Synthesis of new organosoluble poly (ester-amide-imide)s bearing amino acids and 4,4’-(diamidodibenzo) sulfone subunits in the main chain

Esmael Rostami*, Elmira Forouzani, Shayesteh Akhbarzadeh, Zahra Heidari, Roshan Azadmanesh, Laleh Pourhossein, Nilofar Nashibi, Somayeh Sepahvand
Department of chemistry, Payame Noor University, PO BOX 19395-3697 Tehran, (IRAN)
E-mail : esmrostami@yahoo.com

**ABSTRACT**

New poly (ester-amide-imide)s containing aminoacids and 4,4’-(diamidodibenzo) sulfone units were prepared and their solubility and viscosity were evaluated. The viscosities of polyamides are in the range of 0.43-0.47. These polyamides showed good solubility in common organic solvents. Theoretical calculation shows the high free volume of polymer chains.

**KEYWORDS**

Poly (ester-amide-imide); Amino acid; Diphenylsulfone; Synthesis; Theoretical study.

**INTRODUCTION**

Aromatic polyamides and polyimides are high performance polymers with some advantages such as, good thermal stability, efficient mechanical properties, low flammable, good processable, easy applicable and low density materials\[1-4\]. Because of their excellent properties, they are used as good alternatives for a series of industrial materials in applications\[5\]. The new industry and technology requires high performance materials with a series of properties and stable in vigorous conditions such as elevated temperatures, high acidic and basic media and humid and cold regions\[6\]. Polyamides and polyimides are important candidates for these advanced materials have ability to change their properties with a series of improvements and gain desired application\[7\]. Wholly aromatic polyamides (aramides) have a few disadvantages such as poor solubility, difficult processability and high melting and thus restricted applications\[8\]. Several procedures were examined for achieve these drawbacks containing the use of softening aliphatic chains, ethers, esters and sulfides in the polymer main chain, insertion of three dimensional and bulky pendant groups (for example; alkyl, sulfone, thio and ether groups) for avoid crystallinity, close packing and gain low melting, good soluble and processable polymers with good thermal stability\[9-11\].

In continuation of our previous research works on the synthesis of polymers\[12\], in this research work new organosoluble poly (ester-amide-imide)s containing aminoacids and diphenylsulfone in the main chain were synthesized and their properties were studied.

**EXPERIMENTAL**

The reactions for the synthesis of monomer and purification of polymers were carried out in an efficient hood. All the materials were purchased from Merck, Fluka, Across Organics and Aldrich chemical companies. N-Methyl-2-pyrrolidinone (NMP, Merck) was
purified by distillation under reduced pressure over calcium hydride and stored over 4Å molecular sieves. FT-IR spectra were recorded in potassium bromide pellets on a Bruker apparatus. The $^1$H NMR and $^{13}$C NMR spectra were obtained using Bruker Avance DRX 500 MHz apparatus and mass spectra were obtained with Shimadzu GC-MS-QP 1100 EX model. Inherent viscosities ($\eta_{inh} = \ln \eta/c$ at a concentration of 0.5 g dL$^{-1}$) were measured with an Ubbelohde suspended-level viscometer at 30°C using DMSO as solvent. Theoretical studies were performed using Hyperchem 7.0 using semi-empirical functions and AM1 method and then the molecular structures in Figures 3 and 4 were produced using GaussView 5.0.

