polymerization is carried out by heating a mixture of the diamine, dialdehyde, monoamine, and monoaldehyde. In a preferred procedure the diamine and the dialdehyde are mixed at equimolar proportions and this mixture is combined with an equimolar mixture of the monoamine and the monoaldehyde. The molar ratio of the dialdehyde-diamine mixture to the monoaldehyde monoamine mixture can vary from \( 1:1 \) to \( 1:3 \), depending on the particular dialdehyde and diamine used. The ratio required to produce a homogeneous, viscous melt depends on the isomeric nature of the diamine and dialdehyde. For example, a higher proportion of monoamine- monoaldehyde is required for reaction mixtures using p-diamine and p-dialdehyde than for the corresponding meta forms.

When the mixture is heated to a temperature of at least \( 250{\circ}\text{C.} \), and preferably \( 250{\circ}\text{C.} \) to \( 300{\circ}\text{C.} \) and held at this temperature for about two to five hours to produce a fusible black polymer. The mixture is initially formed as a pasty yellow mixture upon combining the liquid monoaldehyde and monoamine with the difunctional reagents, which are solids. Upon being heated the mixture forms a solid and then a viscous melt. The mixture can be heated rapidly to \( 250{\circ}\text{C.} \) or higher, but preferably it is heated at a temperature increase rate of 10 to 30\( {\circ}\text{C.} \) per hour. Polymerization proceeds through increasing stages of molecular weight during heating as evidenced by vivid changes in color of the melt from a bright yellow-orange to dark brown to black. An equilibrium stage is reached upon holding at \( 250{\circ}\text{C.} \) to \( 300{\circ}\text{C.} \), and no further polymerization will occur until the by-product monofunctional Schiff base is rendered insufifiable. The product polymer is then recovered by removing the monofunctional Schiff base, preferably by distillation at a temperature of \( 300{\circ}\text{C.} \) to \( 350{\circ}\text{C.} \).

In an alternate procedure the four reagents are first reacted in a solution system to produce a low-molecular-weight polymeric mixture prior to heating to higher temperatures. This reaction can be carried out by dissolving the diamine, dialdehyde, monoamine and monoaldehyde in an azeotroping hydrocarbon solvent such as benzene or toluene and heating the solution in a Dean-Stark apparatus until the water is no longer eliminated. The resulting condensation product is then recovered by distilling off the solvent. The product can then be converted to a high-molecular weight form by heating in the manner described above. The product polymer, in the form of a fusible, black coherent mass, can be polymerized further in the solid state by heating to a temperature not exceeding about 375\( {\circ}\text{C.} \) This treatment serves to improve the mechanical properties of the polymer. Higher temperatures are normally to be avoided since the polymers would be rendered insufifiable and untractable. However, if subsequent shaping or melting of the product is not desired the polymer can be converted to an insufifiable,
thermally stable form by heating to higher temperatures, for example, 400° to 600° C. at this stage.

In order to avoid oxidation and side-reactions the polymerization reaction and subsequent heating steps are carried out in the absence of moisture and oxygen. The provision of an atmosphere of an inert gas such as nitrogen, helium or argon is suitable for this purpose. For this reason and to allow removal of reaction by-products the reaction is conducted in apparatus provided with distilling equipment and an inert gas inlet. Gas pressure over the reaction mixture is not critical, but a substantially reduced pressure, for example, down to 1 mm. Hg, is preferred in the later heating stages to enhance the removal of volatilized by-products.

The fusible polymer product obtained as described above has a relatively high molecular weight, estimated to be in excess of 20,000, although the insolubility of the polymer has prevented an exact determination. Upon being heated to higher temperatures this material undergoes additional polymerization in the solid state to produce an infusible, tough solid with excellent high-temperature stability and good mechanical properties. Fabrication of the polymer into the desired shape or structure is carried out while it is in the fusible state because of the intractable nature of the infusible material.

