

Synthesis and Characterization of Water-soluble and Carboxy-functional Polyester and Polyamide Based on Ethylenediaminetetraacetic Acid and Their Metal Complexes

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ABSTRACT

Ethylenediaminetetraacetic acid (EDTA) as a suitable and common complexing compound was inserted into the polymer backbone with polyaddition reactions separately between hexamethylenediamine (HMDA) or poly(ethylene glycol) ($\bar{M}_w=1000$, PEG1000) and ethylenediaminetetraacetic acid dianhydride (A-EDTA). The prepared polymers were soluble in water and carboxy functional groups have been connected to the polymer chains. The polymers were characterized by UV-vis, FTIR and ^1H NMR spectroscopy, elemental analysis and thermal gravimetry methods. The carboxy functionalities were measured by titration. The metal complex polymers were separated by dialysis tube and also characterized by spectral techniques and thermal gravimetry.

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Key Words:

ethylenediaminetetraacetic acid;
hexamethylene diamine;
poly(ethylene glycol);
water soluble polymer;
functional polymer;
metal complexation.

INTRODUCTION

Aminocarboxylic acid molecules, such as ethylenediaminetetraacetic acid (EDTA), diethylenetriamine-pentaacetic acid (DTPA), and their derivatives are widely described in the literature [1-3], and their complexing abilities are more particular-

ly used in medicine and analytical chemistry [4-5]. Many polymers bearing such groups have been stable complexes with heavy metal ions [6-9].

In this way, Montembault et al. synthesized polymers with linear structures bearing aminoacetic acid

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Table 1. Experimental conditions and results for the preparation of polyester (1mmol A-EDTA, 1mmol PEG1000) in the melt condition.

Exp. No.	Reaction temp. (°C)	Reaction time (h)	mp (°C)	Yield* (wt.%)
1	50	5	59-60	5
2	85	3	58-60	21
3	85	6	65-68	37 (63 ^{**})
4	85	12	65-68	37
5	95-100	12	-	Gel form

(*) after using dialysis tube; (**) before using dialysis tube.

groups along the polymer chain, by ring-opening polyaddition reaction of EDTA dianhydride (A-EDTA) or DTPA dianhydride (A-DTPA) with some diols and diamines, all as bifunctional monomers [10]. Also, Tuelue et al. reported the preparation, characterization and copper (II) complexing capacity of polyesters, derived from some polyethylene glycols with A-EDTA and A-DTPA [11]. Recently, Geckeler et al. published the synthesis of a water soluble sugar copolymer, with pendant carboxyl groups, that was biodegradable and metal complexing [12].

In this study we report the synthesis and characterization of novel polyamide based on hexamethylene diamine (HMDA) and A-EDTA and its metal complexing properties. Meanwhile, we prepared polyester based on poly (ethylene glycol) with molecular weight of 1000 g.mol⁻¹ (PEG1000) and A-EDTA according to the literature [11] and its various metal complexes were prepared and studied for the first time.

EXPERIMENTAL

Materials and Instruments

EDTA, HMDA, acetic anhydride and PEG1000 were purchased from Merck and used without any further purification. Pyridine and dimethyl formamide were distilled before use.

¹H NMR Spectra were carried out on a Bruker AC 500 spectrometer. The infrared spectra were recorded in the 4000-400 cm⁻¹ range from a Fourier transform Shimadzu 7R-40E spectrometer. UV-vis Spectra were recorded by Shimadzu UV-256 F.W spectrophotometer.

Thermolysis of polymers and their metal complexes were performed with Dupont 950 US to obtain TGA curves. Elemental analyses were carried out on elemental-analyses system of GmbH, Germany. For the separation and purification of polymers and their metal complexes the dialysis tube (B-9652) from Sigma was used.

Synthesis of EDTA Dianhydride (A-EDTA)

EDTA (10.0 g, 34 mmol), pyridine (16 mL) and acetic anhydride (14 mL) were placed in a 100 mL-flask equipped with a condenser and a magnetic stirrer. The reaction was carried out at 65-70°C for 12 h. The resulting anhydride was filtered off and washed thoroughly with acetic anhydride and dry diethyl ether. The white-cream powder was then dried under vacuum at 40-50°C until constant weight was obtained (yield 90-92%) [11].

