Synthesis and Characterization of New Polyesters Containing Azobenzene Unites and Aromatic Diols in Main Chain

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Abstract

4-Nitrobenzoic acid 1 was reacted with glucose in the presence of sodium hydroxide at 50 °C and 4,4’-azodibenzoic acid 2 was obtained in quantitative yield. Then 4,4’-azodibenzoic acid 2 was converted to 4,4’-azodibenzoyl chloride 3 by reaction with thionyl chloride. Solution polycondensation of this diacid chloride 3 with hydroquinone 4a, 2,7-dihydroxy naphtalene 4b, 4,4’- dihydroxy diphenyl sulfone 4c, bisphenol A 4d, 1,4-dihydroxy antraquinone 4e and phenol phethalein 4f was carried out in DMAc solvent and in the presence of pyridine as a base. The polycondensation reaction producing a series of new polyesters 5a-f in high yield, and inherent viscosity between 0.20-0.47 dL/g. The resulting polyesters were characterized by elemental analysis, viscosity measurements, thermal gravimetric analysis (TGA and DTG), solubility test and FT-IR spectroscopy. All of the polymers were soluble at room temperature in polar solvents such as N,N-dimethylacetamide (DMAc), N,N-dimethylformamide (DMF), dimethylsulfoxide (DMSO), tetrahydrofurane (THF) and N-methyl-2-pyrroolidone (NMP).

Key words: 4,4’-azodibenzoyl chloride, aromatic diols, azobenzene moieties, solution polycondensation, inherent viscosity

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Introduction

Azo-containing polymers are macromolecules with azo groups in main or side chain. These polymers have received much attention because of their special properties resulting from isomerization of the azobenzene groups \[^1-^5\]. Depending on the chemical structures, they can reveal liquid crystalline properties and nonlinear optical (NLO) properties or light-induced dichroism and birefringence \[^6-^10\]. Potential applications of the azobenzene polymers include display devices, optical modulators, optical waveguides, holography and reversible optical storage \[^11\]. The photoisomerization of the azobenzene in the azoaromatic polymers is believed to play an important role in the chromophore orientation and subsequent induction of the birefringence imaging on the polymer films \[^1,^3\].

In the previous articles \[^12-13\], we synthesized a series of new poly(amide-imide)s containing azobenzene and hydrocyclic moieties in main chain. In this article, we wish to report the synthesis and characterization of a series of new polyesters from the reaction of 4,4'-azodibenzoyl chloride 3 as a monomer with azobenzene moieties with six different aromatic dilos in DMAc solution and in the presence of pyridine as a base.

EXPERIMENTAL

Materials and Characterization

Fourier transform infrared (FTIR) spectra were recorded on Galaxy series FTIR 5000 spectrophotometer (England). Spectra of solids were performed using KBr pellets. Vibrational transition frequencies are reported in wave number (cm\(^{-1}\)). Band intensities are assigned as weak (w), medium (m), shoulder (sh), strong (s) and broad (br). Inherent viscosities were measured by a standard procedure using a Technico Regd Trad Merk Viscometer. Thermal Gravimetric Analysis (TGA) data for polymers were taken on a Mettler TA4000 System under N\(_2\) atmosphere at a rate of 10 °C/min. Elemental analyses were performed by the Arak Petrochemical Company, Iran.

Monomer Synthesis

4,4'-Azodibenzoyl chloride 3 was prepared according to a typical procedure that was shown in scheme 1 \[^14-15\].

4,4'-Azodibenzoic acid [4,4'-Azodibenzenedicarboxylic acid] 2

4-Nitrobenzoic acid 1 (13 g, 79 mmol) was heated in sodium hydroxide solution (50 g in 250 ml) at 50 °C. A solution of glucose (100 g in 150 ml of water) was added slowly at this temperature with occasional shaking, the reaction mixture was then cooled to ambient temperature and aerated for 8 h with vigorous stirring until orange crystals were formed. The mixture was acidified with dilute acetic acid, and then the liberated diacid was filtered, washed with water and dissolved in hot potassium carbonate solution to get orange colored solution. This solution was concentrated to get orange crystals of potassium salt of diacid. On acidifying with dilute acetic acid, 18 g (86 %) of rose colored 4,4'-azodibenzoic acid 2 was obtained. mp > 300 °C, FT-IR (KBr): 3600-2900 (m, br), 1669 (s, br), 1614 (s), 1579 (s), 1410 (s), 1300-1200 (s, br),
1100-1000 (s, br), 868 (s), 777 (s) cm\(^{-1}\). Analysis: Calculated for C\(_{14}H_{10}N_2O_4\): C, 62.24; H, 3.70; N, 10.36; found: C, 62.4; H, 3.8; N, 10.0.

