Synthesis and Characterization of Ethylene Diamine Tetera Acetic Acid Polyester-amides polymer with Aminoalcohol

Dakhil Nasser Taha  Khudheyer Jawad Kadam
Babylon University, College of Science , Department of Chemistry.
Hutham Abd Al Abd Al Hussain
kerbala University, College of veterinary.
dakhilfia@yahoo.com  khuheyerbable@yahoo.com  huthamabd15@yahoo.com

Abstract
linear aromatic and aliphatic polyester-amides (PEAs) have been synthesized by polycondensation of aliphatic and aromatic aminoalcohol (Ethanol amine, 2-amino-2-methyl-propan-1-ol, m-amino phenol) with Ethylenediaminetetraacetic acid (EDTA) as a favorable and combined complexing compound was joined into the polymer backbone with poly addition reactions. These polymers were characterized by FTIR, \(^1\)H NMR, solubility studies, elemental analysis, Thermal analyses such as TGA were measured, intrinsic viscosity. The poly(ester-amide)s obtained show good thermal stability.

Keywords: poly(ester amide); Ethylenediaminetetraacetic acid; polycondensation

1. Introduction
Poly(ester amide)s (PEAs) have been studied for many years because the presence of ester and amide groups in the same polymer backbone gives them centrist properties between polyester and polyamid (Katsarava et al., 1999,Yujiang et al., 2002, Kai et al., 2005). Polyamides are, compared to polyesters, characterized by better mechanical properties, melting temperatures, higher glass transition (Tg) and a higher solvent resistance, but also a higher water sensitivity (Van et al., 1997).The ester linkage must be hydrolytically disintegrated while their amide must ameliorate thermal and mechanical properties because of the intermolecular hydrogen bonding of the amide groups (Grigat et al., 1998).

Both academic and industrial scientists are interested in researches of PEAs for their potential in biomedical and biological fields(Okamura et al., 2002; Matthew et al., 2008, Xuan et al., 2008). Specific applications of these materials in the biomedical field (e.g., hydrogels, controlled drug delivery systems, and other uses like adhesives and smart materials) (Alfonso et al., 2011)

Poly(ester amid)s can be synthesized from different monomers via ring opening polymerization of L-Lactide and amino acid anhydride (Yutaka et al. 2008),or condensation of dicarboxylic and aminoalcohol (Shantilal et al., 2004), using α-carboxy-α-hydroxy amides as monomers (Villuendas et al., 2001).

In this paper we report the synthesis of PEAs by polycondensation solution of aliphatic and aromatic aminoalcohols (Ethanol amine, 2-Amino-2-methyl-propan-1-
ol, m-Amino phenol) with EDTA their characterization through FTIR, $^1$H NMR, intrinsic viscosity, elemental analysis, solubility studies and TGA analysis.

2. Experimental

2-1. Materials and Instruments

EDTA, Ethanol amine, m-Amino phenol, and 2-Amino-2-methyl-propan-1-ol were purchased from Merck and used without any further purification. Thionyl chloride is obtained commercially from Aldrich. pyridine, chloroform, dimethyl sulphoxide, dimethylformamide, ethanol, acetone were obtained from Merck and used without any further purification.

FTIR Spectra of polymers have been scanned in KBr disk on shimadzu 7R-40E Spectrometer in range of 4000-400 cm$^{-1}$ (Iraq). $^1$H NMR Spectra were taken in DMSO-$d_6$ as a solvent on Bruker AC500spectrometer (Iran). Elemental analysis (C, H and N) for all PEA's was estimated by “Carlo Erba Elemental Analyzer” Ostwald viscometer was used to measure Viscosity of the polymer solutions use DMF as solvent at 30°C(Iraq). Thermolysis of polymers was performed with TGA curves obtain used Mettler TA 4000 system (Switzerland)in Ar atmosphere at a heating rate of 10°C/min in the temperature ranges from 50°C to 800°C(Iran).

2-2. Synthesis of Polyester-amides (general procedure)

EDTA (0.02mole, 3.2g) is introduced in single – neck round bottom flask with a excess of thionyl chloride and a drop of dimethyl formamide (DMF) as a solvent (Bosshard et al., 1959, Velingkar et al., 2009) and equipped with condenser with stirring were refluxed for 2hrs. The excess of thionyl chloride was distillation under reduced pressure.

The EDTA acyl chloride is mixed with aminoalcohol in equivalent mole ratio introduced in single – neck round bottom flask containing DMF as solvent and drop of pyridine as HCl accepter were refluxed for 4hrs. the solvent was evaporated and the product was washed with diethyl ether, dried under vacuum until a constant weight was obtained. The table shows the physical properties of polymers.

