POLYBENZIMIDAZOLES VIA AROMATIC NUCLEOPHILIC DISPLACEMENT

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Abstract

Novel molecular weight controlled and endcapped polybenzimidazoles (PBI) are prepared by the aromatic nucleophilic displacement reaction of di(hydroxyphenylbenzimidazole) monomers with activated aromatic dihalides or activated aromatic dinitro compounds. The PBI are endcapped with mono(hydroxyphenyl)benzimidazoles. The polymerizations are carried out in polar aprotic solvents such as N-methyl-2-pyrrolidinone or N,N-dimethylacetamide using alkali metal bases such as potassium carbonate at elevated temperatures under nitrogen. Mono(hydroxyphenyl)-benzimidazoles are synthesized by reacting phenyl-4-hydroxybenzoate with aromatic (o-diamine)s in diphenylsulfone. Molecular weight controlled and endcapped PBI of new chemical structures are prepared that exhibit a favorable combination of physical and mechanical properties.
![Diagram of chemical reactions](image)
\[
\text{Diphenylsulfone / Toluene} \\
\text{Nitrogen / Heat}
\]

\[
\text{FIG. 2}
\]
FIG. 6

Y = F, Cl, NO₂
X = CO₂, SO₂

DMAC / Toluene
Nitrogen / Heat
K₂CO₃

w = H, CH₃, CH₃O,
POLYBENZIMIDAZOLES VIA AROMATIC NUCLEOPHILIC DISPLACEMENT

ORIGIN OF THE INVENTION

The invention described herein was jointly made by employees of the United States Government and a contract employee in the performance of work under NASA Grant No. NAG-148 and is subject to the provisions of Public Law 96-517 (35 USC 202) in which the contractor has elected not to retain title.

CROSS REFERENCE TO RELATED APPLICATIONS

This application is related to co-pending patent application Ser. No. 07/790,730, filed Apr. 5, 1993, entitled "Poly(N-arylenebenzimidazole) Via Aromatic Nucleophilic Displacement" and co-pending continuation-in-part patent application Ser. No. 95,426, filed October 30, 1991, entitled "Polybenzimidazoles Via Aromatic Nucleophilic Displacement".

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates generally to heterocyclic polymers. In particular it relates to novel polybenzimidazoles and to a novel process for the preparation of molecular weight controlled and endcapped polyimides. In particular it relates to novel polybenzimidazoles and to a novel process for the preparation of molecular weight controlled and endcapped polybenzimidazoles.

2. Description of Related Art

Polybenzimidazoles (PBI) are heterocyclic polymers commonly prepared by the condensation reaction of an aromatic bis(o-diamine) with an aromatic diacid or derivative thereof and having a repeat unit of the general structure

\[ \text{Ar} - \text{N} \rightarrow \text{Ar'} \]

where \( \text{Ar} \) is a tetravalent aromatic radical such as 1,2,4,5-tetrasubstituted benzene. \( \text{Ar} \) may also be a bis(o-diphenylene) having the general structure

\[ \text{Z} - \text{N} \rightarrow \text{N} \rightarrow \text{Z} \]

where \( \text{Z}=\text{nil}, \text{O}, \text{S}, \text{SO}_2, \text{O} = \text{C}, \text{CH}_2 \) or any other appropriate divalent radical. \( \text{Ar}' \) is a divalent aromatic radical which may be 1,3-phenylene, 1,4-phenylene, 4,4'-biphenylene, 4,4'-oxydiphenylene, 4,4'-sulfonyldiphenylene, or any other appropriate divalent radical.


