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SYNTHESIS AND CHARACTERIZATION OF CERTAIN POLYESTER AMIDES

M. Leo Edward*, L. Syed Ahamedhussain & V. Jaisankar*****
PG and Research Department of Chemistry, Presidency College (Autonomous),
Chennai, Tamilnadu

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Abstract:

The introduction of amino phenol unit in polymeric chain enhances the desired properties such as increase in thermal and mechanical properties of polyester amides which finds diverse applications. In this paper, we report on synthesis of polyester amide by condensation method using two different bifunctional symmetric monomer units of amino phenol (OAP and MAP) with acid chloride (TPCl) in presence of cetyltrimethyl ammonium bromide phase transfer as catalyst.

The repeating unit of the synthesized polyester amide has been determined by fourier transform infrared spectroscopy (FTIR) and H^1 proton nuclear magnetic resonance (^{1}HNMR), ^{13}C nuclear magnetic resonance (^{13}CNMR) spectral method. The morphology of the synthesized polyesteramide was studied using SEM. The polymer PEAs indicates that the melting temperature (Tm) based on differential scanning calorimetry (DSC) analysis.

Key Words: Amino Phenol, Acid Chloridepolycondensation & Phase Transfer Catalyst.

Introduction:

Organic polymers generally have long-term stability and good flexibility [1, 2] However, polymers have some disadvantages such as poor thermal and electrical properties and lower in modulus and strength compared with metals and ceramics. Organic polymers have been used in various fields such as electronics, coatings and catalysis. Polyester-amides were prepared by polycondensation reaction of substituted amino phenols with diacid chlorides containing ester groups.

The polyester-amides are a particular class ofpolymers possessing a special structure due to the regular presence of ester and amide groups in the same macromolecular chain, which gives them the properties intermediate between the polyesterand polyamide. Their rigidity caused by the doublebond character of the amide group coupled withextensive hydrogen bonding influences ordering of polyester-amides. [3, 4] Polyesteramides (PEA) seem to be very promising materials combining the favorable properties of aromatic polyesters and polyamides.

The rigidity due to the double-bondcharacter of the amide group coupled with extensive hydrogen bonding influences the ordering of PEAs and consequently enhances the mechanical and thermal stability. As such, the synthesis of PEAs represents a good alternative to overcome the thermal and mechanical limitations of polyester amide [5]. Polyester-amides constitute a promising family of biodegradable materials since they combine a degradable character, afforded by hydrolizable ester groups placed in the backbone, Currently a considerable variety of polyester-amides have been studied including the use of different monomers (amino acids aminoalcohols or carbohydrates) or different polymers microstructures. (e.g., ordered, blocky or random monomers distribution) [6, 7]

The presence of hydrolytically cleavable ester bonds in the backbone and the lowering of the crystallinity make also polyestes - amides promising materials for their use in medical fields. Note also that the incorporation of amino acid moieties may lead to biocompatible materials and, depending on their side groups, to functionalized polymers.

Experimental:

Materials:

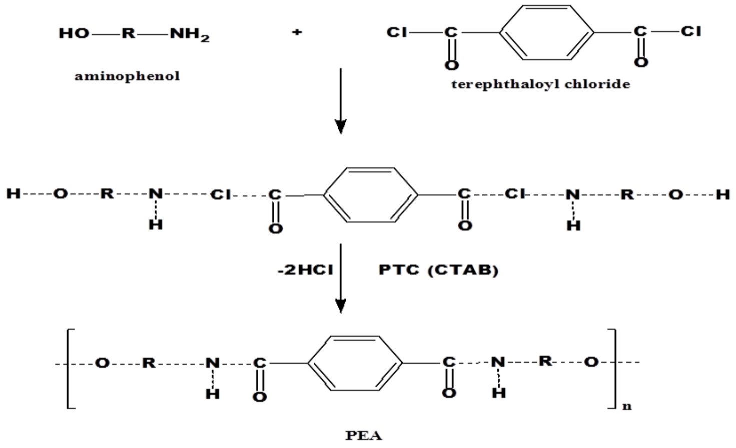
O-aminophenol, m-amino phenol were purchased from sigma aldrich, Terephthaloyl chloride Cetyltrimethyl ammonium bromide. Sodium hydroxide, Chloroform, Acetonewere obtained commercially from SRL.

Synthesis of Polyester Amide:

Initially 0.025 mol sodium hydroxide is added to 0.0125 mol amino phenol and stirred well using magnetic stirrer. Upon stirring required amount of phase transfer catalyst (ie 0.25 mg of cetramide (CTAB) in 10ml of water) was added to it. To this equimolar amount of diadidchloride (TPCL) was prepared using dry Chloroform ($CHCl_3$) was added rapidly and the stirring speed was raised to the maximum and continued for 5 minutes.

