

Synthesis and preliminary findings of poly (Amide-co-Ester Amide)s

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Abstract:

Uncontrolled accumulation of synthetic materials in the environment led to ecological problems, due to their resistance to chemical or biological degradation. One strategy to augment the biodegradability of convenient polymers involves introducing more hydrolysable groups into their structure. Exceptionally important representatives of biodegradable polymers are pseudo-proteins - a new family of synthetic biodegradable polymers based on natural α -amino acids. One of the members of pseudo - proteins class of polymer include poly(ester amide)s, which are characterized by easily synthesis and versatile application.

During the research Poly (Amide-co-Ester Amide)s were synthesized via interfacial polycondensation reaction mechanism, between monomers: Hexamethylenediamine (HDMA) and Tosyl diamine diesters (TDADE) with various diacid chlorides. Solubility of obtained products was studied in various solvents. Structures were checked by FTIR and NMR spectroscopy methods. Mechanical properties were evaluated using Tensile Testing Machine.

Keywords: Polymers, Biodegradability, Pseudo-Proteins, Polyureas, Polyamides.

Introduction:

Humans have used naturally occurring polymers since ancient times, such as polypeptides/proteins (silk and wool), polysaccharides (cellulose and starch), and others. With the development of civilization, the demand to create and replace existing materials with cheaper ones having higher technical characteristics increased. In the 20th century, the advancement of synthetic chemistry led to the creation of synthetic polymers, which were characterized by high technical performance and low cost. However, the uncontrolled accumulation of synthetic polymers in the environment has caused numerous problems. Today, the resistance of these materials to chemical or biological degradation is

considered a serious environmental threat. Most synthetic polymer materials are less susceptible to degradation under natural conditions. Every year, only one-third of polymer waste is recycled, with the remainder being collected in landfills or burned, which cannot completely prevent damage to the ecosystem. It is estimated that the production of polymer products will reach 500 million tons per year by 2050 [1-4]. All this has led to the need to create materials that degrade and "disappear" after performing their assigned function, without polluting the environment. Biodegradable polymers (BP) belong to such materials. Biodegradability is mostly found in the so-called heterochain polymers containing polarized chemical bonds—ester, amide, urethane, urea, etc.—capable of hydrolytic cleavage. Commercially important biodegradable heterochain polymers are polyesters (polyglycolic acid, polylactic acid, polyhydroxyalkanoates, polycaprolactone, etc.), which degrade at the desired rate due to the hydrolysis of the most labile of the listed chemical bonds. Despite this significant advantage, polyesters is characterized by relatively low thermal and mechanical parameters.

Outstanding classes of heterochain polymers with improved thermal and mechanical properties are polyamides (PA), known as nylons, and polyureas (PU) (PU also belongs to polyamides based on carbonic acid). The high degree of crystalline and strong intermolecular interactions between the amide and urea bonds of polymer chains significantly increase the mechanical strength of these polymers. Additionally, the stability of amide/urea bonds (which are hydrolyzed 10^4 - 10^5 times more slowly than ester bonds) makes PA and PU difficult to degrade [5,6].

It is possible to transform PA and PU into degradable materials at the desired rate by combining them with polyesters, leading to the synthesis of hybrid polymers—co-polyesteramides. Various methods for the synthesis of polyester amides have been provided and analyzed by Prof. J. Puijal et al [7]. Prof. R. Katsarava synthesized a new class of biodegradable polymers Pseudo-proteins - based on natural occurring α - amino acid. Obtained polymers includes Poly (Ester urea)s, Poly(Ester Amide)s and Poly(depsipeptide)s and their copolymers [8,9].

Experimental Methods:

Throughout the research, the synthesis and analysis of the copolymers were carried out. The molecular structures of the resulting products were characterized using spectroscopy methods. Mechanical properties were assessed through tensile testing.

