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Preparation and characterization of new thermally stable and optically active polyesters by direct polycondensation reaction promoted by Vilsmeier adduct

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Abstract: Highly soluble and optically active aromatic polyesters **(PE)**s containing phthalimide and flexible chiral groups were prepared with moderate molecular weights by step-growth polymerization of diacid monomer containing pendant 4-[(2L)-phthalimidylpropanoylamino)benzoyl group with several aromatic diols, in a system of tosyl chloride, pyridine (Py) and *N*,*N*-dimethylformamide (DMF) to give a series of new optically active **PE**s with good yield and moderate inherent viscosity ranging from 0.28 to 0.48 dL/g. The aim of this work was to obtain novel optically active **PE**s that was more soluble in common organic solvents while maintaining the high thermal stability. All polymers derived from such a diacid and aromatic diols were highly organosoluble in solvents like *N*-methyl-2-pyrrolidinone, *N*,*N*-dimethylacetamide, DMF, Py, dimethyl sulfoxide. Thermogravimetric analysis data showed that these **PE**s are thermally stable, with 10% weight loss being recorded above 400 °C and showed good thermal stability associated with high glass-transition temperatures above 200 °C as measured by differential scanning calorimetry. All of the above polymers were characterized by FT-IR and specific rotation techniques and some of them were also characterized by ^{1}H-NMR and elemental analyses methods.

*Keywords***:** direct polycondensation; pendant group; optically active polymers; phthalimide

Introduction

Synthesis of optically active polymers is an important field in macromolecular science as they find a wide variety of potential applications based on the chiral structure. The chiral macromolecules have found successful applications in chiral chromatographic separations and shown potential uses in chiral catalytic systems, liquid crystals, optical switches, biomedical devices [1-5]. This circumstance will influence new methodologies for the synthesis of optically active polymers in the coming century. A direct and efficient approach for synthesizing chiral polymers is to introduce chiral elements into the macromolecule backbone or the side chains [6]. We have synthesized a variety of novel chiral monomers and polymers [7-10].

The patent literature reviewed shows that predominant research activities in the past were focused on improving the electrical, thermal and mechanical properties of polymers. There is considerable interest in polymers consisting of aromatic units linked together directly or *via* ester, ketone, ether, thioether, sulfone, amide or imide moieties because they often form the basis of excellent high performance materials. In many cases these polymers also display liquid crystal properties [11]. It can, however, encounter processing difficulties due to their high glass transition or melting temperatures coupled with insolubility in most organic solvents. Hence, expansion of polymers for use at high temperature with better solubility is an important goal. This problem can sometimes be overcome by using a precursor monomer synthetic methodology. One of the approaches to improve solubility of the macromolecules without excessive loss of their high thermal stability is the introduction of flexible and bulky groups into the polymer backbone and using asymmetrically substituted monomers or pendent group [12-15]. If the bulky pendent groups be carefully chosen in the way that they exhibit high thermal stability because this approach generates a separation of chains and lowering the chain packing with a raise of free volumes, it is possible to promote solubility without sacrificing the thermal and mechanical properties to a great extent. Thus thermally stable polyesters (**PE**)s with pendant aromatic or heteroaromatic rings have been reported [16]. Particularly, the introduction of pendent imide rings which are known for their high thermoresistance, will improve both the solubility and thermal stability [17-18]. We are interested in synthesis of fully-aromatic **PE**s containing 4-[(2L)-phthalimidiylpropanoylamino) benzoyl] as pendant group for two reasons. Firstly, the phthalimide moiety and benzoyl unit are stable toward high temperatures, secondly, the chiral L-alanine moiety is a biological active and optically active unit. The amalgamation of amino acid into synthesized polymers is of interest because these combinations create new nonbiological macromolecules with biomimetic structures and properties, and thus have many potential applications, including optical resolution, controlled drug release systems, and biologically active and degradable materials [19].

