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Synthesis and Properties of Novel Soluble and Thermally Stable Optically Active Poly(amide-imide)s from *N,N'*-(4,4'-Oxydiphthaloyl)-bis-L-phenylalanine Diacid Chloride and Aromatic Diamines

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Summary

In this research work, 4,4'-oxydiphthalic anhydride (**1**) was reacted with L-phenylalanine (**2**) in acetic acid and the resulting imide-acid **3** was obtained in high yield. This imide-acid **3** was converted to diacid chloride **4** by reaction with thionyl chloride. The polycondensation reaction of diacid chloride **4** with several aromatic diamines such as 4,4'-sulfonyldianiline (**5a**), 4,4'-diaminodiphenyl methane (**5b**), 4,4'-diaminodiphenylether (**5c**), *p*-phenylenediamine (**5d**)**,** *m*-phenylenediamine (**5e**), and 4,4'-diaminobiphenyl (**5f**) was performed by two conventional methods: low temperature solution polycondensation and short period reflux conditions. Several new thermally stable optically active poly(amide-imide)s with inherent viscosity ranging from 0.34-0.62 dL/g were obtained with high yield. All of the above polymers were fully characterized by ^{1}H-NMR, FT-IR, elemental analyses and specific rotation techniques. Some structural characterizations and physical properties of this new optically active poly (amide-imide)s are reported.

Introduction

The interest for developing new biodegradable and biocompatible polymers, specially polyesters and polyamides, has largely encouraged the use of monomers based on naturally occurring products[1-2]. Both carbohydrate [3-4] and amino acid [1] derived monomers are being currently used as building blocks to generate novel polyamide structures with enhanced biodegradability. For example L-lysine in particular has been used for making polyamides as potential biomaterials [5–9]. Thus polyamides made of citric acid [10] or malic acid [11] and L-lysine were recently investigated for their potential as water-soluble polyelectrolyte drug-carriers. Over the past decade, polyimides have become an important class of polymers that have found a wide range of application as high performance materials in the aerospace and industries electronics [12]. It was the exceptionally high thermal stability, which is the main characteristic of aromatic polyimides that clearly distinguished them from other known polymers [13-15]. Although aromatic polyimides are well recognized as a class of thermally stable engineering materials, their widespread use is limited due to poor handling and processing characteristics. To overcome these problems, various approaches have been developed [16]. One of the successful approaches to increase solubility and moldability of polyimides is the introduction of flexible linkages into polymer backbone [17-18]. An important flexible is ether (-O-) group. It is known to exhibit reasonable thermal stability and good mechanical properties together with excellent moldability. It was observed that the solubility of polyamides, polyimides and poly(amide-imide)s (**PAI**)s [19] was enhanced by incorporating the ether units into the polymer backbone while retaining a satisfying thermal stability. Recently, we synthesized novel optically active polymers by different methods [20-24]. In these polymers, we also used amino acids as chiral inducting agents. These materials are naturally occurring compounds, therefore synthetic polymers based on amino acids are expected to be biodegradable and biocompatible. In this work we describe the synthesis and characterization of a set of new organosoluble, thermally stable and optically active **PAI**s made from L-phenylalanine and 4,4'-oxydiphthalic anhydride with several readily available aromatic diamins by conventional solution polymerization.

Experimental

Materials

4,4'-Diaminodiphenylmethane (**5b**) and 4,4'-diaminobiphenyl (**5f**) was purified by recrystallization from water. 4,4'-Diaminodiphenylether (**5c**), 1,4-phenylenediamine (**5d**), 1,3-phenylenediamine (**5e**), were purified by sublimation. 4,4'-oxydiphthalic anhydride was supplied from T.C.I Chemical Co (Japan). *N,N*-Dimethylacethamide (**DMAc**) was dried over BaO, then distilled in vacuum. The other chemicals were purchased from Fluka Chemical Co. (Buchs, Switzerland), Aldrich Chemical Co. (Milwaukee, WI) and Riedel-deHaen AG (Seelze, Germany), and were used without further purification.