Polymer Synthesis:

Poly (Amide-co-Ester Amide)s synthesized via interfacial polycondensations (system – water/dichloromethane) at room temperature, between monomers of hexamethyl diamine (HDMA) and β -leucine-1,6-hexandiol-di-Para-toluin sulfonate (L6) with various dicarboxylic chlorides - Sebacoil chloride (SC), Terephthaloyl chloride (TC) and Fumaryl chloride (FC) (figure. 1).

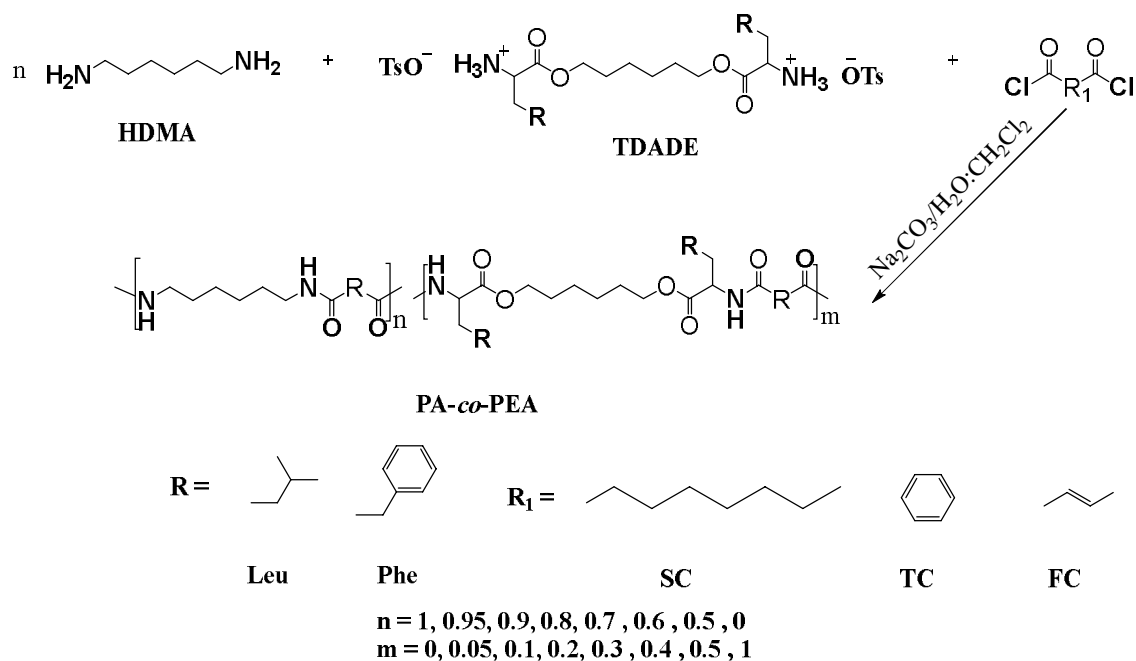


Fig. 1 General Synthesis Scheme of Poly (Amide-*co*- Ester Amide) Copolymers

Characterization: solubility and film forming properties of obtained product were evaluated in different solvents. Infrared Spectra (FT-IR) and Proton magnetic resonance ($^1\text{H-NMR}$) were used to confirm the structures of the obtained products. Mechanical Properties were measured using Tensile test machine.

Solubility: The solubility of obtained products was assessed in various solvents such as Chloroform (CCl_3H), Dichloromethane (CH_2Cl_2), Hexafluoro isopropyl alcohol (HFIP), Acetic acid (AcOH) and Formic acid (HCOOH) was determined at room.

Infrared Spectrum: The FT-IR measurement was conducted on Nicolet (FTIR Thermo Nicolet AVATAR 370) Spectrophotometer (KBr pellets) in the range of $4000\text{-}400\text{ cm}^{-1}$.