To obtain polymer with low melt viscosity, the molecular weight of a polymer can be lowered and controlled by using a stoichiometric imbalance of one of the monomers. This is expressed mathematically by a modification of the Crouthers equation for AA-BB type monomers (Polymer Chemistry: An Introduction, 2nd Ed., M. P. Stevens, Oxford University, New York, 1990, 335-337).

\[ DP = \frac{1 + r}{1 - r} \]

where

\[ DP: \text{degree of polymerization} \]
\[ r: \text{stoichiometric imbalance; } 0.5 < r < 1.0. \]

For \( r = 1 \), there is no stoichiometric imbalance of monomers in the polymerization reaction. The calculated number average molecular weight can then be determined by

\[ M_n = (0.5 \times (\text{MW of repeat unit}) \times (DP)) \]

where

\[ M_n: \text{number average molecular weight} \]
\[ \text{MW of repeat unit}: \text{molecular weight of polymer repeat unit}. \]

Endcapping the polymer is achieved by using 2\( \times (1 - r) \) of a monofunctional reagent in the polymerization reaction based on monofunctional endcapping technology [D. Progar, T. St. Clair, H.Burks, C. Graue, A. Tamaguchi, and M. Ohta, SAMPE J., 52 (January/February 1990)]. An endcapped version of poly[2,2'-bis(phenyl-5,5'-dibenzimidazole)] has recently been reported [M. Jaffe, E. C. Chenvey, W. M. Cooper, M. Glick, and I. Taider, Polym. Prepr., 32(2), 207 (1991)].

SUMMARY OF THE INVENTION

A primary object of the present invention is to provide novel polybenzimidazoles (PBI) compositions of matter.

Another object is to provide a new process to prepare molecular weight controlled and endcapped PBI.
Yet another object is to provide new molecular weight controlled and endcapped PBI that are useful as adhesives, coatings, films, fibers, membranes, moldings, and composite matrices.

According to the present invention, the foregoing and additional objects were obtained by synthesizing molecular weight controlled and endcapped PBI by nucleophilic displacement reaction of di(hydroxyphenyl)benzimidazole monomers with activated aromatic dihalides. Endcapping of the molecular weight controlled polymer was achieved by using a mono(hydroxyphenyl)benzimidazole. The inherent viscosities ($\eta_{inh}$) of the molecular weight controlled and endcapped PBI ranged from 0.55 to 1.65 dL/g and the glass transition temperatures ($T_g$) ranged from 266-274° C. An unendcapped, uncontrolled molecular weight PBI polymer (no stoichiometric imbalance) had an inherent viscosity of 2.00 dL/g and a glass transition temperature of 276° C. Thermogravimetric analysis (TGA) at a heating rate of 2.5° C./min showed no weight loss occurring below 300° C. in air or nitrogen with a 5% weight loss occurring at about 470° C. in air and about 490° C. in nitrogen.

The synthesis of molecular weight controlled and endcapped PBI involved the use of di(hydroxyphenyl)benzimidazoles and mono(hydroxyphenyl)benzimidazoles. The monomers were prepared from phenyl-4-hydroxybenzoate and aromatic bis(o-diamine)s. The catenation of the hydroxy groups may be meta-meta, para-para, or para-meta. The monofunctional benzimidazole, used as an endcapping agent, was prepared from phenyl-4-hydroxybenzoate and o-phenylene diamine. The catenation of the functional group may be para or meta.

**BRIEF DESCRIPTION OF THE DRAWINGS**

For a more complete understanding of the present invention including its objects and benefits, reference should be made to the Description of the Preferred Embodiments, which is set forth below. This description should be read together with the accompanying drawings, wherein:

**FIG. 1** is an equation showing the preparation of monomers according to the present invention from phenyl-4-hydroxybenzoate and aromatic bis(o-diamine)s;

**FIG. 2** is an equation showing the preparation of an endcapping agent according to the present invention from phenyl-4-hydroxybenzoate and o-phenylene diamine;

**FIGS. 3 and 4** are equations showing the general reaction sequence for the synthesis of molecular weight controlled and endcapped polybenzimidazoles according to the present invention; and

**FIGS. 5 and 6** are equations showing the general reaction sequence for the synthesis of molecular weight controlled and unendcapped PBI according to the present invention.

