Dibenzyl Structures on the Macromolecular Chain v.
Polyquinazolinediones and Polybenzimidazoles

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Received 1 June 1993; accepted 6 October 1993

ABSTRACT

Polyquinazolinediones and polybenzimidazoles with dibenzyl structure on the macromolecular chain are synthesized. 4,4'-; 2,4'-Dibenzyl disocyanate and, respective, 3,3', 4,4'-dibenzyldiaminotetramine are used as monomers for the polymer syntheses. Thermogravimetric, IR spectroscopy and elemental analyses of these polymers are determined.

Key Words
heterocyclic polymer, dibenzyl structure, disocyanate, tetramine, quinazolinedione, benzimidazole, thermal stability.

INTRODUCTION

Our previous papers described the syntheses of different polymers from 2,2'-2,4' and 4,4'-dibenzyl diamines (DAB) or disocyanates (DBDI). The influence of the dibenzyl isomers on the aromatic polyamides structure was studied [1,2]. Polyamideimides and polyamides with dibenzyl structures were also investigated. 4,4'-Dibenzyl moieties lead to higher molecular weight and thermal stability than other isomers.

Polyurea and copolyurea syntheses from dibenzyl diamines and/or disocyanates were also studied [3]. 4,4'-Dibenzyl isomers produced high crystalline polyureas which prematurely precipitated from the reaction mixture and which possessed low molecular weight.

2,4'-Dibenzyl diamine or disocyanate lead to high molecular weight polyureas able to form flexible films by casting from the polymer solutions.

2,2'-Dibenzyl isomers can determine in a certain extent the cyclization to low molecular weight oligomers. Starting from these polyureas, poly(parabanic acids) were obtained by the intermolecular reaction with oxalyl chloride [3].

This paper is directed toward the investigation of heterocyclic polymers as polyquinazolinediones and polybenzimidazoles containing dibenzyl systems.

A) Polyquinazolinediones are very thermal stable polymers but they exhibit low solubility in organic solvents [4]. In this work we have obtained polyquinazolinediones by a few step polycondensation of the 3,3'-benzidine dicarboxylic acid (BDA) and 4,4'-or 2,4'-DBDI:
The first step is a polyaddition reaction between isocyanate and amine groups of monomers. The addition reaction takes place by the nucleophilic attack of the amino groups on the carbon atom of the cumulated double bonds from the isocyanate groups resulting urea groups. Thus, we have obtained in the first step of the reaction, polyureas with pendant carboxylic groups on the macromolecular chain (I). These polymers can be transformed, stepwise, into polyimino-benzoxazinone (II), by cyclohydration at 150-180°C. The mechanism of this reaction consists in an elimination of one water molecule between the enolic form of the urea group and the carboxylic group from the ortho position of same aromatic ring (the vicinal carboxylic group), at 150-180°C. At this temperature, a ring closure takes place forming an iminobenzoxazinone structure (II). Finally, the polyiminobenzoxazinones (II) were heated at 230-300°C. When an intramolecular rearrangement was produced and polyquinazolinediones were obtained.
B) Polybenzimidazoles are polymers with high thermal and hydrolytical stability and they exhibit reduced solubilities in organic solvents. This kind of polymer was obtained for the first time by Marvel and Iwakura [5-7] starting from the free base of tetramine derivatives and the aromatic dicarboxylic acids or their derivatives. The aromatic tetramines are sensitive to oxidation and all polycondensation reactions required the use of inert atmosphere and a very careful processing. This is why Iwakura and Yoda [8, 9] used the aromatic tetramine hydrochloride as well as polycondensation factor.

In this work, the reaction of 3,3', 4,4' dibenzyl tetramine hydrochloride and tetraphthalic or isophthalic acid in polyphosphoric acid was used.

EXPERIMENTAL

Materials

2,4'- and 4,4'-DBDI were prepared by original methods [10]. Benzidine -3,3'-dicarboxylic acid (BDA) was prepared as described [11]. 3,3',4,4'-Dibenzyl tetramine hydrochloride (TAB-HCl) was prepared by an original method [12]. Commercial terephthalic and isophthalic acids were purified in the usual manner. The N-methyl-2-pyrrolidone (NMP) solvent was dried on P2O5 and freshly distilled.

Polyphosphoric acid (84% P2O5) (PPA) was prepared by the known procedure [9].

Methods

A. Two procedures were followed for the polyaddition between dibenzyl diisocyanates and benzidine -3,3'-dicarboxylic acid.

a) When NMP was used as solvent, the reaction mixture needed heating at the beginning of the reaction to dissolve the monomers, then, the mixture was stirred at room temperature for 7-8 hours.

The polyurea acids were precipitated in methanol, isolated by filtration and dried at 120 °C.

b) The polyphosphoric acid as a solvent permitted the use of the hydrochloride derivative that produced a foaming due to the evolution of the hydrochloride acid (HCl) at the beginning of the reaction. The reaction temperature was about 150 °C. After 4-5 hours, a clear and very viscous solution was obtained. The polymer was precipitated in water and washed with 5 % Na2CO3 solution, then dried at 120 °C in vacuum.

The reaction conditions and the characterization of the polyurea acids are shown in Table 1. The amounts of reactive materials are also included in Table 1.
Table 3. Polybenzimidazoles synthesis

<table>
<thead>
<tr>
<th>Nr.</th>
<th>Phthalic acid(a) (g)</th>
<th>Monomers</th>
<th>TAB(\cdot)HCl(b) (g)</th>
<th>Solvent PPA(c) (g)</th>
<th>Temp. (°C)</th>
<th>Time (h)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IV(_a)</td>
<td>para, 0.83</td>
<td>2.10</td>
<td>50</td>
<td>200</td>
<td>13</td>
<td>98.5</td>
<td></td>
</tr>
<tr>
<td>IV(_b)</td>
<td>meta, 0.83</td>
<td>2.12</td>
<td>56</td>
<td>200</td>
<td>11</td>
<td>97.8</td>
<td></td>
</tr>
</tbody>
</table>

a) p- and m-phthalic acid are terephthalic and isophthalic acid.
b) 3,3',4,4'-dibenzyl tetramine hydrochloride.
c) PPA = polyphosphoric acid.