Proton Magnetic Resonance: The Proton magnetic resonance instrument for the determination of the samples' structures was provided with a (Magritek Spinsolve 60 MHz) NMR spectrometer. The samples were dissolved in deuterated dimethylsulfoxide (d_6 - DMSO)

Mechanical Properties: Mechanical properties were evaluated on Mark 10™ ESM 303 Motorized Tension Test Stand machine and the results were analyzed using MESUR®gauge Plus software. Tensile strength (MPa), Relative deformation (%), and Young's modulus (GPa) values were determined from the analysis of stress-strain curves of the samples.

Results and Discussion:

Synthesis of PA-co-PEA: The copolymer synthesis reaction was carried out using an interfacial polymerization reaction at room temperature. The system - water/dichloromethane (CH_2Cl_2) was used as a reaction system. Water was used as the inorganic phase, in which the initial monomers -

hexamethylenediamine (HDMA), β -leucine-1,6-hexanediol-di-para-toluene sulfonate (L6), and Na_2CO_3 (H^+ binder) were dissolved in water to which are added the chloranhydrides of the corresponding dicarboxylic acids dissolved in CH_2Cl_2 . Co-polycondensation reaction was carried out under stirring conditions for 1 hour. obtained copolymers of polyamides with poly(ester amide)s **PA-co-PEA**. Poly (hexamethylene sebacylamide) (PHS), poly(hexamethylene Terephthalamide) (PHT) and poly(hexamethylene fumarylamide) (PHF) copolymers with the corresponding poly (Ester amide)s obtained : $[\text{PHS}]_n\text{-co-}[\text{8L6}]_m$ $[\text{PHT}]_n\text{-co-}[\text{L6,TC}]_m$ and $[\text{PHF}]_n\text{-co-}[\text{L6,FC}]_m$. The molar ratios of HDMA and L6 monomers were 0.95:0.5, 0.9:0.1, 0.8:0.2, 0.7:0.3, 0.6:0.4, 0.5:0.5. The corresponding homopolymers were also obtained (n:m = 1:0 and 0:1)

Solubility: Solubility tests were performed using a different solvent. It was found that increased segment of PEA in copolymers increases solubility in polar organic solvents. The Solubility test of obtained copolymers is shown in table 1.

	n:m	CHCl_3	CH_2Cl_2	HFIP	AcOH	HCOOH
$[\text{PHS}]_n\text{-co-}[\text{8L6}]_m$	1:0	-	-	-	±	±
	0.95:0.05	-	-	-	±	±
	0.9:0.1	-	-	±	±	±
	0.8:0.2	-	-	+	±	±
	0.7:0.3	-	-	+	±	+
	0.6:0.4	±	±	+	+	+
	0.5:0.5	+	+	+	+	+
	0:1	+	+	+	+	+
$[\text{PHT}]_n\text{-co-}[\text{TC,L6}]_m$	1:0	-	-	-	-	-
	0.95:0.05	-	-	-	-	-
	0.9:0.1	-	-	-	-	-
	0.8:0.2	-	-	-	-	-
	0.7:0.3	-	-	±	-	-
	0.6:0.4	±	±	±	-	-
	0.5:0.5	+	+	+	-	+

	0:1	+	+	+	-	-
[PHF] _n - <i>co</i> -[FC,L6] _m	1:0	-	-	-	-	-
	0.95:0.05	-	-	-	-	-
	0.9:0.1	-	-	-	-	-
	0.8:0.2	-	-	-	-	-
	0.7:0.3	-	-	-	-	-
	0.6:0.4	-	-	-	-	-
	0.5:0.5	-	-	-	-	-
	0:1	±	±	±	±	±

+ Fully Dissolved ± Half dissolved – Does not dissolve

Table 1 solubility of obtained Product (100 mg/ml)

Spectroscopy:

Infrared spectra: Fourier Transform Infrared (FT-IR) Spectroscopy is a technique used to obtain an infrared spectrum for analyzing polymers. Only one infrared spectra of sample was recorded - [PHT]_{0.5}-*co*-[TC, L6]_{0.5} (figure 2).