In a preferred fabrication procedure the fusible polymer is ground or crushed, and the resulting particles are compressed into the desired shape and heated to a temperature of 400° to 600° C. to effect further solid-state polymerization and consolidation. This reaction is enhanced by providing a small amount, for example, 0.5 to 1 weight percent of a Lewis acid catalyst in the polymer body prior to heating. Examples of suitable Lewis acid catalysts include zinc chloride, aluminum chloride, boron trifluoride, titanium tetrachloride, zirconium tetrachloride, merccuric bromide, cobolt iodide, nickel chloride, boron trifluoride, titanum tetrachloride, zirconium tetrachloride, phosphoric acid, trimethylamine hydrobromide, trimethylamine hydrochloride, trimethylamine hydrobromide, phosphoric acid, tributylphosphonium chloride and p-toluenesulfonic acid. Holding at a temperature of 400° to 600° C. for a period of 5 to 20 minutes is generally suitable, although longer times are necessary for massive structures. During this treatment, small amounts of reactant by-products are formed, and they as well as any remaining mono- and difunctional Schiff base can be removed by further heating the molded form under an inert atmosphere at a temperature of 700° to 1,000° C. for 1 to 4 hours or more. The latter treatment serves to impart a higher degree of thermal stability to the final product.

For the fabrication of composite heat shields, for which Schiff base polymers are a particularly attractive material, the fusible polymer can be intermingled with other desired components of the composite, for example, reinforcing fibers of a refractory material such as fiberglass or silica, prior to the 400° to 600° C. heat treatment.

The invention is illustrated by the following examples:

EXAMPLE I

Equimolar quantities (0.004 M each) of benzaldehyde, aniline, p-phenylenediamine, and terephthaldehyde are mixed in a reaction tube. The resulting mixture immediately turns yellow and solidifies. The tube is then fitted with a condenser, a receiver, and a nitrogen inlet, and the mixture is heated to 220° C. for two hours under atmospheric pressure. During heating the mixture melts and changes in color from yellow to brown-black. The mixture is then cooled, and 0.824 gram of black amorphous polymer is recovered. Water and benzylidene aniline are found in the receiver.

EXAMPLE II

The reactants of Example I are mixed at the same quantities, the two amines being first combined in a mortar and the two aldehydes being added thereto with rapid stirring. The mixture rapidly forms a pasty mass and then a solid. The solid is then removed from the mortar and placed in the reaction tube of Example I. The mixture is then heated under a nitrogen atmosphere to 260° C. for twelve and one-half hours, to 370° to 390° C. for one hour, to 414° C. for seven hours, all at atmospheric pressure, and for 4 hours at 400° C. and 1.5 mm. Hg pressure. The mixture is then allowed to cool, and a dull, black amorphous polymer is recovered at a yield of 100%. Benzylideneaniline is found in the receiver, and water and aniline in an attached Dry Ice-acetone trap.

EXAMPLE III

A series of polymerization reactions is conducted by the following procedure. For each reaction an arylene diamine, either p- or m-phenylenediamine, is mixed with an arylene dialdehyde, either p- or m-phthaldehyd, at equimolar proportions, and the mixture is placed in a glass polymerization reactor. Aniline and benzaldehyde are mixed in a reaction tube. The resulting mixture is then transferred to a reaction tube and heated under a nitrogen atmosphere to 260° C. for twelve and one-half hours, to 370° to 390° C. for one hour, to 414° C. for seven hours, all at atmospheric pressure, and to 360° for nine hours at 1.5 mm. Hg pressure. The mixture is then cooled, and a black, shiny polymer is recovered.

EXAMPLE IV

A series of polymerization reactions is conducted by the following procedure. For each reaction an arylene diamine, either p- or m-phenylenediamine, is mixed with an arylene dialdehyde, either p- or m-phthaldehyd, at equimolar proportions, and the mixture is placed in a glass polymerization reactor. Aniline and benzaldehyde are then added at varying molar proportions. The reaction mixture is then flushed with nitrogen and heated under a nitrogen atmosphere according to the following schedule: one hour at 120° C., one hour at 200° C., and four hours at 300° C., all at atmospheric pressure, to produce a fusible, black polymer. The mixture is then heated at 300° C. for four hours at 0.5 to 1.5 mm. Hg and for eighteen hours at 400° C. at 0.5 to 1.5 mm. Hg. The mixture is then cooled, and the yield is determined. In a number of cases, a sample of the product is then ground and heated under nitrogen for one hour at 600° C. at atmospheric pressure and for four hours at 600° C. and 0.5 to 1.5 mm. Hg. The final yield at this temperature is then determined. The results obtained may be seen by reference to the following table:

<table>
<thead>
<tr>
<th>Data on Direct Synthesis of Poly Schiff Bases</th>
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<tr>
<td>One mole diamine</td>
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<tr>
<td>Meta</td>
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Yields in excess of 100% of theory are due to the retention of by-products such as benzylidene aniline, which is held tenaciously by the polymer; the excess can be removed by prolonged heating of the ground polymer at 300° to 400° C. or for shorter times at 600° C. or higher under an inert atmosphere.