Table 4. Polybenzimidazoles characterization

<table>
<thead>
<tr>
<th>Nr.</th>
<th>(\eta_{inh})(d) (\text{dl/g})</th>
<th>N%</th>
<th>Calcd.</th>
<th>Found</th>
<th>(T_{loss}) °C</th>
<th>5% Loss of weight</th>
<th>15% Loss of weight</th>
<th>25% Loss of weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>IV(_a)</td>
<td>0.23</td>
<td>16.67</td>
<td>16.70</td>
<td>365</td>
<td>435</td>
<td>510</td>
<td>555</td>
<td></td>
</tr>
<tr>
<td>IV(_b)</td>
<td>0.32</td>
<td>16.67</td>
<td>17.14</td>
<td>370</td>
<td>440</td>
<td>500</td>
<td>550</td>
<td></td>
</tr>
</tbody>
</table>

a) Measured at a concentration of 0.5 g/100 ml in concentrated sulphuric acid at 25°C.

RESULTS AND DISCUSSION

A) The polyurea acids were characterized by TGA, IR-spectra, elemental analysis and inherent viscosities. The analysis confirmed the polyurea acid structure. The IR-spectra exhibit an absorption band at 1660 cm\(^{-1}\) due to the urea carbonyl groups and at 2800-3300 cm\(^{-1}\) attributed to NH groups; also, a large band assigne to the free carboxyl group was observed at 2500-3000 cm\(^{-1}\) (Figure 1).

As we show above, the effective cyclization temperatures were determined from TGA. The polyurea acids (I\(_a\),b) with 4,4'-dibenzyl structure (Table 1) exhibit a weight loss between 150-180 °C which represents 8-9% (corresponding to two moles of water on a structural unit) with simultaneously cyclization to iminobenzoxazinone.

The calculated weight loss are in good agreement with those found (5,5 and 6,2%). The decomposition temperature of this polymers is higher than 370 °C.

The second step of the reaction consists of a cyclodehydration reaction by the heating of polyureas at 230-355°C, followed by an intramolecular rearrangement. By prolonged thermal treatments in vacuum, polyquinoxalinediones were obtained directly, without evidence of the iminobenzoxazinone intermediate structures.

The polymers were characterized as shown in Table 2. The infrared spectra show the disappearance of the absorption band characteristic to free carboxylic groups in the region of 2800-3000 cm\(^{-1}\) and, also, the changing of the urea carbonyl band from 1670 cm\(^{-1}\) to a new carboxylic band characteristic of the quinoxalinedione heterocycle at 1760 cm\(^{-1}\) (Figure 2).

These polymers show a high thermal stability, the decomposition temperature ranging from 380 to 450 °C as determined by TGA. The weight loss rates are different: the weight loss of the polymers
Fig. 1. IR Absorption spectra of polyureas I:
I_{ab} - polyureas from 4,4' - DBDI
I_{c} - polyurea from 2,4' - DBDI

Fig. 2. IR Absorption spectra of polyquinazolinediones III
III_{ab} - polyquinazolinedione from 4,4' - DBDI
III_{c} - polyquinazolinedione from 2,4' - DBDI
Fig.3. IR Absorption spectra of polybenzimidazoles IV.
IVa (para-phenylene structure)
IVb (meta-phenylene structure)

with 2,4'-dibenzyl structure is higher than those of the polyquinazolinedione obtained from 4,4'-DBDI.

The values for nitrogen by elemental analyses are in agreement with the calculated ones (Table 2).

B) In this paper, we used the poly-condensation reaction of 3,3',4,4'-dibenzyl tetramine hydrochloride and terephthalic or isophthalic acid in PPA solution. This solvent permits the use of hydrochloride tetramine because the pure tetramine is very sensitive to oxidation. PPA acts as dehydrating agent too, and finally, polybenzimidazoles are obtained.

The characteristics of polymers are shown in Table 4. The polymers presented high thermal stability. Thus, they decomposed without melting at temperature higher than 365-370 °C in air; a 5% weight loss was observed at 435-440 °C, a 15% weight loss at 500-510 °C and a 25% weight loss at over 550 °C, finally, leading to black residue.

The viscosity measurements were made on the polymer solutions in concentrated H2SO4, at 25°C. The low molecular weight of these polymers are explained by the tendency of the monomers to crystallize with the dibenzyl structure, determining the premature precipitation from the reaction mixture.

The polymer are brown powders. The color of the polymers is due to the benzimidazole chromophore groups and to the conjugation with the aromatic ring of the carboxylic acids.
The infrared absorption spectra of polybenzimidazoles derived from 3,3',4,4'-dibenzyl tetramine showed strong absorption bands at 1610 cm\(^{-1}\) and 1440 cm\(^{-1}\) characteristic to the benzimidazole rings [6] and two peaks at 800 and 850 cm\(^{-1}\) corresponding to the p- or m- disubstituted benzene ring (Figure 3).

**CONCLUSIONS**

The series of studies about the influence of dibenzyl structures on some type of heterocyclic polymers with high thermal stability has been continued.

The polymers with quinazolinedione or benzimidazole rings were synthesized and characterized.

As in our previous studies, a superior crystallinity of polymers with dibenzyl structures was observed and, consequently, they showed a high thermal stability.

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