4,4′-Azodibenzoyl chloride 3

Into a 100 mL round-bottomed flask were placed (4 g, 14.8 mmol) of 4,4′-azodibenoic acid 2, 15 mL of thionyl chloride and 0.2 ml triethylamine. The mixture was heated on an oil bath up to 60°C, until the suspension mixture was converted to a clear solution. Then, the solution was stirred for over night at room temperature. Unreacted thionyl chloride was removed under reduced pressure and the residue was washed with dry n-hexane two times to leave 4.3 g (95%) of red crystals of 4,4′-Azodibenzoyl chloride. mp 177-179°C, FT-IR (KBr): 1776 (s), 1732 (m, br), 1595 (m), 1408 (m), 1195 (s, br), 885 (s), 804 (m), 646 (m) cm\(^{-1}\). Analysis: Calculated for C\(_{14}H_8N_2O_2Cl_2\): C, 54.72; H, 2.60; N, 9.12; found: C, 54.9; H, 2.8; N, 8.9.

\[
\begin{array}{c}
\text{O}_2\text{N-} \quad \text{CO}_2\text{H} \\
1)
\text{NaOH} \\
\text{Glucose, } 50^\circ\text{C} \\
2) \text{CH}_3\text{COOH} \\
\text{SOCl}_2
\end{array}
\]

Scheme 1

**Polymer Synthesis**

The new polyesters 5a-f were prepared by two different methods such as solution and bulk polycondensation using the following general procedure: Taking polymer 5a as an example that was prepared from the reaction of 4,4′-azodibenzoyl chloride 3 and hydroquinone 4a:

**Method A: Solution polycondensation with pyridine as a base**

Into a 25 mL round-bottomed flask was fitted with a stirring bar were placed (0.22 g, 2 mmol) hydroquinone 4a and 1.5 mL of DMAc. The mixture was cooled in an ice-water bath, and (0.32 g, 4 mmol) of pyridine was added to this solution. Then (0.54 g, 2 mmol) of diacid chloride 3 was added all at once. The polymerization proceeded as the acid chloride was dissolved. The reaction mixture was stirred in an ice-water bath for 1 hr, the cooling bath was removed, the stirring continued at room temperature for overnight and then heated at 80°C for 12 h. The reaction mixture was poured into 50 mL of methanol, The precipitated polymer was collected by filtration, washed thoroughly with methanol and dried at 80°C for 12 hr under vacuum to leave 0.58 g (85%) of polymer 5a.

**Method B: Bulk polycondensation**

Into a 25 mL round-bottom flask fitted with a stirring bar were added (0.54 g, 2 mmol) of diacid chloride 3 and (0.22 g, 2 mmol) of hydroquinone 4a. Then the reaction mixture was heated at 60°C for 4 h and 120°C for 1 h. Intensive stirring and dynamic vacuum enable the removal of HCl. The solid was poured into 50 mL of
methanol. The resulting polymer was filtered off and dried to yield 0.40 g (58%) of solid polymer 5a.

RESULTS AND DISCUSSION

Polymer Synthesis

Polyesters 5a-f were synthesized by solution polycondensation reactions of an equimolar mixture of monomer 3 with six different derivatives aromatic diols 4a-f as shown in Scheme 2.

At first, polymer 5a was prepared from the reaction monomer 3 and hydroquinone 4a by two different methods. In method A, polymerization reaction was carried out in DMAc solution at low temperature, then was heated at higher temperature in the presence of pyridine as a base. The resulting polymer had moderate inherent viscosity and high yield. In method B, polymerization reaction was carried out under bulk condition at higher temperature and in vacuum. The resulting polymer had low inherent viscosity and low yield. In the solution method the resulting polymer had higher viscosity and higher yield in comparison with the bulk method. According to these results we selected the method A for the synthesis of the other polymers.

