



Synthesis and Characterisation of water soluble EDTA functionalized polyesters for environmental applications

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ARTICLE INFO

Article history:

Received: 1 July 2014;

Received in revised form:

21 August 2014;

Accepted: 3 September 2014;

Keywords

Copolyesters, Metal complex,
Polymer chain, Viscosity.

ABSTRACT

In recent years, preparation of polymer materials either soluble or insoluble in water with various functional groups has been developed, which can absorb metal ions in aqueous and non-aqueous media. In general, functionalized polymers for metal ion complexation can be prepared either by derivation of a basic polymer (precursor) with the desired ligand or by polymerization of the corresponding ligand derivatives. Among functionalized polymers, those containing EDTA have attracted much attention. EDTA with amino carboxylic acid groups can be introduced into or graft onto the backbone of polymer chains. Polymers bearing such groups can form stable complexes with various heavy metal ions. Therefore, we attempted to prepare new complexing polymer materials, which can be used in wastewater treatment. The synthesised random copolyesters were characterized by viscosity measurements, solubility studies, and spectral analysis. Thermal studies were also made on these copolyesters.

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Introduction

Polymers have become essential in every walk of human life from simple household items to high technological applications. Such a wide use of polymers in various fields, because of their versatility and mass-production ability, is considered as a serious source of environmental pollution. Carboxyl functionalised metal complexes are becoming increasingly important as they are used as environment friendly structural materials for environmental remediation of municipal and industrial wastewater¹⁻⁵. Polyesters are the most important and widely used class of polymers which fall under heterochain macromolecular compounds possessing carboxylate esters as part of the repeating unit. Polyesters are usually prepared by the condensation of a diacids or its derivatives with a diol. It is possible to bring about profound changes in the properties of polyesters by copolymerisation and the extent to which the polymer retains the desirable properties of homopolymers depends on the chemical microstructure and copolymer composition^{6,7}. The vast interest in commercial utilization of copolyesters has necessitated the determination of composition and microstructure as an important adjunct to copolymer technology^{8,9}.

Carboxyl functional polyesters with EDTA-Metal complexes are water soluble polymers and are used for the removal of metal ion from industrial waste¹¹⁻¹⁵. This concept of chemoremediation in the liquid homogeneous phase using polymer reagents is considered as a green technology process^{16,17}. It is based on the retention of polymer-member complexes in aqueous solution according to their molecular size by using membrane filtration. The efficient and selective separation of inorganic ions can be achieved by using water-soluble polymeric reagents with chelating groups¹⁸⁻²⁰.

Nowadays, considerable efforts have been taken on the synthesis and characterisation of water soluble polymers with potential applications in chemoremediation technology²⁰⁻²⁴. Aliphatic polyesters are of interest for such applications because

of their biocompatibility and biodegradation properties^{25,26}. In accordance with the green chemistry principle, catalyst free synthesis has emerged as a potential route to synthesis of polyesters with appropriate mechanical integrity, suitable surface characteristics and compatibility for complexing ability²⁷⁻²⁹.

In this investigation, we report on the synthesis and characterization of water soluble citric acid based polymer with EDTA. The introduction of EDTA unit in the repeating unit of synthesized copolyester chain is expected to introduce metal complexing ability of the polyester.

Experimental methods:

Materials:

Chloroform (MERCK,AR) was used as such. Methanol (MERCK,AR) was refluxed over quicklime for six hours by distilled (b.pt. 65°C) method. ANALAR samples of Acetone, Dimethyl formamide and 1,4 dioxane were used as such. Samples of citric acid, ethylene glycol, sebacic acid and suberic acid (MERCK) were used as such.

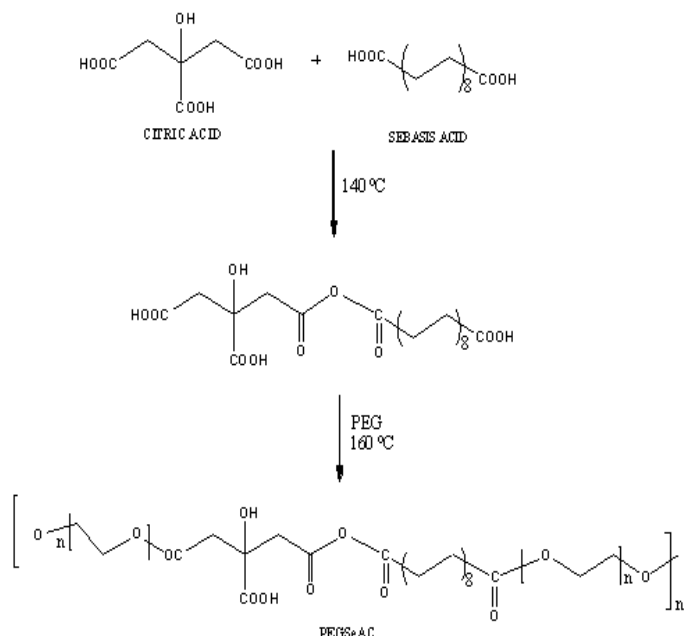
Synthesis of random copolyesters and their EDTA metal complexes:

The scheme of synthesis of copolyesters involving poly (ethylene glycol) citric acid and sebacic acid is presented as follows.