Direct polycondensation as a mild condition method for the synthesis of **PE**s and corresponding copolymers has been used in the authors' laboratory [20-21]. The processes which are operative under mild conditions and adaptable to the direct polycondensations of free dicarboxylic acids and aromatic diols, can be more useful techniques for polyesterification. Several condensing agents suitable for the direct polycondensation reaction such as diphenyl chlorophosphate and arylsulfonyl chlorides have been developed in the past decades [22-23]. However, there are few which have been well studied for the direct synthesis of the aliphatic and aliphatic-aromatic **PE**s. It has been reported that Vilsmeier adduct derived from tosyl chloride (TsCl) and dimethylformamide (DMF) in pyridine (Py) has been successfully used as a suitable condensing agent for the synthesis of aromatic **PE**s by the direct polycondensation of aromatic dicarboxylic acids and bisphenols and also of hydroxybenzoic acids [24-25]. In this article we wish to report the synthesis and characterization of new optically active **PE**s from aromatic diols and 5-[4-(2-phthalimidylpropanoylamino)benzoylamino] isophthalic acid as a monomer containing preformed imide group under Vilsmeier adduct derived from arylsulfonyl chlorides and DMF in Py.

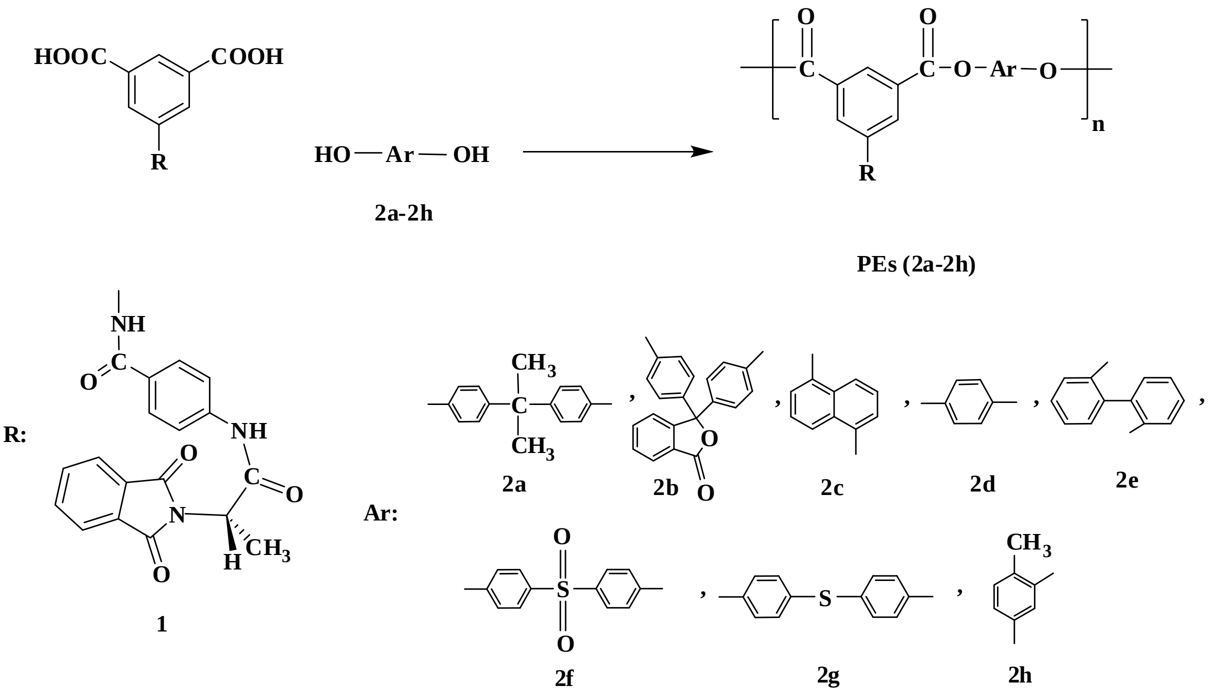
Results and Discussion

Monomer Synthesis

5-[4-(2-Phthalimidylpropanoylamino)benzoylamino]isophthalic acid (**1**) was synthesized by a five-step route as in previously reported procedures [18].

Polymer Synthesis

PEs **2a-2h** were synthesized by the direct polycondensation reactions of an equimolar mixture of monomer **1** with several different aromatic diols, such as bisphenol-A (**2a**), phenolphthalein (**2b**), 1,5-naphthalenediol (**2c**), hydroquinone (**2d**), bisphenyl-2,2'-diol (**2e**), 4,4'-dihydroxydiphenyl sulfone (**2f**), 4,4'-dihydroxydiphenyl sulfide (**2g**) and 1,3-dihydroxytoluene (**2h**) in a system of TsCl/Py/DMF (Scheme I). In this work for the polycondensation reaction of aromatic diacid and aromatic diols, a Vilsmeier adduct was prepared by dissolving TsCl in a mixed solvent of Py and DMF.