The IR spectra of [PHT]_{0.5}-*co*-[TC, L6]_{0.5} sample exhibited characteristic absorption bands listed as follows (figure 3): 3303.91 (-NH-C=O secondary amide), 2935.96 (C-H), 2867.58 (C-H) 1734.10 (C=O ester), 1625.25 (C=C aromatic), 1536.95 C=C aromatic)

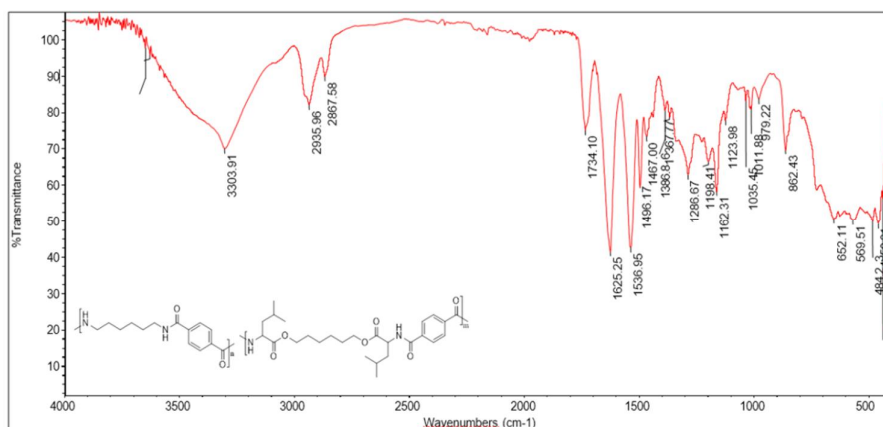


Fig 2. Infrared spectra of [PHT]_{0.5}-*co*-[TC,L6]_{0.5}

Proton Magnetic Resonance: The observed NMR spectrum of [PHT]_{0.5}-co-[TC,L6]_{0.5} is consistent with the expected chemical shifts and splitting patterns based on its structure. The chemical shifts align with typical values for [PHT]_{0.5}-co-[TC,L6]_{0.5}. Figure 4 shows the ¹H-NMR spectra of [PHT]_{0.5}-co-[TC,L6]_{0.5} in deuterated dimethyl sulfoxide. The chemical shifts at 8.67 ppm were attributed to the amid bonds. ¹H NMR (60 MHz, DMSO): δ 8.67 (d, J = 7.4 Hz, 1H NH-CO amide), 7.79 (s, 1H aromatic), 5.57 (s, 1H aromatic), 4.08 (dt, J = 24.2, 6.9 Hz, 3H), 3.49 (s, 7H), 2.35 (s, 0H), 1.33 (d, J = 17.7 Hz, 9H CH₂-), 0.75 (s, 5H CH₃-).

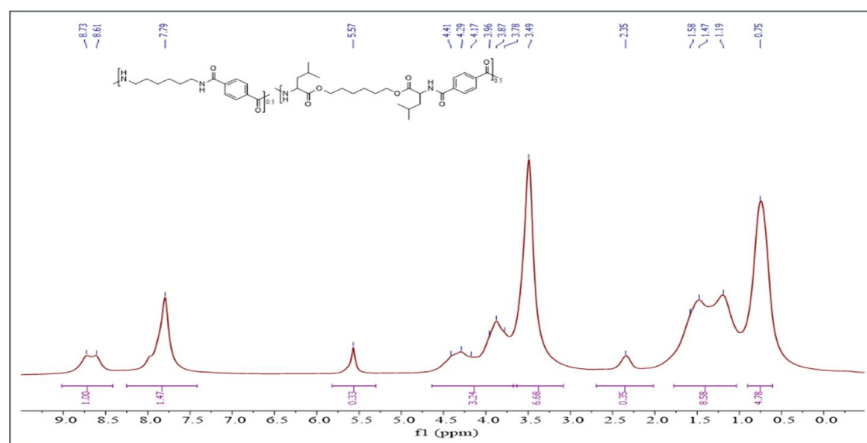


Fig. 3 ¹H-NMR Spectra of [PHT]_{0.5}-co-[TC,L6]_{0.5}

Mechanical Properties:

The mechanical properties of the obtained polymers were studied using film samples that were cast from appropriate solvents. Test samples were then cut from these films using a die sample cutter.