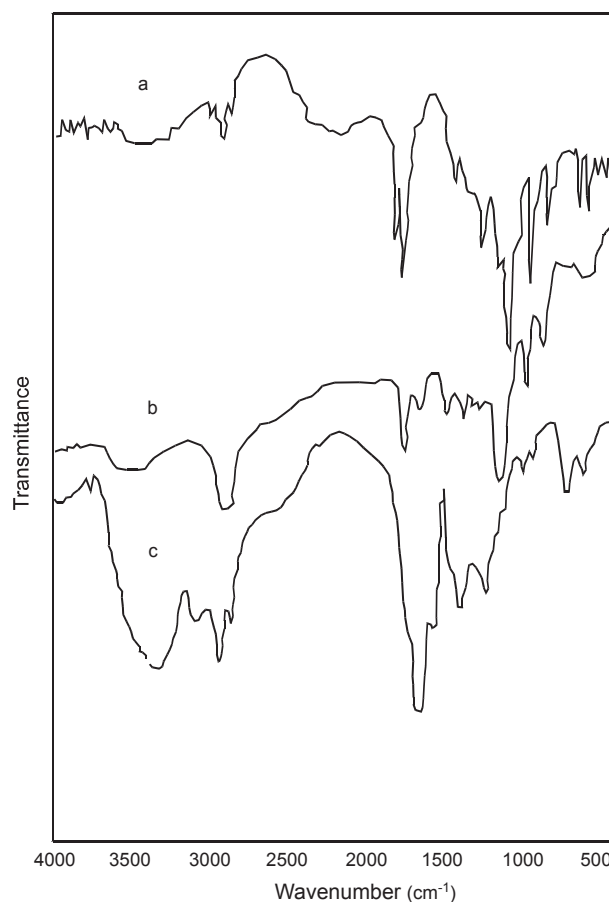


Figure 1. FTIR Spectra of (a) A-EDTA, (b) polyester, and (c) polyamide.

Table 2. Experimental conditions and results for the preparation of polyamide.

Exp. No.	A-EDTA g(mmol)	HMDA g(mmol)	Solvent (mL)	Reaction time(h)/temp.(°C)	mp (°C)	Yield (wt. %)
1	0.512(2)	0.332(2)	methanol (10)	24/r.t.	145-148	78
2	0.256(1)	0.116(1)	toluene (10)	7/40 48/80	(98-100)* 186-190 (100-105)*	87
3	0.256(1)	0.116(1)	toluene (10)	24/reflux	187-190	96
4	0.256(1)	0.116(1)	DMF (1.5)	24/r.t. 24/45	116-120*	33*

(*) after purification by dialysis tube; DMF: dimethyl formamide; A-EDTA: ethylenediaminetetraacetic acid dianhydride; HMDA; hexamethylene diamine.

Preparation of Polyester

PEG1000 (1.0 g, 1 mmol) was melted under nitrogen atmosphere in an oil bath at 85°C. To the molten, 0.256 g (1 mmol) of well-powdered, dry A-EDTA was slowly added and the mixture was stirred for 5 h. The product was made in contact with toluene and cold acetone to purification (yield 63% and mp 65-68°C). For more purification, the polyester was dissolved in 10 mL water, filtered and transferred to a dialysis tube (yield 37% and mp 68°C). The experimental conditions and results are also presented in Table 1.

Preparation of Polyamide (General Procedure)

The A-EDTA and HMDA in equivalent mole ratios were introduced in a single-neck round-bottom flask containing freshly dried solvents and equipped with a condenser, stirred in defined temperature and time. Then the solvent was evaporated and the residue was washed with acetone and diethyl ether. Finally, it was

dried under vacuum until a constant weight was obtained. Dialysis tube was used for more purification of polyamide. The preparation conditions and some physical and spectroscopic results were presented in Tables 2 and 3.