**DESCRIPTION OF THE PREFERRED EMBODIMENTS**

In one aspect, the present invention is a molecular weight controlled and endcapped poly(benzimidazole) consisting of repeat units having the general structural formula

```
wherein the catenation of oxygen is selected from the group consisting of the group consisting of meta-meta, para-para, and para-meta. Ar is a radical selected from the group consisting of
```

and Z is a radical selected from the group consisting of
X is a radical selected from the group consisting of

EC is a radical selected from the group consisting of:

wherein EC is a radical selected from the group consisting of:
V is selected from the group consisting of OH, Cl, F, NO₂; and the catenation of V is selected from meta and para. Also reacted is an activated aromatic dihalide or aromatic dinitro compound having the general structure

wherein Y is selected from the group consisting of Cl, F, and NO₂. The reaction is carried out in a polar aprotic solvent selected from the group consisting of N,N-dimethylacetamide, N-methyl-2-pyrrolidinone, sulfolane, diphenylsulfone, N-cyclohexyl-2-pyrrolidinone, and dimethylsulfoxide. The reaction is also carried out in the presence of an alkali metal base selected from the group consisting of potassium carbonate, sodium carbonate, potassium hydroxide, and sodium hydroxide, and the reaction is carried out with the application of heat.

Especially advantageous results are achieved if X is

wherein X is a radical selected from the group consisting from

and EC is

W is H, V is OH, Y is Cl or F, preferably F, and the solvent is N,N-dimethylacetamide.

In other aspects, the present invention is a molecular weight controlled and endcapped poly(benzimidazole): film, fiber, molding, adhesive, and matrix resin for composites.

In yet another aspect the present invention is a molecular weight controlled and unendcapped poly(benzimidazole) consisting of repeat units having the general structural formula
wherein the catenation of oxygen is selected from the group consisting of meta-meta, para-para, and para-meta. Y is F, Cl, or NO2; and Ar is a radical selected from the group of

\[ \text{Z} \text{ is a radical selected from the group consisting of} \]

\[ \text{X is a radical selected from the group consisting of} \]
Y is selected from the group consisting of C1, F, and NO2. The reaction is carried out in a polar aprotic solvent selected from the group consisting of N,N-dimethylacetamide, N-methyl-2-pyrrolidinone, sulfolane, diphenylsulfone, N-cyclohexyl-2-pyrrolidinone, and dimethylsulfoxide. The reaction is also carried out in the presence of an alkali metal base selected from the group consisting of potassium carbonate, sodium carbonate, potassium hydroxide, and sodium hydroxide, and the reaction is carried out with the application of heat.

In other aspects, the present invention is a molecular weight controlled and unendcapped poly(benzimidazole): film, fiber, molding, adhesive, and matrix resin for composites.

Having generally described the invention a more complete understanding thereof can be obtained by reference to the following examples, which are provided herein for purposes of illustration only and do not limit the invention.

**EXAMPLE 1**

Endcap Synthesis

The following example illustrates the reaction sequence in FIG. 2 for the preparation of the endcapping agent.

2-(4-Hydroxyphenyl)benzimidazole

A mixture of 1,2-diaminobenzene (25.17 g, 0.233 mol), phenyl-4-hydroxyphenylbenzoate (50.17 g, 0.234 mol), diphenylsulfone (121.15 g), and toluene (100 ml) were heated under a nitrogen atmosphere for 16 hours at 150° C. The toluene was removed and the temperature increased to 260° C. and maintained for two and one-half hours. A vacuum was subsequently applied and the temperature increased to 290° C. and maintained for one and one-half hours. The warm reaction mixture was precipitated in toluene, washed in hot toluene, and subsequently dried at 110° C. to afford 45.00 g (92% crude yield) of a red-tan powder, m.p. (DTA) 279° C. (broad).

The solid was recrystallized from 40% aqueous ethanol using charcoal to afford a light tan crystalline product (31.46 g, 64% yield). The compound exhibited a sharp melt by DTA with an endothermic minimum at 280° C.