Poly (ethylene citrate-co-ethylene suberate), PECSu and Poly (ethylene citrate-co-ethylene sebacate), PECSs were synthesized by catalyst free melt condensation method. In the synthesis of each copolyester, citric acid, ethylene glycol and suberic acid/sebacic acid were used. As an example, the synthesis of copolyesters, Poly (ethylene citrate-co-ethylene sebacate), PECSs, is described as follows. The reaction mixture containing sebacic acid (8.7g,0.05mol) and citric acid (9.6g,0.05mol) were heated in an oil bath in nitrogen atmosphere.

The temperature of the reaction mixture was raised to 140°C for 30 minutes. When the mixture of citric acid and sebacic acid

were melted, ethylene glycol (10ml,0.05mol) was added to the mixture. Then the temperature was gradually raised in 10°C steps and the final reaction temperature maintained at 160°C for 2 hours to remove the water as the esterification byproduct. Subsequently the pressure of the reaction system is gradually decreased and condensation polymerisation was continued under a final reduced pressure lower than 0.5mm Hg. applied for 2 hours. Finally, the reaction was terminated when the viscosity of the reaction mixture is so high the rotation is not possible.



The viscous slurry of prepolymer was then dissolved in acetone and the solution cast into Teflon molds and post polymerized at 70 °C for 2 days to obtain the polyester films. These polyester films were cleaned by continuous washings with distilled water and dried under vacuum. The diacids and diols used in the preparation of copolyester along with yields are given in table 2.1.

Table 2.1 Comonomers used and the yield of synthesised copolyesters

S.No	Polymer	Common diol	Common acid	Diacid	% yield
1.	PECSu	EG	Citric acid	Suberic acid	67
2.	PECSe	EG	Citric acid	Sebacic acid	73

Synthesis of EDTA Dianhydride (A-EDTA):

EDTA (10g, 34mmol), pyridine (16 mL) and acetyl chloride(14mL) were placed in a 100mL flask equipped with a condenser and a magnetic stirrer. The reaction was carried out at 70°C for 12hours. The resulting anhydride was filtered off and washed thoroughly with dry diethyl ether. The white cream powder was then dried under vacuum until constant weight was obtained.

Preparation of EDTA functionalised polyester :

The polyester (1g, 1 mmol) was melted under nitrogen atmosphere in an oil bath at 85C. To the molten polyester, well powdered dry A-EDTA (0.256g, 1 mmol) was slowly added and the mixture was stirred for 5 hours. The product was washed with toluene and cold acetone for purification.

Preparation of metal complex polymer

A solution of 2 mmol metal nitrate was dissolved in twice distilled water 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 in water was added.

Characterisation of random copolyesters :

All the random copolyesters synthesized were characterized by viscosity measurements, solubility studies, and spectral analysis. Thermal studies were also made on these copolyesters.

Solubility

Solubility of all the random copolyesters were determined in various solvents qualitatively. About 100mg of the polymer was taken in small stoppered test tube containing 5ml of the solvent. The mixture was kept for 24 hours with occasional shaking.

Viscosity measurements

The inherent viscosity [η_{inh}] of the random copolyesters was determined in chloroform using Ubbelohde Viscometer in which the pure solvent had a flow time of 60 seconds. All the copolyesters were dissolved in chloroform to prepare 1% wt solution at room temperature.

FT Infrared spectra

IR spectra of all the copolyesters were recorded by Perkin Elmer IR spectrometer in the range of 4000 to 400 cm^{-1} . The samples were embedded in KBr pellets.

Nuclear magnetic resonance spectra

The ^1H NMR Spectra of the copolyesters were recorded in CDCl_3 solvent with TMS as the reference using JEOL Model GS X 300. ^{13}C NMR Spectra of the copolyesters were recorded using DMSO-d₆ solvent.

UV-Visible Spectra

UV-Visible spectra of the metal complex solutions are recorded using ELICO Double beam UV-Visible spectrophotometer.