The tensile strength of the samples was measured using a Mark-10 ESM 303 tensile testing machine and MESUR®gauge Plus software. The mechanical properties of the [PHT]_n-co-[TC,L6]_m copolymers were measured for various compositions (n:m=0.5:0.5 and 0:1). The samples were cast from solutions dissolved in hexafluoroisopropyl alcohol (HFIP). Analysis of stress – Strain curves (figure 4) of obtained samples, mechanical properties (Tensile Strength, Elongation to Break and Young's Modulus) were obtained (Table 2). Only the copolymer of Polyhexamethylene terephthalamide (PHT) with the corresponding polyesteramide [TC,L6] has demonstrated exceptional mechanical properties, as shown below. When the polyesteramide ratio exceeds 0.6, the copolymer exhibits low solubility in HFIP, making it impossible to measure. Further studies are needed to explore the mechanical properties of other polyamides.

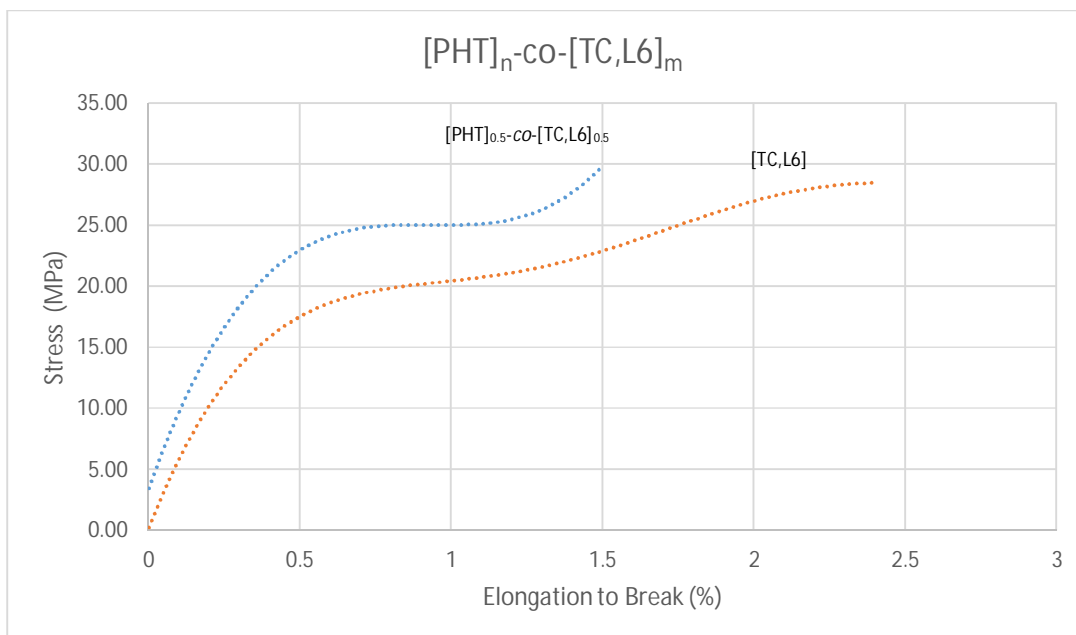


Fig. 4 Stress-strain curve of $[PHT]_n\text{-co-}[TC,L6]_m$

Sample	n:m	Tensile Strength (MPa)	Elongation to Break (%)	Young's Modulus- (GPa)
$[PHT]_n\text{-co-}[TC,L6]_m$	0.5:0.5	30	1.5	0.92
	0:1	28	2.4	0.52

Table 2. Mechanical properties of $[PHT]_n\text{-co-}[TC,L6]_m$

Conclusion:

Poly(amide-co-ester amide) copolymers were synthesized by interfacial polycondensation in a water-dichloromethane system. The copolymers $[PHS]_n\text{-co-}[8L6]_m$, $[PHT]_n\text{-co-}[TC,L6]_m$, and $[PHF]_n\text{-co-}[FC,L6]_m$ were obtained with varying ratios of monomers.