To precipitate the formed polyesteramide, 200 ml of acetone was added. And the precipitate was collected and washed sereval times using acetone with water to remove the unreacted monomers, alkalisalts, and filtered. Then the polymer was dried in a vacuum oven at 40^0C.

General Scheme Polyester Amide:



Result and Discussion:

The polycondensation of OAP, MAP, with TPCl leading polymer was first carried out by the interfacial method [8]. In general, the selection of an adequate solvent in an organic phase is most essential for the production of high-molecular- weight polymers [9]. Yields of the different polymer samples involving aromatic diacid chloride moiety in polymer chain are inthe range from 78% to 75%. All the PEAs are solid powders. PEAs are light to dark brown powders. Polyester-amide from diacid chloride and aminophenols yield.

Code	Repeat unit	Appearance	Yield%
P_1	$[\text{-O-Ph-NH-CO-Ph-O}]_n$ [o-AP+TPCL]	Light Brown Powder	78
P_2	$[\text{-O-Ph-NH-CO-Ph-O-}]_n$ [m-AP+TPCL]	Light Brown Powder	75

Solubility:

Relative solubilities of polyester-amides of diacidchlorides + aminophenol (++) Soluble at room temperature, (+) soluble on heating, (±) partially soluble on heating, and (-) insoluble.

Solvent	H_2SO_4	DMSO	DMF	DHF	Dioxane	$CHCl_3$	CH_3OH	C_2H_5OH	$(CH_3)_2CO$
P_1	++	++	++	±	±	±	-	-	-
P_2	++	++	++	±	±	±	-	-	-

Elemental Analysis C, H and N% Contents in the Polyester-Amide:

Polyester-amide	C%		H%		N%	
	Calc.	Obs.	Cals.	Obs	Cals.	Obs.
P_1	75.6	65.03	4.68	4.02	.56	6.98
P_2	73	69.50	4.05	3.78	6.56	4.58

Infrared Spectroscopy:

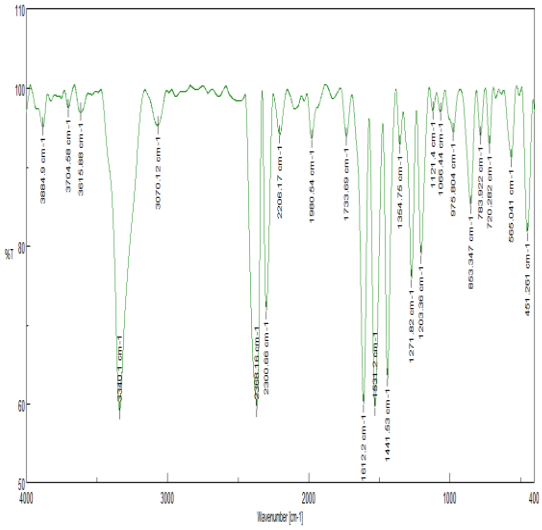


Figure 1: (a) P1

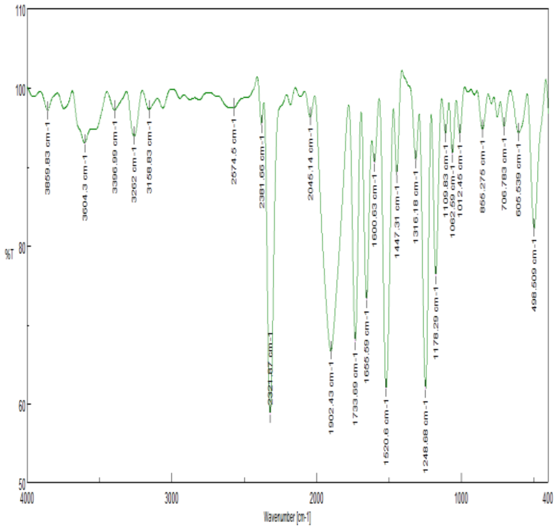


Figure 1: (b) P2

Figure 2 (a,b) Infrared Spectroscopy of Polyester Amide: The formation of polyester amide is confirmed from the typical characteristic Bands observed around1700-1735cm^{-1}dueto the ester stretch,1600±15cm^{-1}dueto the stretch in Amide bands,1246±25,cm^{-1} and 1009±7cm^{-1} correspond to C-O-C symmetic andasymmentric stretch and bending vibration in all PEAs. In all polymer the N-H bending and N-H stretching for 2^{0} amide were observed at 1540 ± 5 and 3280 ± 5 cm^{-1}due to the C=C aromatic at 1610 , 151 5 and 1435 cm^{-1}due tothe C-H stretch of aromatic ring2574cm^{-1},2341cm^{-1}.