Results and discussion

The random copolyesters were characterised by solubility studies, viscosity measurements, spectral studies and thermal analysis. The copolyesters were functionalised with ethylene diamine tetra acetic acid and then complexed with metal ions.

Solubility

The dissolution of a polymer in a solvent is a more complex process compared to low molecular weight compounds.

There are two stages involved during the dissolution of a polymer in a solvent which is a slow process. In the first stage, solvent molecules slowly diffuse into the polymer to produce a swollen gel. Then in the second stage, the swollen gel becomes soluble and gives a clear solution. The solubility of the synthesised random copolyesters was tested qualitatively in various organic solvents and the results are presented in Table 3.1.

Table 3.1 Solubility of Random Copolyesters

Sl.No	Polyme r	Aceton e	CHCl 3	DMS O	Methano l	Ethano l	TH F	DM F	Wate r
1	PECSu	+++	+++	--	++	--	++	++	--
2	PECSe	+++	+++	--	++	--	++	++	--

+++ = Freely Soluble

-- = Insoluble

++ = Partially soluble

Viscosity

The presence of small amount of a polymeric material dissolved in a solvent significantly increases the viscosity of the solvent. Such an increase in viscosity is dependent on the concentration and molecular weight of the polymer and its interaction with solvent. Inherent viscosity, η_{inh} , is an important parameter in the polymer characterisation since it relates to the inherent ability of a polymer to increase the viscosity of a particular solvent at a given temperature. The inherent viscosities

of the synthesised random copolyesters were determined in chloroform at 30°C using Ubbelohde viscometer. The inherent viscosity values of the synthesised copolyesters 0.75 and 0.78 dL/g for PECSu and PECSe respectively.

Table 3.2 Inherent viscosity data of random copolyesters

S.No	Copolyester	Inherent viscosity (dL/g)
1.	PECSu	0.75
2.	PECSe	0.78

Spectral Methods of Analysis

In the present investigation, FT-IR, ^1H NMR and ^{13}C NMR spectroscopy methods have been employed to determine the structure of the repeating units in the two synthesised random copolyesters.

FT-IR Spectroscopy

IR spectroscopy is the most extensively used tool for the identification of polymer structure and the analysis of functional groups¹⁶⁻¹⁸. Most polymers absorb electromagnetic radiation in the IR region because their molecules undergo transitions between vibration states of different energies causing absorption and emission. The IR spectra have been recorded for all the random copolyesters synthesised and spectra of typical polyesters are presented given below. The broad peaks centered at 3475 cm^{-1} and 3325 cm^{-1} are assigned due to the hydrogen bonded hydroxyl group stretching vibration and O-H of the hydrogen bonded carboxyl groups.

Table 3.3 IR spectral data of random copolyesters

Absorption (cm ⁻¹)	Frequency	Assignment
3325 – 3475		Hydrogen bonded hydroxyl O-H stretching vibrations
2933 – 2929		C-H stretching vibrations of methylene group
1720 – 1716		C=O stretching vibrations of ester group
1114-1112		Aliphatic C-C stretching
1195 – 1125		C-O stretching vibrations of ester groups

The characteristic IR absorption frequencies of the random copolyesters observed at 1720 to 1716 cm^{-1} due to the ester C=O stretching and 1195 to 1111 cm^{-1} due to the ester C-O stretching indicate that the polyester chain is present in all polymers. However, the carbonyl stretching frequencies are altered by the length of the flexible spacer in the polymer backbone. It is observed that the ester carbonyl, C=O stretching frequency decreases with increase in the length of the spacer groups. This suggests that the ester carbonyl bond strength decreases with increase in the length of the spacer groups in the repeating unit of the main chain of the polyester.

Table 3.4 IR absorption frequencies and assignment of groups

Copolyester	Absorption frequency, cm ⁻¹			
	-C=O Stretching of ester group	-C-O- Stretching of ester group	Aliphatic -CH ₂ Stretching	Aliphatic -CH ₂ - bending
PECSu	1716.6	1111,1114.8	2933.7	943.1
PECSe	1720.5	1195.8, 1203.5	2929.8	939.3