Table 1 lists the physical properties of the prepared poly(ester amide)

<table>
<thead>
<tr>
<th>Poln. code</th>
<th>color</th>
<th>Conversion</th>
<th>solubility</th>
<th>$\eta_{inh}$</th>
<th>Softin tsp/c°</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>Faint brown</td>
<td>90</td>
<td>+ + - + - +</td>
<td>0.18</td>
<td>&gt;300</td>
</tr>
<tr>
<td>A2</td>
<td>Dark yellow</td>
<td>70</td>
<td>+ + - + - +</td>
<td>0.31</td>
<td>&gt;300</td>
</tr>
<tr>
<td>A3</td>
<td>Faint red</td>
<td>85</td>
<td>+ + - + - +</td>
<td>0.22</td>
<td>&gt;300</td>
</tr>
</tbody>
</table>
3. Results and Discussion

The interaction of amine alcohol with EDTA and process conditions are illustrated in Scheme I. The new functionalized polymers were soluble in water and common organic solvents. The activation of EDTA carboxylic function was carried out by using an excess of thionyl chloride and catalytic amount of dimethylformamide in standard manner. The polymerization technique is relatively simple and polymers with higher molecular weights in good yields.

FTIR spectra of formation PEA is confirmed from the typical characteristic bands observed around 1660±15 cm⁻¹ (˃C=O stretch in amide) and 1700-1735 cm⁻¹ (˃C=O stretch in ester).

The FT-IR absorption spectrum of condensed polymer A₁ figure (1) shows the new ˃C=O amide band at 1665 cm⁻¹ and new ˃C=O of ester was observed at 1739 cm⁻¹. NH amide band at 3200 cm⁻¹. The ν OH carboxylic acid revealed a broad band at (3445-2900) cm⁻¹. The FT-IR absorption spectrum of condensed polymer A₂ figure (2) shows the ν C=O amide band at 1606 cm⁻¹ and ν C=O of ester was observed at 1735 cm⁻¹. The other absorptions were observed at 3090 and 2850 cm⁻¹ which are attributed to CH aromatic and aliphatic respectively and NH amide band at 3250. The FT-IR absorption spectrum of condensed polymer A₃ figure (3) shows the ν C=O amide band at 1606 cm⁻¹ and ν C=O of ester was observed at 1730 cm⁻¹.

¹H NMR for polymer A₁ Fig. (4) shows the following signals : - NH- amide δ (8.2 ppm), -CH₂-O-C=O δ (4.4 ppm), 4CH₂C=O δ (3.4 ppm) and (δ = 2.8) corresponding to the methylene proton next to the tertiary amine of the backbone polymer and 2COOH δ (9.05 ppm). ¹H NMR for polymer A₂ Fig. (5) shows the following signals : -NH- amide δ (7.9 ppm), Ar-H different environments δ (6.7-7.2 ppm), 4CH₂C=O δ (3.4 ppm) and 2COOH δ (9.05 ppm). ¹H NMR for polymer A₃ Fig. (6) shows the following signals : -NH- amide δ (8.04 ppm), -CH₂-O-C=O δ (3.6 ppm), 4CH₂C=O δ (3.4 ppm), 2CH₃ (δ = 1.2) and 2CH2-N (2.9) and 2COOH δ (9.1 ppm).

The elemental analysis of PEAs is shown in Table 2. The observed percentages of C, H and N contents in PEAs agree with those theoretically calculated.
Fig(1) FT.IR spectra of EDTA- Ethanol amine Condensed polymer $A_1$

Fig(2) FT.IR spectra of EDTA- m-Amino phenol Condensed polymer $A_2$
Fig (3) FT-IR spectra of EDTA- 2-Amino-2-methyl-propan-1-ol Condensed polymer A₃

Fig (4) $^1$H NMR spectrum for prepared polymer A₁
Fig (5)$^1$H NMR spectrum for prepared polymer $A_2$

Fig (6)$^1$H NMR spectrum for prepared polymer $A_3$

Table 2. Elemental analysis C, H and N % contents in the polyester-amides.

<table>
<thead>
<tr>
<th>Polyester-amides</th>
<th>C (%)</th>
<th>H (%)</th>
<th>N (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>calc.</td>
<td>obs.</td>
<td>calc.</td>
</tr>
<tr>
<td>$A_1$</td>
<td>34.12</td>
<td>34.93</td>
<td>5.43</td>
</tr>
<tr>
<td>$A_2$</td>
<td>57.67</td>
<td>57.23</td>
<td>4.55</td>
</tr>
<tr>
<td>$A_3$</td>
<td>44.74</td>
<td>44.49</td>
<td>6.12</td>
</tr>
</tbody>
</table>
4. Thermal Gravimetry (TG) Analysis

The TG curves for pure poly(ester amide) of A_1 and A_3 are shown in Figures 7 and 8, respectively which show good thermal stability, the major decomposition of polymer A_1 started at 300°C and complete around 700°C. The polymer A_3 shows a three-step weight loss. The first observed weight loss 55% appeared at 330°C, and the second weight loss 75% is observed between 500°C and 600°C. The third weight loss process begins at 700°C and is due to the decomposition of polymer chain.

![Fig(7) Thermograms of polymer A_1](image)

**Fig(7) Thermograms of polymer A_1**

![Fig(8) Thermograms of polymer A_3](image)

**Fig(8) Thermograms of polymer A_3**

**Conclusion**

The poly(ester amide)s synthesis is quickly prepared in a two-step reaction in the solution of polycondensation, which can be soluble in water, DMF, DMSO and ethanol at room temperature. The polymers were obtained in good yields at 70 °C in 4 h with DMF as the solvent. The poly(ester amide)s have pendant carboxyl groups which refer to EDTA may be able to bind metal ions in aqueous solutions. TG analysis shows good thermal stability of prepared poly(ester amide)s.
References