**Synthesis of dichloroamide (3)**

To acetonitrile (30 mL) were added 4,4'-diaminodiphenyl sulfone (1, 1mmol, 0.25g), triethylamine (2mmol, 0.28mL) and chloroacetyl chloride (2mmol, 0.16mL) at room temperature. The reaction mixture was stirred at room temperature for 48 hours. After completion of the reaction (monitored by TLC), water was added and the resulting white precipitate was filtered and recrystallized in ethanol to afford a white solid in 94% yield; IR (KBr): 3598, 3508, 3114, 2987, 1684, 1654, 1302, 1107, 836 cm$^{-1}$; $^1$H NMR (500 MHz, DMSO-d$_6$) $\delta$: 4.24 (s, 4H), 7.75 (d, J= 9Hz, 4H), 7.85 (d, J= 9Hz, 4H), 10.68 (S, 2H) ppm; $^{13}$C NMR (125 MHz, DMSO-d$_6$) $\delta$: 166.27, 143.75, 136.64, 129.44, 120.34, 44.39 ppm; MS (EI) m/z (relative intensity %): 405 [M+1]$^+$ (3), 404 [M]$^+$ (6), 403 [M-1]$^+$ (7), 402 [M-2]$^+$ (33), 401 [M-3]$^+$ (23), 400 [M-4]$^+$ (54), 324 (31), 216 (29), 184 (32), 140 (71), 108 (100), 77 (24), 36 (57); Analytical calculated for C$_{16}$H$_{14}$Cl$_2$N$_2$O$_4$S (M=401.26): C, 47.89; H, 3.52; Found, C, 47.86; H, 3.51; N, 7.03.

**Synthesis of diimide-acids (8-10)**

To Pyromellitic dianhydride (4, 1mmol) was added aminoacids (5-7, 2mmol) and glacial acetic acid (30mL)
at room temperature. The mixture was stirred at room temperature for 1h and then was refluxed for 24h. After completion of the reaction (monitored by TLC), water was added and the mixture was left for 24h. Then, the resulting white precipitate was filtered and recrystallized in ethanol to afford diimide-acids (8, 9, 10) in good yields.

**Synthesis of polymers (11-13)**

Polyamides were synthesized through the nucleo-
philic reaction of dichloroamide (3) with various diacids (8-10) as shown in Scheme 3. A typical example for the preparation of polyamide (11) is given. To 3 (1mmol, 0.40g) in quartz tube were added 8 (1mmol, 0.51g), NMP (4mL) and triethylamine (2mmol, 0.28mL). The mixture was stirred at room temperature for 30min. and then, irradiated under microwave in 600W for 9 Min. (3×3 Min.) and the rest time of 10
Min. (2×5 Min.). After cooling to room temperature, the resulting viscose reaction mixture was poured into 300 mL of boiling methanol. The resulting crude product was precipitated and then filtered. The resulting polymer (11) was washed with hot methanol (50 mL), hot water (twice, 50 mL) and then hot methanol (50 mL), respectively; and dried under vacuum at 100 °C overnight. Spectral data, viscosity and solubility of these polyamides were reported in the following tables and figures.

RESULTS AND DISCUSSION

In this research work, we wish to report the synthesis and characterization of poly (ester-amide-imide) s obtained from the reaction of a new dichloroamidemonomer (3), containing amide and sulfone units, and aromatic rings. 3 was prepared from the reaction of 4,4′-diaminodiphenyl sulfone and chloroacetyl chloride in acetonitrile in the presence of triethylamine (Scheme 1).

Diimide-acids (8-10) were prepared from the reaction of Pyromellitic dianhydride (4) and amino acids (l-phenyl alanine (5), l-methionine (6) and β-alanine (7)) in refluxing glacial acetic acid in good yields (Scheme 2). FT-IR spectrum of 8 is appeared in Figure 1. poly (ester-amide-imide)s (11-13) were prepared from the reaction of dichloroamide (3) and diimide-acids (5-7) in NMP under microwave irradiation (Scheme 3). FT-IR spectrum of 11 is appeared in Figure 2, and showed the corresponding structure according to the main functional groups. FT-IR and 1H NMR spectra of polymers summarized in TABLE 1 and are in agreement with corresponding structures. The inherent viscosities and the yields of polyamides were reported in TABLE 2.