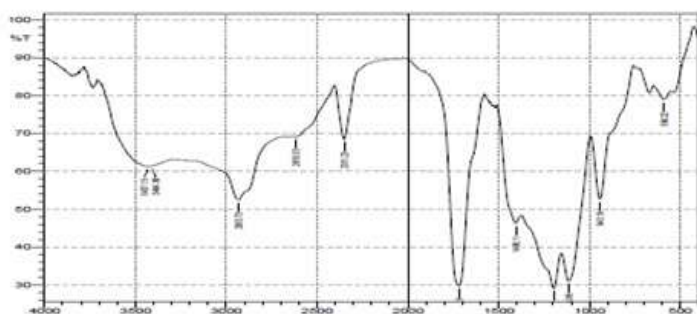


Fig 3.1(a) IR spectrum of copolyesters, PECSu

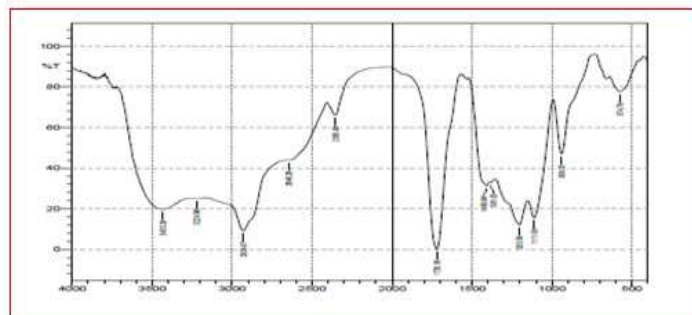


Fig 3.1(b) IR spectrum of copolyesters, PECSe

^1H NMR Spectral Analysis

The structure of the repeating units present in the copolyester can be analysed qualitatively and quantitatively by ^1H NMR spectroscopy²⁶.

Table 3.5 ^1H NMR spectral data of random copolyesters

Chemical shift, δ , (ppm)	Type of protons
7.2 – 7.4	Terminal methylene protons of dicarboxylic acid
4.0 – 4.2	Terminal protons of ethylene glycol
3.5 – 3.8	Central methylene protons of ethylene glycol
2.2 – 2.9	Methylene protons of citric acid
1.2 – 1.6	Central methylene protons of dicarboxylic acid

The ^1H NMR spectra of these copolyesters show signals characteristic signals of terminal and central methylene proton resonances of ethylene glycol at about 4.1ppm and between 1.2 and 1.6ppm respectively. The terminal methylene protons of dicarboxylic acids show signals in the range, 2.1-2.9 ppm.

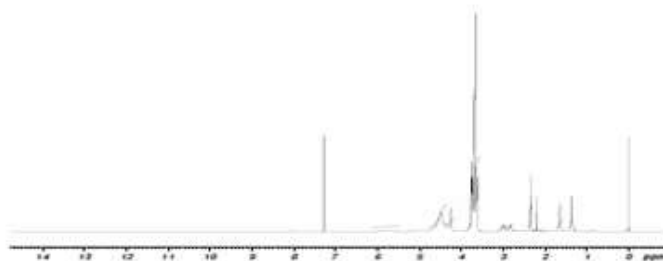


Fig 3.2(a) ^1H NMR spectra of copolyester PECSu

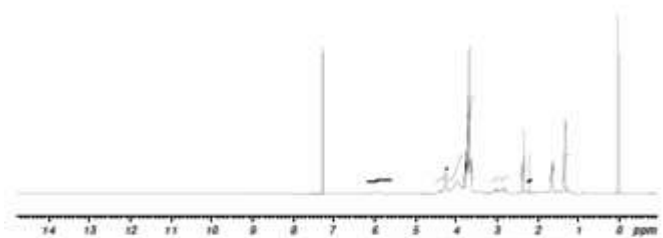


Fig 3.2(b) ^1H NMR spectra of copolyesters, PECSe

^{13}C NMR spectral analysis

^{13}C NMR spectroscopy is an important spectral method in the analysis of fine structure of polymers. The ^{13}C NMR chemical shift values for the synthesised copolyesters and the corresponding assignments are presented in Table 3.6.

Table 3.6. ^{13}C NMR spectral data of copolyesters

Chemical shift, δ (ppm)	Type of carbon
175 – 180	Ester carbon - C = O
75-80	Central carbon of citric acid
62 – 65	Methylene carbon attached to oxygen, - O-CH ₂
33 – 34	Methylene carbon attached to ester, - O-CH ₂
23 & 26	Central and terminal methylene carbons of ethylene glycol and dicarboxylic acids

^{13}C NMR spectroscopy has significant role in the study of the structure of the repeating units present in the aliphatic-aromatic copolyesters. The carbons present in different environments are differentiated in the proposed structure given in ^{13}C NMR spectrum of corresponding polyesters which are presented in Figures 3.3(a) and 3.3(b).