Table 1. Synthesis and some physical properties of polyesters 5a

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Method</th>
<th>Yield (%)</th>
<th>( \eta_{inh} (dL/g) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>5a</td>
<td>A</td>
<td>85</td>
<td>0.47</td>
</tr>
<tr>
<td>5a</td>
<td>B</td>
<td>58</td>
<td>0.15</td>
</tr>
</tbody>
</table>

\(^a\) Measured at a concentration of 0.5g/dL in DMF at 25ºC
Polymer Characterization

Synthesis and some physical properties of polyester 5a-f are summarized in Table 2. These polymers have inherent viscosities in a range between 0.20-0.47 dL/g and have red color. The structures of these polymers were confirmed as polyester by means of FT-IR spectroscopy and elemental analyses (Table 3). These polymer show absorption bands between 1690-1670 cm\(^{-1}\) due to ester carbonyl groups. Absorption bands around 1650-1600 cm\(^{-1}\) and 1350-1460 are due to aromatics ring vibrations, methyl and methylene stretching, respectively. Absorption bands around 1200-1000 cm\(^{-1}\) which correspond to C-O stretching of ester (See Appendix A).

Table 2. Synthesis and some physical properties of Polyesters 5a-f

<table>
<thead>
<tr>
<th>Aromatic diol</th>
<th>Polymer</th>
<th>Yield (%)</th>
<th>(\eta_{inh})(dL/g) (^d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4a</td>
<td>5a</td>
<td>85</td>
<td>0.47</td>
</tr>
<tr>
<td>4b</td>
<td>5b</td>
<td>82</td>
<td>0.28</td>
</tr>
<tr>
<td>4c</td>
<td>5c</td>
<td>80</td>
<td>0.25</td>
</tr>
<tr>
<td>4d</td>
<td>5d</td>
<td>86</td>
<td>0.24</td>
</tr>
<tr>
<td>4e</td>
<td>5e</td>
<td>90</td>
<td>0.29</td>
</tr>
<tr>
<td>4f</td>
<td>5f</td>
<td>81</td>
<td>0.23</td>
</tr>
</tbody>
</table>

Measured at a concentration of 0.5g /dL in DMF at 25°C.

The elemental analysis values of the resulting polymers were in good agreement with the calculated values for the proposed structures (Table 3).
Table 3. Elemental Analysis of polyesters 5a-f

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Formula</th>
<th>C%</th>
<th>H%</th>
<th>N%</th>
</tr>
</thead>
<tbody>
<tr>
<td>5a</td>
<td>C_{20}H_{12}N_{2}O_{4}</td>
<td>69.8</td>
<td>3.5</td>
<td>8.1</td>
</tr>
<tr>
<td></td>
<td>(344.29)_n</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>C_{24}H_{14}N_{2}O_{4}</td>
<td>72.3</td>
<td>3.0</td>
<td>6.1</td>
</tr>
<tr>
<td></td>
<td>(394.35)_n</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5c</td>
<td>C_{26}H_{16}N_{2}O_{6}S</td>
<td>64.4</td>
<td>3.3</td>
<td>5.8</td>
</tr>
<tr>
<td></td>
<td>(484.39)_n</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5d</td>
<td>C_{29}H_{22}N_{2}O_{4}</td>
<td>75.3</td>
<td>4.8</td>
<td>6.0</td>
</tr>
<tr>
<td></td>
<td>(462.46)_n</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5e</td>
<td>C_{28}H_{14}N_{4}O_{6}</td>
<td>70.9</td>
<td>2.9</td>
<td>5.9</td>
</tr>
<tr>
<td></td>
<td>(474.39)_n</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5f</td>
<td>C_{34}H_{20}N_{2}O_{6}</td>
<td>73.9</td>
<td>3.6</td>
<td>5.1</td>
</tr>
<tr>
<td></td>
<td>(562.5)_n</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The solubility of polyesters 5a-f were investigated as 0.01 g of polymeric sample in 2 ml of solvent. All of the polymers are soluble in organic solvents such as DMF, DMAc, DMSO and THF at room temperature, and are insoluble in solvents such as acetone, chloroform, methylene chloride, methanol, ethanol and water.