Anal. calcd for C13H10N2O: C, 74.27%; H, 4.79%; N, 13.32%; Found: C, 74.21%; H, 4.75%; N, 13.21%.

**EXAMPLE 2**

Molecular Weight Controlled and Endcapped Poly(arylene ether benzimidazole) Synthesis

0% Stoichiometric Offset, 0% Endcapped PBI

The following example illustrates the reaction sequence for the preparation of high molecular weight polymer where X is equal to an isophthaloyl group, Y is F, and Z is 5,5'-nil, the catenation of the hydroxy groups is para-para, and the stoichiometric imbalance is 0% (r=1).

Into a 100 ml three necked round bottom flask equipped with nitrogen inlet, thermometer, mechanical stirrer, and Dean Stark trap was placed 5,5'-bis[2-(4-hydroxyphenyl)benzimidazole] (2.092 g, 4.9 mmol),
13
1,3-bis(4-fluorobenzoyl)benzene (1.5707 g, 4.9 mmol), pulverized anhydrous potassium carbonate (1.7379 g, 12.6 mmol), dry DMAc (18 ml, 18% solids w/w) and toluene (50 ml). The mixture was heated to 140°-150°C for three and one-half hours and then heated to 155°-160°C. After about two hours the viscous reaction mixture was diluted with 21 ml DMAc (9.0% solids w/w) and stirring continued at 155°-160°C. The viscous reaction mixture was diluted again with 25 ml DMAc (5.7% solids w/w) after an additional three-quarter hours. The viscous solution was precipitated in a water/acetic acid (10/1) mixture, washed successively in hot water and methanol and dried at 110°C to provide a light brown polymer (2.48 g, 73% yield) with a 18.3% solids W/W) and toluene (250 ml). The mixture was heated to 140°-150°C for seven and one-half hours and then heated to 155°-160°C. After about one and one-half hours the viscous reaction mixture was diluted with 600 ml DMAc (10.0% solids w/w) and stirring continued for an additional one-half hour at 155°-160°C and the reaction mixture was cooled. The viscous solution was precipitated in a water/acetic acid (10/1) mixture, washed successively in hot water and methanol and dried at 110°C to provide a light tan polymer (115.2 g, 97% yield) with a Tg of 274°C. The inherent viscosity of 0.5% solution in DMAc at 25°C was 1.42 dL/g. Unoriented thin films cast from a DMAc solution gave tensile strength, tensile modulus, and elongation at 23°C of 18.7 ksi, 582 ksi, and 30%, respectively; and at 232°C of 12.0 ksi, 406 ksi, and 12%, respectively.

EXAMPLE 3
1.5% Stoichiometric Offset, 3% Endcapped PBI

The following example illustrates the reaction sequence in FIG. 3 for the preparation of the molecular weight controlled and endcapped polymer where X is equal to an isophthalamoyl group, Y is F, and Z is 5,5'-nil, the catenation of the hydroxy groups is para-para and the stoichiometric imbalance is 1.5% (r = 0.985). The endcapping reagent [3%, 2×(1-r)] is 2-(4-hydroxyphenyl)benzimidazole.