Polyester Amide	>C=O Stretching of ester group cm^{-1}	>C=O Stretching of amide cm^{-1}	C-O-C Symmetric and asymmetric stretch and bending cm^{-1}	N-H Stretching 2^{0} amide cm^{-1}	C=C aromatic ring cm^{-1}	C-H stretching cm^{-1}
P_1	1733.69	1655.59	1248.68 1063.59 1012.45	1520.6 3262	1600 1447	2574 2381
P2	1733.69	1612.2	1271.82 1066	1531.2	1414	2368 2300

^{1}H NMR Spectral Analysis:

structure of the repeating units present in the polyester amide can be analysed qualitatively , quantitatively and microstructure of the polymer was determined by ^{1}H NMR spectroscopy taken in DMSO – d$_6$ using TMS internal reference .[10,11] The chemical shift value can be explained on the basic of structural units present in the polyester amide. Meta –disubstituted aromatic ring with amide or ester bonds can be expected to exhibit three signals: a singlet doublet and a triplet [12] furthermore, corresponding peaks for aromatic protons substituted by ester groups will be observed downfield from those for aromatic protons substituted by amide groups, based on the chemical shifts of model compounds.

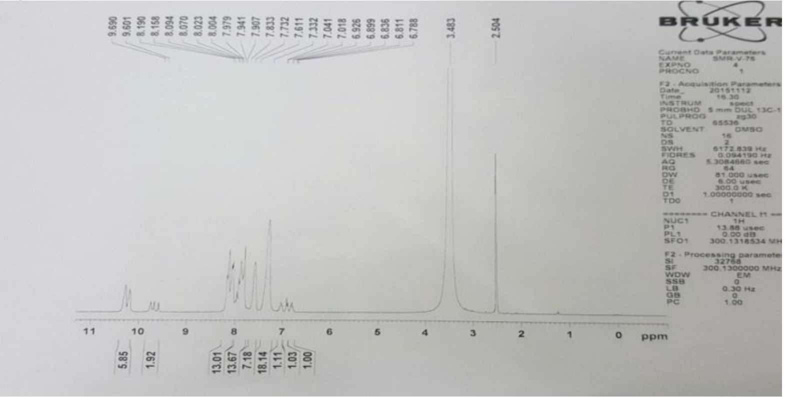


Figure 2: (a) ^{1}H NMR Spectra of polyester amide

The NMR spectra of the polymer were in agreement with the proposed Structure of polyester-amide ^{1}H of two Ar-H ortho –NH-CO- group of adoublet at δ 7.32- 7.61 and two Ar-H ortho to –COO- group appeared around δ 6.64-6.76 ppm. And group of terephthaloyl moiety showed δ at 8.04-9.28 ppm.

^{13}CNMR Spectral Analysis:

^{13}CNMR is an important spectral method in the analysis of fine structure of polymers [13, 14]. The ^{13}C resonance of organic compounds are found over a chemical shiftrange of 300ppm compared with less than 20 ppm for protons. The proton decoupled ^{13}C NMR spectra of this polyester amide have been recorded in DMSO-d6 with as internal standard. The ^{13}C NMR chemical shift values for the synthesized polyester amide and the corresponding assignments are presented in given bellow. Structure of polyester-amide ^{13}C of two Ar-H ortho –NH-CO- group of adoublet at δ 162-179 and two Ar-H ortho to –COO- group appeared around δ 164-169 ppm. and 2^{o} group of –NH- 30-45, and ester 80 40ppmgroups.

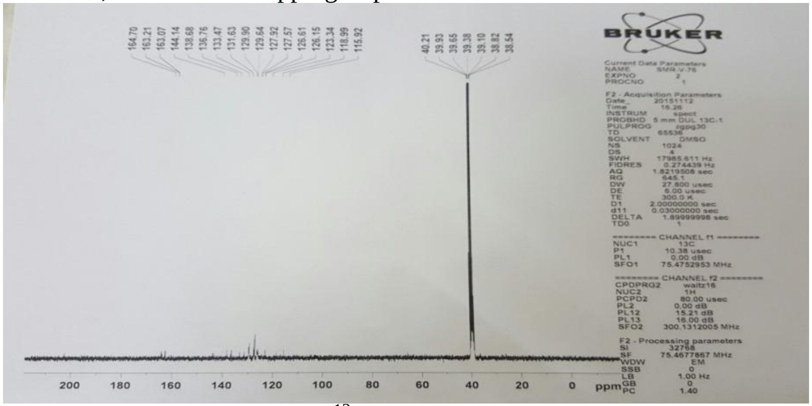


Figure 3: (a) P_1 ^{13}CNMR of polyester amide

Conclusion:

In this investigation, two polyester amides based on o-amino phenol/ m-amino phenol and terephthaloyl acid chloride as a common monomer. The polymers are synthesized by melt polycondensation using CTAB as a phase transfer catalyst. The synthesized polesteramides are soluble in DMSO and DMF and insoluble in common solvent such as acetone and chloroform. The elemental composition of the two synthesized polymer have been determined using elemental analysis. d. Further, the synthesizedpolyesteramidesare characterized by FTIR, ^{1}H NMR, and ^{13}C NMR spectral methods. The synthesized polyester-amides have potential applications in medical field.

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