**Thermal Properties**

The thermal properties of two polyester 5a and 5c were investigated by means of differential scanning calorimetry (DSC) as well as the thermogravimetric analysis (TGA) and derivative thermogravimetric (DTG) analysis in a nitrogen atmosphere at a heating rate of 10 °C/min and thermal data are summarized in Table 4. All of these polymers show similar decomposition behavior. Initial decomposition temperature, 5% and 10% weight loss (T_{5}, T_{10}) and char yields at 600 °C for polymer 5a and 5c are summarized in Table 4. These polymers exhibited good resistance to thermal decomposition up to 315 °C in nitrogen and began to decompose gradually above that temperature. The temperature of 5% weight loss for all the polymers ranged from 315 to 320 °C and the residual weight for these polymers at 600°C ranged from 10 to 12.0 % in nitrogen (Fig. 1).
Table IV. Thermal behavior of polyesters 5a, c

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$T_5$ (°C) b</th>
<th>$T_{10}$ (°C) c</th>
<th>Char Yield d</th>
</tr>
</thead>
<tbody>
<tr>
<td>5a</td>
<td>380-385</td>
<td>455-460</td>
<td>47%</td>
</tr>
<tr>
<td>5c</td>
<td>320-325</td>
<td>380-385</td>
<td>52%</td>
</tr>
</tbody>
</table>

a Glass transition temperature. b,c Temperature at which 5% and 10% weight loss was recorded by TGA at heating rate of 10°C/min in N$_2$ respectively. dPercentage weight of material left undecomposed after TGA analysis 600°C.

CONCLUSIONS

The present work has shown that 4,4′-azodibenzoyl chloride 3 is an interesting monomer which have azobenzene moieties. Thus, a series of new polyesters 5a-f were synthesized by solution polycondensation reaction using the monomer 3 with six different derivatives of aromatic diols 4a-f DMAc solution and in the presence of pyridine as a base. These new polyesters are soluble in various organic solvents and have good thermal stability.

Appendix A. The polyesters 5a-h analyses using FT-IR

**Polymer 5a**

FT-IR (KBr): 3065 (w), 2925 (w), 1695-1670 (s, br), 1597 (w), 1428 (m), 1284 (m), 1208 (s, br), 1179 (w), 1063 (m), 882 (m), 772 (m), 699 (w) cm$^{-1}$.
**Polymer 5b**

FT-IR (KBr): 3064 (w), 2925 (w), 1690-1680 (s, br), 1600 (w), 1577 (w), 1421 (m), 1286 (s, br), 1208 (s, br), 1178 (w), 865 (m), 775 (m), 693 (w) cm\(^{-1}\).

**Polymer 5c**

FT-IR (KBr): 3065 (w), 2920 (w), 1690-1670 (s, br), 1597 (m), 1485 (w), 1280-1240 (s, br), 1206 (m), 1057 (m), 999 (w), 772 (m), 695 (w) cm\(^{-1}\).

**Polymer 5d**

FT-IR (KBr): 3075 (w), 2935 (w), 1695-1685 (s, br), 1629 (w), 1492 (w), 1280-1230 (s, br), 1152 (m), 1050 (w), 865 (m), 776 (m), 693 (w) cm\(^{-1}\).

**Polymer 5e**

FT-IR (KBr): 3075 (w), 2925 (w), 1680-1675 (s, br), 1597 (w), 1420 (m), 1285-1250 (s, br), 1206 (m), 1057 (m), 999 (w), 772 (m), 695 (w) cm\(^{-1}\).

**Polymer 5f**

FT-IR (KBr): 3065 (w), 2926 (w), 1690-1670 (s, br), 1598 (w), 1428 (m), 1285-1270 (s, br), 1206 (w), 1068 (m), 925 (w), 864 (w), 773 (m), 690 (w) cm\(^{-1}\).

**References**