Into a 2000 ml three necked round bottom flask equipped with nitrogen inlet, thermometer, mechanical stirrer, and Dean Stark trap was placed 5,5'-bis[2-(4-hydroxyphenyl)benzimidazole] (30.2497 g, 72.3 mmol), 1,3-bis(4-fluorobenzoyl)benzene (23.6544 g, 73.4 mmol), 2-(4-hydroxyphenyl)benzimidazole (6.8629 g, 2.2 mmol), pulverized anhydrous potassium carbonate (25.8851 g, 187.3 mmol), dry DMAc (250 ml, 18.8% solids w/w) and toluene (225 ml). The mixture was heated to 140°-150°C for five hours and then heated to 155°-160°C. The viscous reaction mixture was diluted again with 250 ml of DMAc (7.2% solids w/w) after an additional one hour. Stirring was continued for one and one-quarter hour at 155°-160°C. After about one hour the viscous reaction mixture was diluted with 250 ml DMAc (10.4% solids w/w) and stirring continued at 155°-160°C and the reaction mixture was cooled. The viscous solution was precipitated in a water/acetic acid (10/1) mixture, washed successively in hot water and methanol and dried at 110°C to provide a light tan polymer (47.3 g, 92% yield) with a Tg of 274°C. The inherent viscosity of 0.5% solution in DMAc at 25°C was 1.65 dL/g. Unoriented thin films cast from a DMAc solution gave tensile strength, tensile modulus, and elongation at 23°C of 1.81 ksi, 524 ksi, and 12%, respectively; at 177°C of 14.0 ksi, 447 ksi, and 7%, respectively; and at 232°C of 12.4 ksi, 409 ksi, and 7%, respectively. The mixture was heated to 140°-150°C for seven and one-half hours and then heated to 155°-160°C. After about one and one-half hours the viscous reaction mixture was diluted with 600 ml DMAc (10.0% solids w/w) and stirring continued for an additional one-half hour at 155°-160°C and the reaction mixture was cooled. The viscous solution was precipitated in a water/acetic acid (10/1) mixture, washed successively in hot water and methanol, and dried at 110°C to provide a light tan polymer (56.9890 g, 92.0% yield) with a Tg of 274°C. The inherent viscosity of 0.5% solution in DMAc at 25°C was 1.42 dL/g. Unoriented thin films cast from a DMAc solution gave tensile strength, tensile modulus, and elongation at 23°C of 18.7 ksi, 582 ksi, and 30%, respectively; at 177°C of 13.6 ksi, 429 ksi, and 11%, respectively; and at 232°C of 12.0 ksi, 406 ksi, and 12%, respectively.

EXAMPLE 4
3.0% Stoichiometric Offset, 6% Endcapped PBI

The following example illustrates the reaction sequence in FIG. 3 for the preparation of the molecular weight controlled and endcapped polymer where X is equal to an isophthalamoyl group, Y is F, and Z is 5,5'-nil, the catenation of the hydroxy groups is para-para and the stoichiometric imbalance is 3.0% (r = 0.97). The endcapping reagent [6%, 2×(1-r)] is 2-(4-hydroxyphenyl)benzimidazole.

Into a 2000 ml three necked round bottom flask equipped with nitrogen inlet, thermometer, mechanical stirrer, and Dean Stark trap was placed 5,5'-bis[2-(4-hydroxyphenyl)benzimidazole] (68.7930 g, 164.4 mmol), 1,3-bis(4-fluorobenzoyl)benzene (54.6260 g, 169.5 mmol), 2-(4-hydroxyphenyl)benzimidazole (2.1379 g, 10.2 mmol), pulverized anhydrous potassium carbonate (59.83 g, 432.9 mmol), dry DMAc (600 ml, 18.3% solids w/w) and toluene (250 ml). The mixture was heated to 140°-150°C for seven and one-half hours and then heated to 155°-160°C. After about one and one-half hours the viscous reaction mixture was diluted with 600 ml DMAc (10.0% solids w/w) and stirring continued for an additional one-half hour at 155°-160°C and the reaction mixture was cooled. The viscous solution was precipitated in a water/acetic acid (10/1) mixture, washed successively in hot water and methanol, and dried at 110°C to provide a light tan polymer (96.85 g, 96% yield) with a Tg of 266°C. The inherent viscosity of 0.5% solution in DMAc at 25°C was 0.55 dL/g. Unoriented thin films cast from a DMAc solution gave tensile strength, tensile modulus, and elongation at 23°C of 16.5 ksi, 530 ksi, and 22%,
respectively, at 177°C of 13.1 ksi, 426 ksi, and 23%, respectively; and at 232°C of 10.3 ksi, 384 ksi, and 10%, respectively. GIC = 2.2 (in lb./in². (Fracture toughness, critical strain energy release rate.)