The solubility and film-forming ability of the copolymers were tested in various organic and inorganic solvents. The solubility of $[PHS]_n\text{-co-}[8L6]_m$ in solvents increased with a higher proportion of the poly(ester amide) fraction, but obtaining films for mechanical evaluation from the solution was not possible. $[PHT]_n\text{-co-}[TC, L6]_m$ copolymers dissolved easily in organic solvents, and films were obtained for mechanical property assessment. In contrast, the $[PHF]_n\text{-co-}[FC,L6]_m$ type of products did not dissolve

in any solvents, nor could films be obtained from their solutions; thus, their spectral and mechanical properties were not evaluated.

It should be noted that increasing the proportion of the PEA segment in polyamides enhances their solubility in polar organic solvents, such as HFIP, CHCl_3 and CH_2Cl_2 . The molecular structure of the obtained copolymers was confirmed by FT-IR and NMR analysis. The IR and ^1H NMR spectra of $[\text{PHT}]_{0.5}\text{-co-}[\text{TC,L6}]_{0.5}$ revealed the presence of specific bonds in the polymer structure.

The mechanical properties, including tensile strength, elongation at break (%), and Young's modulus, of the $[\text{PHT}]_n\text{-co-}[\text{TC,L6}]_m$ copolymers were measured. It was determined that the tensile strength decreases with an increasing proportion of the PEA fraction in the polyamides group.

Research is still ongoing, and further insights will reveal the potential applications of the materials obtained.

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პოლი(ამიდ-თანა-ესტერ ამიდები)ს სინთეზი და წინასწარი დასკვნები

რუსლან დავითაძე, მაია ვანიძე, ალექო კალანდია

აბსტრაქტი:

სინთეზური მასალების უკონტროლო დაგროვებამ გარემოში, ქიმიური ან ბიოლოგიური დეგრადაციისადმი მათი მდგრადობის გამო გამოიწვია ეკოლოგიური პრობლემები, არსებული პოლიმერების ბიოდეგრადუნარიანობის გაზრდის ერთ-ერთი სტრატეგია მოიცავს მათ სტრუქტურაში მეტად ჰიდროლიზირებადი ჯგუფების შეყვანას. ბიოდეგრადირებადი პოლიმერების განსაკუთრებულად მნიშვნელოვანი წარმომადგენლები არიან ფსევდოპროტეინები - სინთეზური ბიოდეგრადირებადი პოლიმერების ახალი ოჯახი ბუნებრივი α -ამინომჟავების საფუძველზე. ფსევდო-პროტეინების ჯგუფის ერთ-ერთ წარმომადგენელია პოლი(ესტერი ამიდები), რომლებიც ხასიათდებიან მარტივის სინთეზის და მრავალმხრივი გამოყენებით.

კვლევის პერიოდის დასინთეზირდა პოლი(ამიდ-თანა-ესტერ ამიდები) ინტეფაზური პოლიკონდენსაციის რეაქციის გამოყენებით, საწყისი პრეკურსორების: ჰექსამეთილენდიამინის (HDMA) და ტოსილ დიამინის დიესტერების (TDADE) ურთერთქმედების დიკარბომჟავების ქლორიდებთან. მიღებული პროდუქტების ხსნადობა შესწავლილ იქნა სხვადასხვა გამხსნელებში. სტრუქტურები შემოწმდა ინფრაწითელი და ბმრ სპექტროსკოპიის მეთოდებით გამოყენებით. მექანიკური თვისებები შეფასდა ნიმუშების გაჭიმვის ხელსაწყო გამოყენებით.

საკვანძო სიტყვები: პოლიმერები, ბიოდეგრადაცია, ფსევდო-პროტეინები, პოლიმარდოვანები, პოლიამიდები.