Instrument

Proton nuclear magnetic resonance ^{1}H-NMR (500MHz) spectra were recorded on a Bruker, Avance 500 instrument (Rheinstetten, Germany). Proton resonances are designated as singlet (s), doublet (d), doublet of doublet (dd) and multiplet (m). FT-IR spectra were recorded on (Jasco-680, Japan) spectrophotometer. Spectra of solids were carried out using KBr pellets. Vibrational transition frequencies are reported in wavenumber (cm^{-1}). Band intensities are assigned as weak (w), medium (m), strong (s) and broad (br). Inherent viscosities were measured by a standard procedure using a Cannon Fenske Routine Viscometer (Mianz, Germany). Specific Rotations were measured by a Jasco-1030 Polarimeter (Japan). Thermal Gravimetric Analysis (TGA) data for polymers were taken on TGA 7 Perkin Elmer (Jugeshein, Germany) in nitrogen atmosphere at a rate of 40^{o}C/min. Elemental analysis were performed by Malek-Ashtar University of Technology, Tehran, I. R. Iran.

Synthesis of Monomer

N,N'-(4,4'-Oxydiphthaloyl)-bis-L-phenylalanine diacid (3)

Into a 50-mL round-bottomed flask 1.00 g (3.22 × 10^{-3} mol) of 4,4'-oxydiphthalic anhydride (**1**), 1.3 g (8 × 10^{-3} mol) of L-phenylalanine (**2**), 30 mL of acetic acid and a

stirring bar were placed. The mixture was stirred at room temperature for 3 h and then was refluxed for 10 h. The solvent was removed under reduced pressure and 5 mL of cold concentrated HCl was added to the residue. A white precipitate was formed, washed with cold water, and was added to it enough amount of ether that was converted to a clear solution. The ether was removed under reduced pressure to give 1.76 g (90.6 %) of compound **3**. mp: 119-120 °C (decomposed), $[\alpha]_D^{25}$: 118.0° [0.050 g in 10 mL of *N,N*-dimethylformamide (DMF)]. FT-IR (KBr, cm^{-1}): 2924, (s, br), 1775 (m), 1718(s), 1609(w), 1474 (w), 1383 (s), 1276 (w), 1235 (w), 1104 (w), 828 (w), 749 (w), 700 (w), 558 (w). ^{1}H-NMR (500 MHz, DMSO-d_6, δ ppm): 3.45-3.55 (dd, 2H, J_1 = 14.09 Hz, J_2 = 4.66 Hz), 5.10-5.1 8 (dd, 2H, J_1 = 11.63 Hz, J_2 = 4.64 Hz), 7.10-7.25 (m, 10H), 7.45-7.55 (dd, 2H, J_1 = 8.16 Hz, J_2 = 1.69 Hz), 7.54 (s, 2H), 7.87-7.89 (d, 2H, J = 8.15 Hz).605 .MS: m/z = 605, 604 (M$^+$).
Found: C, 72.03%; H, 4.31%; N, 7.41%; ($C_{46}H_{32}N_4O_8$ requires C, 71.87%; H, 4.19%; N, 7.28%).

*N,N'-(4,4'-Oxydiphthaloyl)-bis-L-Phenylalanine diacid chloride (**4**)*

Into a 25-mL, round-bottomed flask, were placed 1.00 g (1.65 × 10^{-3} mol) of compound **3** and 3 mL (an excess amount) of thionyl chloride. The mixture was heated by an oil bath up to 50 °C until the suspension mixture was converted to a clear solution and was heated for 2h. Unreacted thionyl chloride was removed under reduced pressure and was washed with dry ether three times to leave 0.98 g (93.2%) of pale yellow solid. mp: 82-84 °C , $[\alpha]_D^{25}$: −155.7° (0.050 g in 10 mL of DMF). FT-IR (KBr, cm^{-1}): 3029 (w), 1776 (m), 1719(s), 1473 (w), 1381(s), 769 (s), 699 (w). ^{1}H NMR (500 MHz, DMSO- d_6, δ, ppm): 3.25-3.75 (dd, 2H, distorted), 5.10- 5.13 (dd, 2H, J_1 = 11.6 Hz, J_2 = 4.60 Hz), 7.10-7.20 (m, 10H), 7.50-7.55 (dd, 2H, J_1 = 10.1 Hz, J_2 = 3.8 Hz), 7.52-7.54 (s, 2H), 7.87-7.89 (d, 2H, J = 8.14 Hz).
Found: C, 63.86%; H, 3.48%; N, 4.81%; ($C_{34}H_{22}N_2O_7$ Cl_2 requires C, 63.66%; H, 3.48%; N, 4.81%).