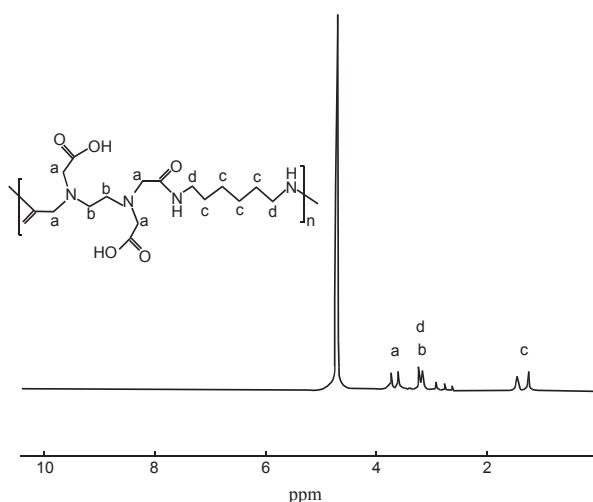
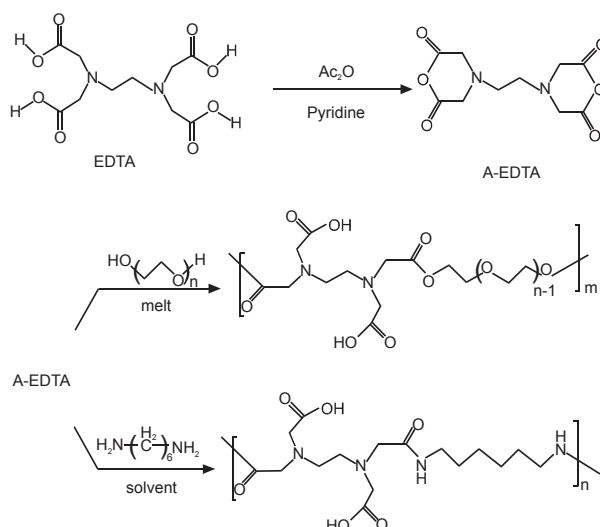
Preparation of Metal Complex Polymer

A solution of 2.0 mmol metal nitrate was dissolved in twice distilled water (3-5 mL) and its pH was adjusted to the defined value by adding a small volume of KOH or HCl aqueous solutions. Then, a solution of 0.15 mmol polyester or polyamide in water (3-5 mL) was added. The metal complex polymers can be prepared at different pHs and purified by dialysis tube or membrane filtration.