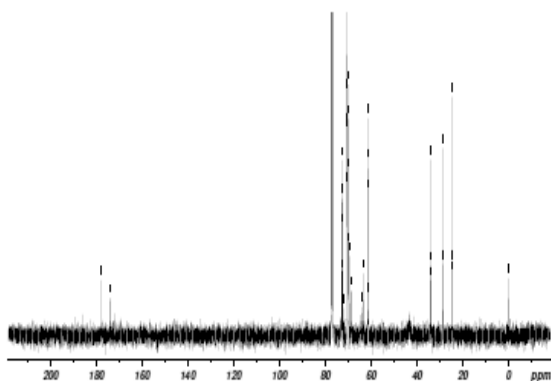


Fig.3.3(a) ^{13}C NMR spectra of copolyesters, PECSu

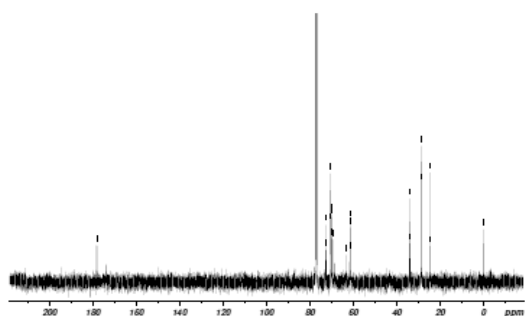


Fig. 3.3(b) ^{13}C NMR spectra of copolyester PECSe
Characterisation of metal complex polymer

The metal complex polymer solutions are characterized by UV-Visible spectroscopy. PECSe-EDTA-Co and PECSe-EDTA-Ni solutions were prepared and the corresponding λ_{max} was measured. The shift in the absorption bands shows the metal binding on these polyesters. The following table 3.7 shows the absorption bands of the metal complex polymers.

Table 3.7 UV-Visible spectral data of metal complex polymer

Polymer-EDTA-metal	Colour	UV-Vis, λ_{max} (nm)
PECSe-EDTA-Co	Violet	232, 530 (508*)
PECSe-EDTA-Ni	Green	248, 730 (716*)

The table shows the characteristic shift in absorption observed for the metal polymer complexes which confirms the formation of metal binding on polymers. UV-Visible spectrum of corresponding polyester-EDTA-metal complexes are presented in Figures 3.4(a) and 3.4(b).

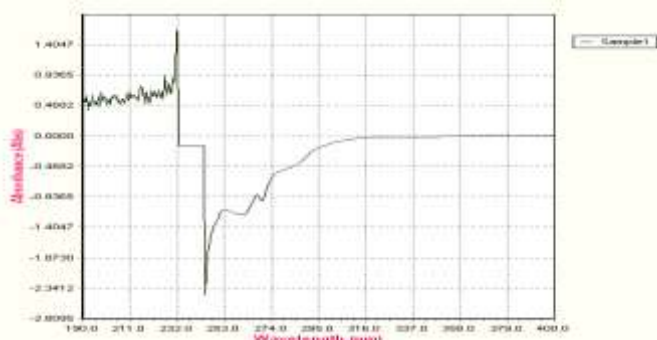


Fig.3.4 (a) UV spectrum of PECSe-EDTA-Co complex

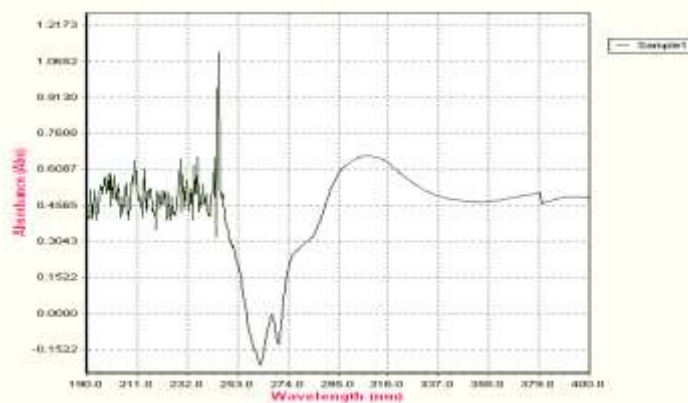


Fig.3.4 (b) UV spectrum of PECSe-EDTA-Ni Complex
Conclusion:

In this investigation, two citric acid based novel polyesters, PECSu and PECSe are synthesised by catalyst free melt polycondensation method. The synthesised polyesters are characterised by FTIR, ^1H NMR and ^{13}C NMR spectral methods. The synthesised PECSu polyester is functionalised with EDTA dianhydride. The EDTA functionalised polyester is water soluble and is used for complexing with metal ions. Hence, the synthesised chelating polymers can be used for the removal of nickel and cadmium ions by complexing with water soluble EDTA functionalised polymers and characterised by UV-Visible spectroscopy. Thus, the synthesised EDTA functionalised water soluble polyesters are used in chemoremediation technology in water treatment methods.

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