The solubility behavior of polymers was investigated qualitatively in a series of organic solvents such as N-methylpyrrolidinone (NMP), N, N-dimethylformamide (DMF), tetrahydrofuran (THF), dimethylsulfoxide (DMSO), N, N-dimethylacetamide (DMAc) and m-cresol, and the results are summarized in TABLE 3. All the polymers showed reliable solubility in polar organic solvents. This might be due to the presence of phenyl sulfone units which decreased intramolecular and intramolecular hydrogen bonding but thiomethoxyd aliphatic groups increases the intramolecular hydrogen bonding and flexibility and then decrease the crystallinity and close paking. On the other hand, sulfone units reduced the flexibility and increased close packing and crystallinity. Also, the aminoacid structure varies the solubility. Theoretical studies on the monomer of 12 showed the high free volume in the

<table>
<thead>
<tr>
<th>Polymer</th>
<th>IR (cm⁻¹)</th>
<th>¹H NMR (500 MHz, DMSO-d₆): δ (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>11</td>
<td>3368, 3146, 2993, 1716, 1693, 1386, 1107.</td>
<td>3.12-3.15 (b, 4H), 5.31 (S, 4H), 6.71 (t, J= 8.5 Hz, 2H), 6.73-7.24 (m, 10H), 7.71-7.73 (b, 4H), 7.81-7.83 (b, 4H), 8.14-8.16 (b, 2H), 9.29.</td>
</tr>
<tr>
<td>12</td>
<td>3366, 3281, 2983, 2431, 1719, 1685, 1401, 1041, 986, 834.</td>
<td>3.15 (s, 6H), 4.56 (S, 4H), 4.73 (S, 4H), 6.99-7.01 (b, 2H), 7.21-7.82 (m, 8H), 8.13-8.16 (m, 2H), 10.56 (S, 2H).</td>
</tr>
<tr>
<td>13</td>
<td>3366, 3158, 2986, 2434, 1701, 1688, 1577, 1126, 1040, 990.</td>
<td>3.77-3.89 (m, 8H), 4.62 (S, 4H), 7.56-7.83 (m, 8H), 8.15 (s, 2H), 10.55 (S, 2H).</td>
</tr>
</tbody>
</table>

**TABLE 2 : Inherent viscosity and the yields of polymers (11-13)**

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Yield (%)</th>
<th>ηinhl (g/dL)²</th>
</tr>
</thead>
<tbody>
<tr>
<td>11</td>
<td>91</td>
<td>0.47</td>
</tr>
<tr>
<td>12</td>
<td>88</td>
<td>0.45</td>
</tr>
<tr>
<td>13</td>
<td>86</td>
<td>0.43</td>
</tr>
</tbody>
</table>

²Measured at a polymer concentration of 0.5 g/dL in DMSO solvent at 30 °C

<table>
<thead>
<tr>
<th>Polymer</th>
<th>NMP</th>
<th>DMAC</th>
<th>DMF</th>
<th>DMSO</th>
<th>m-Cresol</th>
<th>THF</th>
</tr>
</thead>
<tbody>
<tr>
<td>11</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>+</td>
</tr>
<tr>
<td>12</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>13</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>±</td>
</tr>
</tbody>
</table>

(++) Soluble at room temperature; (+) soluble upon heating; (±) partially soluble; *Solubility measured at a polymer concentration of 0.05 g/ml
molecule. This phenomenon decreases the crystallinity and close packing, and increase the solubility of polymers (Figure 3 and 4). According to the above discussions the solubility of polymers were affected by the several variables and the solubility varies according to the structure of amino acid in the di-acid monomer (8-10). The viscosities of polymers were measured in DMSO at 30 °C and are in the range of 0.43-0.47 (TABLE 2).

CONCLUSION

A series of new poly (ester-amide-imide)s bearing aminoacids and diphenylsulfone in the main chain were successfully prepared in nucleophilic conditions under microwave irradiation (MW). The polymers showed reliable solubility and viscosity. This is due to the presence of diphenylsulfone and aliphatic groups of amino acids in the presence of tetrahedral sulfone functional group. Thus, we afforded polymers with improved solubility. Theoretical study showed the high free volume and describes the solubility.

ACKNOWLEDGEMENT

The financial support of this work by Payame Noor University (PNU) Research Council is acknowledged.

REFERENCES


[10] M.Ghaemy, M.Hassanzadeh, S.M.A.Nasab,