Polymer Synthesis

All of the polymers were synthesized with two different methods*:*

Method I: Low temperature solution polycondensation

Taking polymer **6aI** as an example, the general procedure consisted of adding 0.20 g (3.1 × 10^{-4} mol) of diacid chloride **4** to a cooled (-5.0 °C) and stirring solution of 0.076 g (3.1 × 10^{-4} mol) of diamine **5a** in 0.25 mL of 1-methyl-2-pyrrolidone (NMP). After the reagents dissolved completely, 0.1 mL of trimethysilyl chloride (TMSC) was added and reaction was allowed to proceed for 2h under a blanket of nitrogen. Then the temperature was raised to room temperature. The reaction mixture was stirred for 5h. The viscous solution was poured into 40 mL of of methanol and the precipitated solid was filtered off and dried at 80 °C for 10 h under vacuum to leave 0.19 g (76.2%) of solid polymer **6aI.** FT- IR (KBr): 3343 (m, br), 2966 (m, sh), 1781 (s), 1723 (s), 1590 (s), 1529(s), 1378 (s), 1152 (s), 1105 (s), 921 (w) cm^{-1}.

The other **PAI**s **(6bI-6fI)** were prepared with similar procedures. All of spectra were recorded with KBr pellets.

Polymer **6bI**. FT-IR (KBr): 3381 (w, br), 3029 (w), 1780 (m), 1721(s), 1600 (m), 1514 (m), 1378 (s), 1147 (m), 1104 (m), 918 (w), 820 (m), 741 (m), 700 (w), 671 cm^{-1} (w).

Polymer **6cI**. FT-IR (KBr): 3343(w, br), 2965(w), 1780 (m), 1723(s), 1590 (m), 1529(m), 1387 (s), 1150 (s), 1105 (m), 921 (w), 742 (w), 672 cm^{-1} (w).

Polymer **6dI**. FT-IR (KBr): 3375 (w, br), 3028 (w), 1781 (m), 1723(s), 1604 (w), 1514 (m), 1382 (s), 1242 (w), 1147 (w), 1105 (w), 742 (m), 634 cm^{-1}(w).

Polymer **6eI**. FT-IR (KBr): 3364 (w, br), 2966 (m), 1780 (m), 1723 (s), 1602(w), 1529 1378 (m), 1147 (m), 1078 (w), 920 (w), 745 (m), 672 cm^{-1} (m).

Polymer **6f** FT-IR (KBr): 3369 (m, br), 2965 (m), 2361 (w), 1724 (s), 1601 (w), 1504 (m), 1378 (s), 1147 (m), 1056 (w), 921 (w), 819 (w), 746 (m), 672 (m), 634 cm^{-1} (m).

Method II: High temperature solution polycondensation

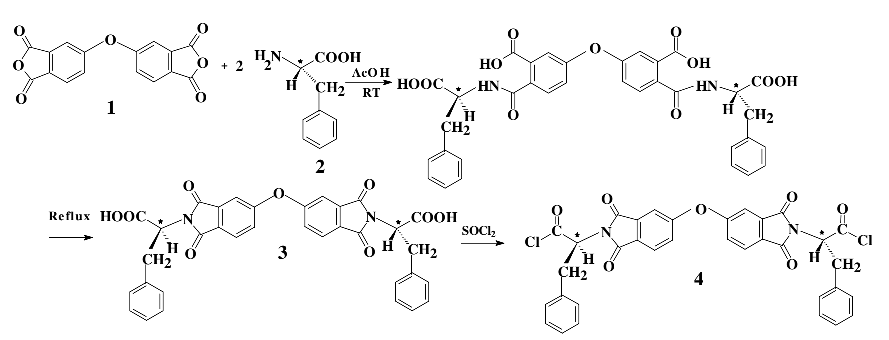
Taking polymer **6aII** as an example, into a 5-mL round-bottomed flask were placed 0.20 g (3.1 × 10^{-4} mol) of diacid chloride **4**, 0.076 g (3.1 × 10^{-4} mol) of diamine **5a**, 0.25 mL of DMAc and 0.05 mL of TMSC was added. The mixture was refluxed for one min. The viscous solution was poured into 40 mL of methanol and the precipitated solid was filtered off and dried at 80°C for 10 h under vacuum to leave 0.22 g (86. 3%) of polymer **6aII**.