RESULTS AND DISCUSSION

Synthesis

Polyester and polyamide were prepared from diol and

**Figure 2.** ¹H NMR Spectrum of polyamide in D₂O.**Scheme I**

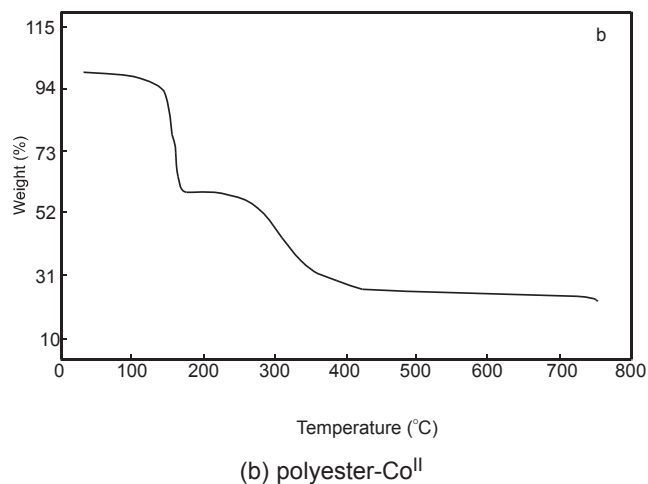
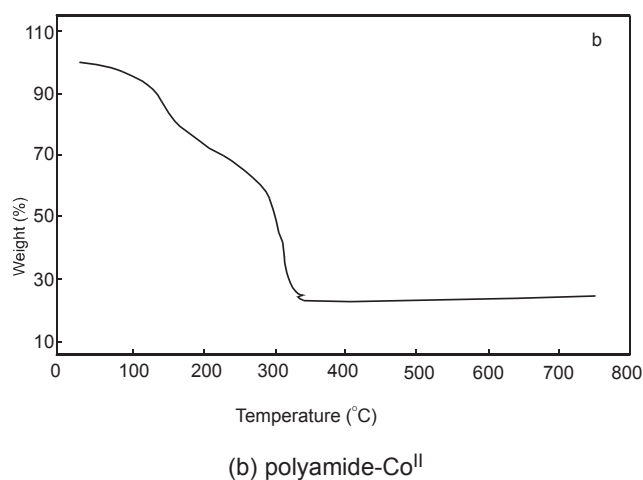
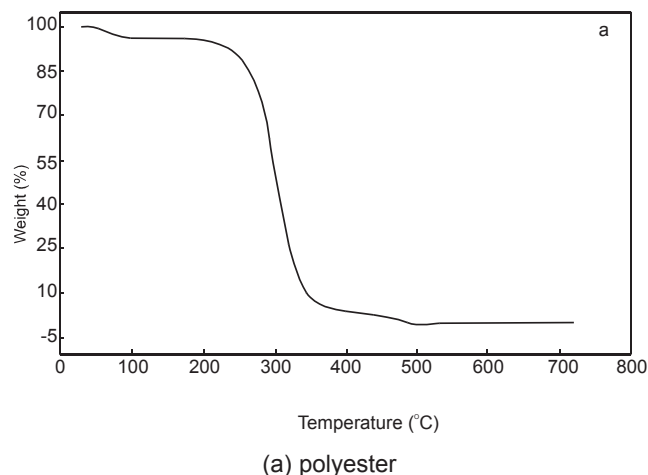
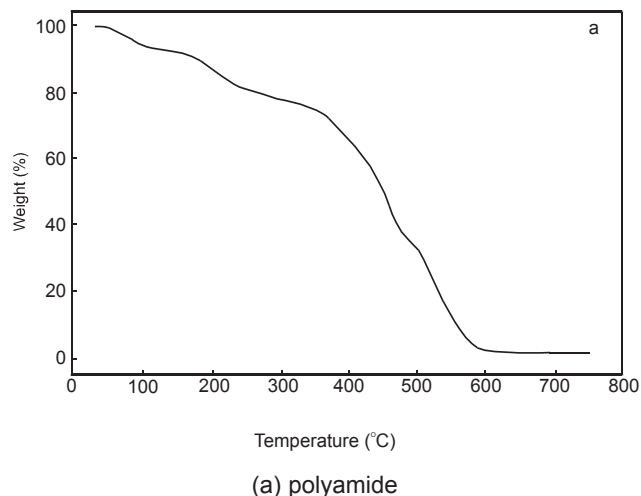


Figure 3. TG Curves.

diamine and activated ethylenediaminetetraacetic acid (EDTA), in the form of dianhydride, in a one step polyaddition reaction. EDTA which represents a ligand for a variety of metal ions and their incorporation into a polymer chain with a high solubilizing power yield effective polymeric complexants. Therefore, the dianhydride of EDTA was synthesized according to the method of Tuelue et al.[9] at 65-70°C with about 90 percent yield (Scheme I). The polyaddition reactions of A-EDTA with PEG1000 and HMDA were performed in the melt and solution, system, respectively (Scheme I). The solution polyadditions were carried out using a variety of solvents such as toluene, methanol and dimethylformamide.

The content of carboxylic acid pendant groups in the polyester and polyamide were determined by titration using 0.01 N NaOH (Table 3). Because of the relatively high molecular masses of the building block of

Figure 4. TG Curves.

PEG1000 in polyester in comparison to polyamide, its content of carboxylic acid is relatively low.

According to the experimental results (Table 1), using higher temperature, produce insoluble cross-linked polyester in gel form.

Spectroscopic Characterization

The FTIR spectra of polyamide and polyester exhibited the prominent amide band at 1657 cm^{-1} and ester band at 1749 cm^{-1} , respectively. Simultaneously, the bands of the dianhydride group, i.e. bands at 1765 and 1819 cm^{-1} , disappeared. Figure 1 shows FTIR spectra of the prepared polymers and their comparison with A-EDTA.

The ^1H NMR spectra of the prepared polymers were obtained in D_2O solvent (Table 3). The ^1H NMR spectrum of polyamide was shown in Figure 2 including the signal assignments in the corresponding formula. The ^1H NMR spectra of polyester show peaks that

Table 3. The physical and spectroscopy results for the prepared polyamide (PA) and polyester (PES).