**EXAMPLE V**

A mixture of one mole of m-phenylenediamine, one mole of m-phenylenedialdehyde, two moles of aniline and two moles of benzaldehyde as 10% solution in toluene are reacted in a Dean-Stark apparatus at reflux whereby a black polymer is formed and recovering said polymer; the excess can be removed by distilling off the toluene at 15 mm. Hg pressure, leaving a quantitative yield of product. The product was transferred to the glass polymerization reactor and at equimolar proportions and the molar ratio of said monoamine and said monoaldehyde are combined ing a quantitative yield of product. The product was said monoamine and said monoaldehyde are combined at an aromatic monoaldehyde of the formula RCHO where R is said aryl radical, heating the resulting mixture under an inert atmosphere to a temperature of at least 250° C. whereby a black polymer is formed and recovering said polymer.

1. The process of claim 1 wherein said diamine and said aldehyde are combined at equimolar proportions, said monoamine and said monoaldehyde are combined at equimolar proportions and the molar ratio of said aldehyde and said diamine to said monoaldehyde and said monoamine is from 1:1 to 1:3.

2. A process for preparation of a fusible polymer consisting essentially of repeating units of the formula

\[
\text{HCArCH=NArN=}
\]

where n has a numerical value of at least 5 and Ar is an arylene moiety selected from the class consisting of a phenylene group, a diphenylene group and a group consisting of two phenylene groups linked by a component of the class consisting of O, S, SO₂, CH₃, C₆H₅, CH₂ and SO₃, N—CH₂, C≡O, and NH which comprises combining an aromatic diamine of the formula H₂NArNH₂ where Ar is said arylene moiety with an aromatic dialdehyde of the formula OHCArCHO where Ar is said arylene moiety, an aromatic monoaldehyde of the formula RNH₂ where R is an aryl radical selected from the group consisting of C₆H₅, CH₃C₆H₄, (CH₃)₂C₆H₄, (CH₃)₃C₆H₄, C₆H₅C₆H₄, C₆H₅OC₆H₄, C₆H₅SC₆H₄ and CH₃OC₆H₄ and an aromatic monoaldehyde of the formula RCHO where R is said aryl radical, heating the resulting mixture under an inert atmosphere to a temperature of at least 250° C. whereby a black polymer is formed and recovering said polymer.

3. A process for preparation of a fusible polymer consisting essentially of repeating units of the formula

\[
\text{HCArCH=NArN=}
\]

where n has a numerical value of at least 5 and Ar is an arylene moiety selected from the class consisting of a phenylene group, a diphenylene group and a group consisting of two phenylene groups linked by a component of the class consisting of O, S, SO₂, CH₃, C₆H₅, CH₂ and SO₃, N—CH₂, C≡O, and NH which comprises combining an aromatic diamine of the formula H₂NArNH₂ where Ar is said arylene moiety with an aromatic dialdehyde of the formula OHCArCHO where Ar is said arylene moiety, an aromatic monoaldehyde of the formula RNH₂ where R is an aryl radical selected from the group consisting of C₆H₅, CH₃C₆H₄, (CH₃)₂C₆H₄, (CH₃)₃C₆H₄, C₆H₅C₆H₄, C₆H₅OC₆H₄, C₆H₅SC₆H₄ and CH₃OC₆H₄ and an aromatic monoaldehyde of the formula RCHO where R is said aryl radical, heating the resulting mixture under an inert atmosphere to a temperature of about 250° to 300° C. under an inert atmosphere whereby a fusible black polymer is formed and recovering said polymer.

4. The process of claim 3 wherein said mixture is held at said temperature for 2 to 5 hours.

5. The process of claim 3 wherein said arylene moiety is phenylene.

**References Cited**

UNITED STATES PATENTS


WILLIAM H. SHORT, Primary Examiner

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U.S. Cl. X.R.