The other PAIs (**6bII-6fII**) were prepared with similar procedures.

Results and Discussion

Monomer Synthesis

The asymmetric diacid compound **3** was synthesized by the reaction of dianhydride **1** with two moles of L-phenylalanine (**2**) in acetic acid solution. In this two steps reaction, the intermediate amic acid was not isolated and ring closure for the formation of imide ring was performed under refluxing conditions (Scheme 1).



Scheme 1. Synthesis of monomer 4

The diacid **3** was converted to diacid chloride derivative **4** by reaction with thionyl chloride at room temperature. The chemical structure and purity of the compounds **3** and **4** were proved using elemental analysis, FT-IR and ^{1}H-NMR spectroscopic techniques. The ^{1}H-NMR spectrum (500 MHz) of compound (**3**) is shown in Figure 1. The doublet of doublet between 5.10-5.13 ppm is assigned to the protons of the chiral center.

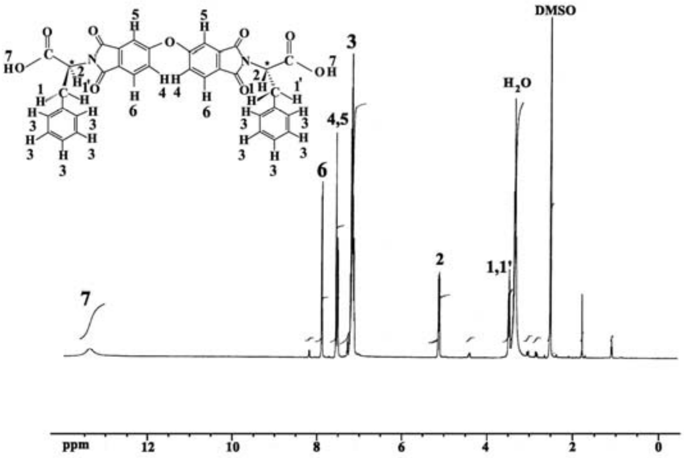
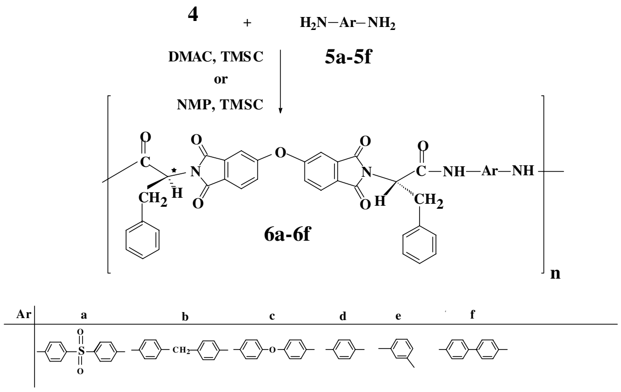


Figure 1. ^{1}H NMR (500 MHz) Spectrum of diacid (**3**) in DMSO-d_6 at rt

Polymer Synthesis

The polymerization of diacid chloride **4** with aromatic diamines **5a-5f** was performed under low temperature (method I), reflux condition (method II) polycondensation reaction (Scheme 2). In method I, polycondensation reaction was performed in cold NMP solution (–5 °C) in the presence of small amount of TMSC. In this method the



Scheme 2. Ploycondensation reactions of monomer **4** with aromatic diamines

polymerization reactions occurred at lower temperature in a period of 2 h. In method II polycondensation reactions were proceeded rapidly at the reflux temperature of solvent in 1 min. We obtained comparable yields and viscosity of **PAIs 6a-6f** frommethods I and II. The reaction yields and some physical data of the solution polycondensations are listed in Tables 1 and 2.