Polymer characterization and unoriented thin film properties are presented in Table 1. Adhesive properties of the 3% stoichiometric imbalance and endcapped polymer are presented in Table 2. Adhesive properties of the 7% stoichiometric imbalance and endcapped polymer are presented in Table 3, and composite properties of the 7% stoichiometric imbalance and endcapped polymer are presented in Table 4.

**TABLE 1**
CHARACTERIZATION OF MOLECULAR WEIGHT CONTROLLED PAEBI

<table>
<thead>
<tr>
<th>STOICHIOMETRIC IMBALANCE</th>
<th>0%</th>
<th>1.5%</th>
<th>3%</th>
<th>7%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tg, °C. (powder)</td>
<td>276</td>
<td>274</td>
<td>274</td>
<td>266</td>
</tr>
<tr>
<td>Tg, °C. (film)</td>
<td>284</td>
<td>287</td>
<td>284</td>
<td>273</td>
</tr>
<tr>
<td>Temp. of 5% wt. loss air/N2</td>
<td>476/515</td>
<td>467/511</td>
<td>467/507</td>
<td>470/472</td>
</tr>
<tr>
<td>Tensile Strength, ksi</td>
<td>18.1/14.0/12.4</td>
<td>18.1/14.0/11.7</td>
<td>18.7/13.6/12.0</td>
<td>16.5/13.1/10.3</td>
</tr>
<tr>
<td>Tensile Modulus, ksi</td>
<td>582/429/406</td>
<td>524/423/384</td>
<td>582/429/406</td>
<td>530/426/384</td>
</tr>
<tr>
<td>Elong. at break, %</td>
<td>14/7/7</td>
<td>12/6/5</td>
<td>30/11/12</td>
<td>22/13/10</td>
</tr>
<tr>
<td>GIC (in lb./in²)</td>
<td>4.9</td>
<td>5.7</td>
<td>2.2</td>
<td>1.42</td>
</tr>
</tbody>
</table>

**TABLE 2**
PRELIMINARY Ti-to-Ti TENSILE SHEAR PROPERTIES

<table>
<thead>
<tr>
<th>TEST TEMPERATURE, °C.</th>
<th>STRENGTH, ksi</th>
<th>MODE, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>23</td>
<td>2524</td>
<td>~60 Adh.3</td>
</tr>
<tr>
<td>177</td>
<td>2276</td>
<td>~55 Adh.</td>
</tr>
<tr>
<td>200</td>
<td>2034</td>
<td>~70 Adh.</td>
</tr>
<tr>
<td>232</td>
<td>2207</td>
<td>~100 Coh.</td>
</tr>
</tbody>
</table>

3 Specimens bonded at 250 psi/330°C/15 minutes

**TABLE 3**
PRELIMINARY Ti-to-Ti TENSILE SHEAR PROPERTIES

<table>
<thead>
<tr>
<th>Test Strength, psi</th>
<th>Failure, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>23</td>
<td>3236 -90 Adh</td>
</tr>
<tr>
<td>177</td>
<td>2235 -90 Adh</td>
</tr>
<tr>
<td>200</td>
<td>2019 -80 Adh</td>
</tr>
<tr>
<td>232</td>
<td>1649 -50 Adh</td>
</tr>
</tbody>
</table>

3 Mole % molecular weight controlled endcapped PAEBI, $\eta_{inh} = 1.42$ dL/g, $T_g = 276°$ C.

We claim:

1. A molecular weight controlled and endcapped poly(benzimidazole) consisting of repeat units having the general structural formula