Polymer	State (colour)	Solvents	f _{COOH}	FTIR (cm ⁻¹)	¹ H NMR (ppm)	Reduced weight (wt.%) at 250°C	Elemental analysis (wt.%)
PA	Solid (white)	water, DMSO, DMF, methanol*, acetone*	4 (5.3**)	O-H 3535	1.2-1.4 8H _c	16	(C) 50.23 (51.6**) (H) 7.75 (7.5**) (N) 14.43(15.05**)
				C=O 1657	3.1-3.3 4H _b , 4H _d		
				N-H 1564	3.6-3.8 8H _a		
				C-N 1395			
PES	Solid (white)	water, DMSO, DMF, methanol, acetone*	1.3 (1.5**)	O-H 3508	3.2-4.4	7	(C) 50.96 (49.6**) (H) 8.20 (8.16**) (N) 1.92 (2**)
				C=O 1749			
				C-N 1356			
				C-O 1117			

(*) slightly soluble; (**) theoretical data.

are in good agreement with the prepared polyester based on PEG400 prepared by Tuelue et al.[9].

Thermal Gravimetry (TG) Analysis

The TG curves for pure polyamide and polyester are shown in Figures 3 and 4, respectively. The corresponding polymer-Co^{II} complexes were also shown for comparison. The polyamide shows a three-step weight loss. The first observed weight loss appeared up to 100°C due to the removal of water, and the second weight loss observed between 100°C and 300°C may

be accounted for the elimination of water and formation of amide cycle. The third weight loss process begins at 380°C is due to the decomposition of polymer chain.

However, the polyamide-Co^{II} complex shows two principal weight loss up to 350°C. The weight loss between 100°C and 200°C is due to removal of water from the complex. The next weight loss begins at 250°C corresponds to the decomposition of polymer complex and formation of cobalt oxide above 350°C.

The polyester shows a low decrease of weight at

Table 4. Physical and spectroscopy results of the polyamide (PA) and polyester (PES).

Polymer-metal	Colour	UV-vis λ _{max} (nm)	FTIR (cm ⁻¹)	Reduced weight (wt.%) at 250 (°C)
PES-Cu	Blue	201, 750 (817.6*)	C-O 1107	-
			C-N 1354	
PES-Ni	Green	204, 723 (716*)	C-O 1157	-
			C-N 1387	
PES-Co	Violet	213, 529 (508*)	C-O 1109	42
			C-N 1395	
PA-Cu	Blue	210, 796 (817.6*)	C-O 1203	-
			C-N 1387	
PA-Ni	Green	207, 722 (716*)	C-O 1400	-
			C-N 1355	
PA-Co	Dark-pink	208, 514 (508*)	C-O 1233	32
			C-N 1395	

(*) λ_{max} of metal salts in water.

100°C and the main weight loss at 250°C that attributed to removal of adsorbed water and decomposition of polyester, respectively. The polyester-Co^{II} also shows two weight losses. The first weight loss is completed at 180°C, which is due to the removal of water from the complex and the second weight loss process occurs at 250°C due to the decomposition of polymer. The plateau observed above 400°C in which the final weight was 25 percent corresponds to the metal oxides.

Metal Complex Polymer Separation

The metal complex polymer solutions were purified from free metal ions by aqueous-phase dialysis in membrane tubing with a 12,000-14,000 molecular-mass cut-off or membrane filtration. After evaporation of water the coloured solid and a hygroscopic, completely water-soluble polymers were isolated. Some results and characteristic data for the metal complexes of the polyamide and the polyester were presented in Table 4. The changes in IR and visible absorption bands confirm the creation of metal binding on polymers.

Further studies on the metal binding capacities and other properties of polyester and polyamide are underway.

CONCLUSION

The results show that water soluble polyesters and polyamide can be conveniently and quickly prepared in a one-step reaction in the melt or in solution.

The linear polyester and polyamide have pendant carboxyl groups and are able to bind metal ions in aqueous solutions.

Using membrane in the form of a dialysis tube is a suitable method for separation and preconcentration of metal ions from aqueous solutions.

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