Table 1. Some Physical Properties of PAIs **6aI-6fI** Prepared by Method I

Diamine	Polymer					
	Polymer code	Yield (%)	η_{inh}(dL/g)	$[\alpha]_{589}^{25}$	$[\alpha]_{577}^{25}$	$[\alpha]_{546}^{25}$
5a	**6aI**	76.2	0.39	-54.1	-100.3	-94.2
5b	**6bI**	90.3	0.57	-56.3	-110.3	-101.2
5c	**6cI**	71.5	0.53	-60.4	-124.2	-112.3
5d	**6dI**	74.3	0.46	-69.1	-89.3	-88.2
5e	**6eI**	65.2	0.38	-74.1	-90.1	-78.3
5f	**6fI**	61.3	0.35	-64.5	-92.1	-90.3

Structural Characterization of Polymers

The structures of these polymers were confirmed as **PAIs** by means of elemental analysis, FT-IR and ^{1}H-NMR spectroscopy. Elemental analysis data of the resulting polymers are listed in Table 3.

Table 2. Some Physical Properties of PAIs **6aII-6fII** Prepared by Method II

Diamine	Polymer					
	Polymer code	Yield (%)	η_{inh}(dL/g)	$[\alpha]_{589}^{25}$	$[\alpha]_{577}^{25}$	$[\alpha]_{546}^{25}$
5a	**6aII**	86.3	0.41	-64.2	-122.5	-121.3
5b	**6bII**	90.4	0.62	-60.3	-110.3	-100.1
5c	**6cII**	91.5	0.55	-40.2	-97.2	-96.3
5d	**6dII**	75.3	0.43	-67.1	-79.3	-78.5
5e	**6eII**	74.2	0.33	-60.1	-88.4	-80.3
5f	**6fII**	64.3	0.44	-54.3	-80.3	-66.5

FT-IR spectra of all polymers show the characteristic absorption peaks for the imide ring at 1718 and 1780 cm^{-1} due to the symmetrical and asymmetrical carbonyl stretching vibrations. Bands of amide N-H groups appeared around 3381-3343 cm^{-1} (hydrogen band) and 1514-1590 cm^{-1} (amide II band). All of them exhibited strong absorptions at 1380 cm^{-1} that show the presence of the imide heterocycle ring in these polymers. The ^{1}H-NMR spectra of **PAI-6dI** is shown in Figures 2. The pattern of spectra is similar to those of monomer diacid chloride and corresponding diamine. The two equivalent amidic hydrogens are seen in similar chemical shift.

All polymers are soluble in organic polar solvents such as DMAc, DMF, NMP and DMSO, Therefore they readily form thin film in these solvents, but, they are insoluble in solvents such as chloroform, acetonitrile, methanol, cyclohexane and water.

Table 3. Elemental Analysis of PAIs **6aI – 6fI**

Polymer	Formula		Elemental Analysis (%) C	H	N	Moisture Content (%)[a]
6aI	$(C_{46}H_{32}N_4O_9S)_n$	Calcd	67.64	3.94	6.85	0.5
	$(818)_n$	Found	67.60	4.03	7.01	
		Corr[b]	67.93	4.00	7.04	
6bI	$(C_{47}H_{34}N_4O_7)_n$	Calcd	73.62	4.46	7.30	0.55
	$(767)_n$	Found	73.62	4.89	7.81	
		Corr[b]	74.00	4.86	7.84	
6cI	$(C_{46}H_{32}N_4O_8)_n$	Calcd	71.87	4.19	7.28	0.25
	$(769)_n$	Found	72.03	4.31	7.41	
		Corr[b]	72.18	4.29	7.42	
6dI	$(C_{40}H_{28}N_4O_7)_n$	Calcd	71.00	4.17	8.28	0.15
	$(677)_n$	Found	71.09	4.21	8.69	
		Corr[b]	71.19	4.20	8.70	
6eI	$(C_{40}H_{28}N_4O_7)_n$	Calcd	71.00	4.17	8.28	0.13
	$(677)_n$	Found	71.01	4.20	8.83	
		Corr[b]	71.10	4.19	8.84	
6fI	$(C_{46}H_{32}N_4O_7)_n$	Calcd	73.40	4.28	7.44	0.18
	$(753)_n$	Found	73.41	4.28	7.88	
		Corr[b]	73.50	4.27	7.89	

[a] Moisture Intake (%) = $\frac{(\mathbf{W}-\mathbf{W_0})}{\mathbf{W_0}}\times 100$, W= weight of polymer sample after standing at room temperature and W_0= weight of polymer sample after dried in vacuum at 100 °C for 10 h.

[b] Corrected value for C and N = Found value $\times\frac{(100+\textbf{moisture content})}{100}$, and Corrected value for H = Found value $\times\frac{(100-\textbf{moisture content})}{100}$.