**TABLE 4**
PRELIMINARY PROPERTIES OF CARBON FIBER (AS-4) UNIDIRECTIONAL COMPOSITES

<table>
<thead>
<tr>
<th>H</th>
<th>H</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Ar$_n$N$_m$)$_n$N$_m$Ar$_n$</td>
<td>(Ar$_n$N$_m$)$_n$N$_m$Ar$_n$</td>
</tr>
</tbody>
</table>

where $Ar = \ldots$

<table>
<thead>
<tr>
<th>PROPERTY</th>
<th>15</th>
<th>16</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile Strength, ksi</td>
<td>18.2/14.0/12.4</td>
<td>582/429/406</td>
</tr>
<tr>
<td>Tensile Modulus, ksi</td>
<td>582/429/406</td>
<td>530/426/384</td>
</tr>
<tr>
<td>Elong. at break, %</td>
<td>14/7/7</td>
<td>30/11/12</td>
</tr>
<tr>
<td>GIC (in lb./in²)</td>
<td>4.9</td>
<td>2.2</td>
</tr>
</tbody>
</table>

3 Adh.: Adhesive, Coh.:

3 Specimens bonded at 250 psi/330°C/15 minutes

3 Mole % molecular weight controlled endcapped PAEBI, $\eta_{inh} = 0.52$ dL/g, $T_g = 265°$ C.

3 Specimens bonded at 250 psi/330°C/15 minutes

3 Adh.: Adhesive, Coh.:
wherein the catenation of oxygen is selected from the group consisting of meta-meta, para-para, and para-meta; wherein Ar is a radical selected from the group consisting of

wherein Z is a bond or Z is a radical selected from the group consisting of

and

wherein X is a radical selected from the group consisting of
wherein EC is a radical selected from the group consisting of:

\[
\begin{align*}
\text{CH}_2\text{N}=\text{N} & \quad \text{and} \\
\text{CH}_3\text{N}=\text{N} &
\end{align*}
\]

wherein W is a radical selected from the group consisting of

\[
\begin{align*}
\text{H} & , \text{CH}_3, \text{CH}_3\text{O} & \\
\text{and} & \\
\text{O} & \\
\end{align*}
\]

wherein n is an integer between 4 and 1000.

2. The molecular weight controlled and endcapped poly(benzimidazole) of claim 1, wherein Ar is a radical having the formula of

\[
\begin{align*}
\text{X} & = \text{radical having the formula} \\
\text{EC} & = \text{radical having the formula} \\
\text{W} & = \text{radical represented by H.}
\end{align*}
\]

3. A process for synthesizing molecular weight controlled and endcapped poly(benzimidazole)s by aromatic nucleophilic displacement which comprises reacting (A) di(hydroxyphenyl)benzimidazole, (B) a monofunctional benzimidazole having the general structure

\[
\begin{align*}
\text{Y} & \\
\text{wherein X is a radical selected from the group consisting of} \\
\text{and} & \\
\text{EC} & \text{is a radical having the formula} \\
\text{W} & \text{is a radical represented by H.}
\end{align*}
\]
droxide, and wherein said reaction is carried out with the application of heat.

4. The process of claim 3, wherein X is

5. Ar is

10

15

20

25

W is H, and V is OH.

5. The process of claim 4, wherein Y is selected from the group consisting of Cl, F, and NO2; wherein said reaction is carried out in a polar aprotic solvent selected from the group consisting of N,N-dimethylacetamide, N-methyl-2-pyrrolidinone, sulfolane, diphenylsulfone, N-cyclohexyl-2-pyrrolidinone, and dimethylsulfoxide; wherein said reaction is also carried out in the presence of an alkali metal base selected from the group consisting of potassium carbonate, sodium carbonate, potassium hydroxide, and sodium hydroxide, and wherein said reaction is carried out with the application of heat.

6. The process of claim 5, wherein Y is F, and the solvent is N,N-dimethylacetamide.

7. A film prepared from the molecular weight controlled and endcapped poly(benzimidazole) of claim 1.

8. A fiber prepared from the molecular weight controlled and endcapped poly(benzimidazole) of claim 1.

9. A molding prepared from the molecular weight controlled and endcapped poly(benzimidazole) of claim 1.

10. An adhesive prepared from the molecular weight controlled and endcapped poly(benzimidazole) of claim 1.

11. A matrix resin for composites prepared from the molecular weight controlled and endcapped poly(benzimidazole) of claim 1.