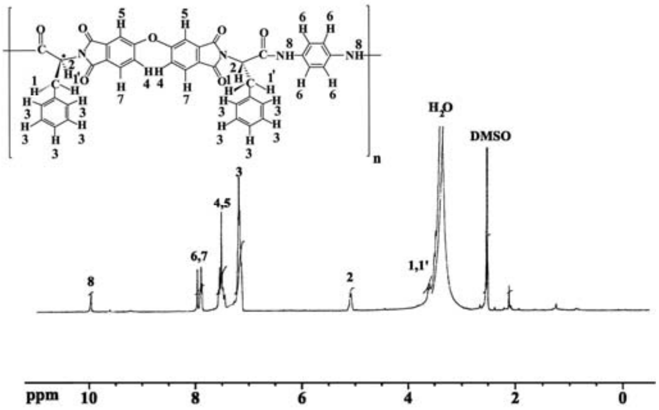


Figure 2. ^{1}H NMR (500 MHz) Spectrum of PAI-**6dI** in DMSO-d_6 at rt

Thermal Properties

All polymers possess char residue above 40% at 500 ^{o}C under nitrogen atmosphere. Poly(amide–imide) **6b** possess considerably low char residue at 600 ^{o}C compared to another polymer due to the presence of phenyl methylene group, which is less thermally stable than that of phenyl sulfone group. Typical TGA curves of representative polymers are shown in Figures 3. The temperatures of 5% and 10% weight loss together with char yield at 600 ^{o}C for PAIs **6aI, 6bI** and **6dI** have been calculated from their thermograms. The thermoanalyses data of PAIs **6aI, 6bI** and **6dI** are summarized in Table 4**.**

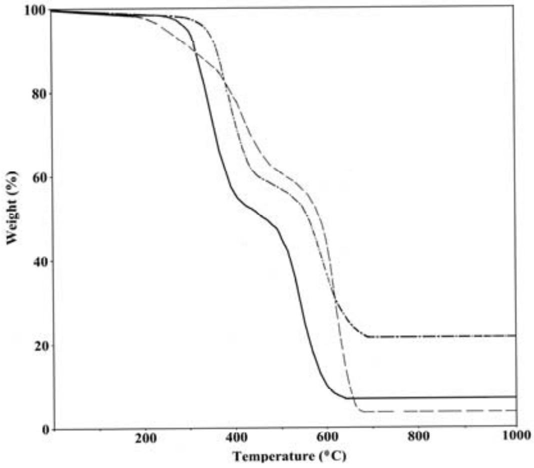


Figure 3. TGA PAI-6aI (.-.-.-.-) PAI-6bI (——) and PAI-6dI (----) with a heating rate of 40^{o}C/min in nitrogen atmosphere

Table 4. Thermal properties of PAIs **6aI**, **6bI** and **6dI**

Polymer	T_0 (^{o}C)^{a}	T_5 (^{o}C)^{b}	T_{10} (^{o}C)^{c}	Char Yield (%)^{d}
6aI	322	361	389	43
6bI	267	311	324	10
6dI	222	272	322	51

[a] Temperature at which 5% weight loss was recorded by TGA at heating rate of 40 ^{o}C/min in N_2.

[b] Temperature at which 5% weight loss was recorded by TGA at heating rate of 40 ^{o}C/min in N_2.

[c] Temperature at which 10% weight loss was recorded by TGA at heating rate of 40 ^{o}C/min in N_2.

[d] Percentage weight of material left undecomposed after TGA analysis at maximum temperature 600 ^{o}C in N_2.

Conclusion

A series of new type optically active aliphatic-aromatic **PAI**s bearing ether groups in the main chain with moderate to high molecular weights was successfully synthesized. These polymers showed excellent solubilities and could be made into film upon casting. Besides, these polymers were characterized by excellent thermal stability as well as demonstrating a good combination of properties and processability. The polycondensation lead to the formation of polymers having inherent viscosity ranging from 0.34-0.62 dL/g. TMSC activates the diamine monomers [25]. The synthetic polymers are expected to have potential as packing materials in chromatography technique. Furthermore the resulting polymers due to the presence of amino acid moieties could have biodegradability and biocompatibility properties, so could be environmentally friendly.

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