Scheme I. Polycondensation reactions of (2L)-5-[2-phthalimidylpropanoylamino)-benzoylamino] isophthalic acid **(1)** with aromatic diols .

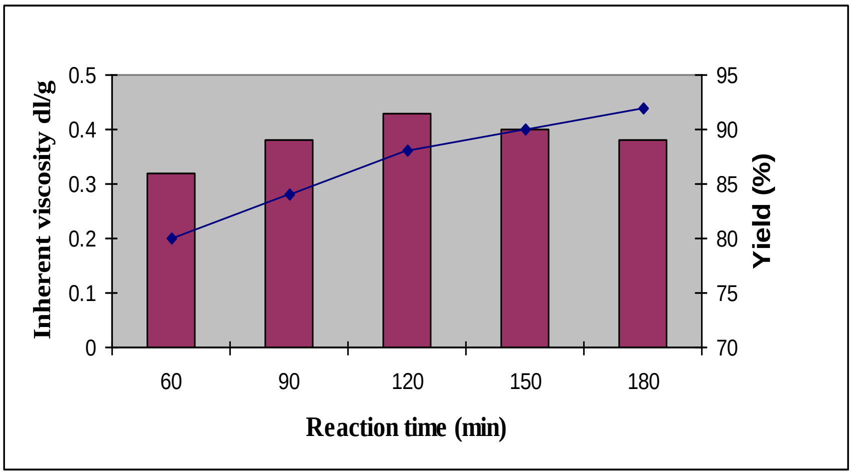


Fig. 1. Effect of the amount of DMF added to TsCl on the inherent viscosity and yield of **PE2a** at 120 °C for 2 h with an aging time of 30 min (for TsCl = 1.0 mmol diacid = 0.20 mmol).

The polycondensation reaction was carried out in the following way: TsCl was dissolved in Py and after a certain period (aging time) the solution was treated with DMF for 30 min. The reaction mixture was added to a solution of diacid in Py. After a period of time a solution of diol in Py was added and the whole solution was maintained at elevated temperature for several hours. Polycondensation reaction was performed by varying the aging time of the initial reaction of TsCl and Py, the amount of DMF, the molar ratio of TsCl/diacid, Py/diacid and the time of heating. Polycondensation of diacid with aromatic diols was carried by varying the aging time of the initial reaction of TsCl and Py, TsCl was dissolved in Py at room temperature and kept at this temperature for 30 min according to previously reported procedures that the suitable aging time is 30 min [8]. The yield and viscosity of the resulting **PE**s were affected by the amount of DMF. From this data it is clear that a ratio of DMF/diacid should be about 7, in order to obtain polymers with high yield and inherent viscosity. Further addition of DMF did not improve the molecular weights and yields (Fig. 1). The effect of reaction time on inherent viscosity and yield of resulting **PE**s is shown in Fig. 2.

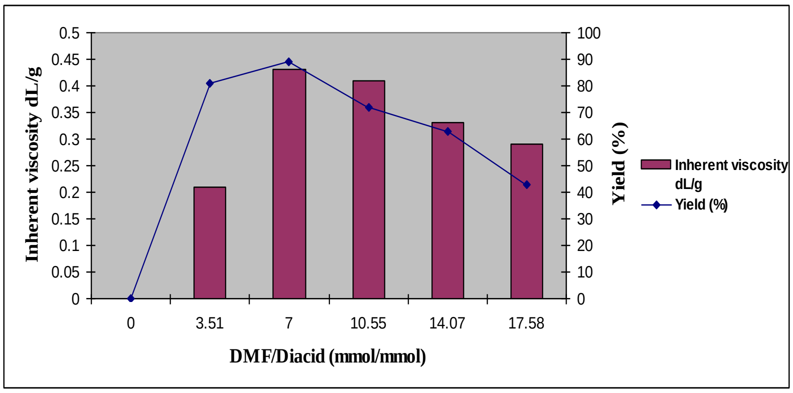


Fig. 2. Effect of reaction time on the inherent viscosity of **PE2a** at 120 °C with an aging time of 30 min (for TsCl =1.0 mmol, diacid = 0.20 mmol, DMF mmol, DMF = 1.40 mmol).

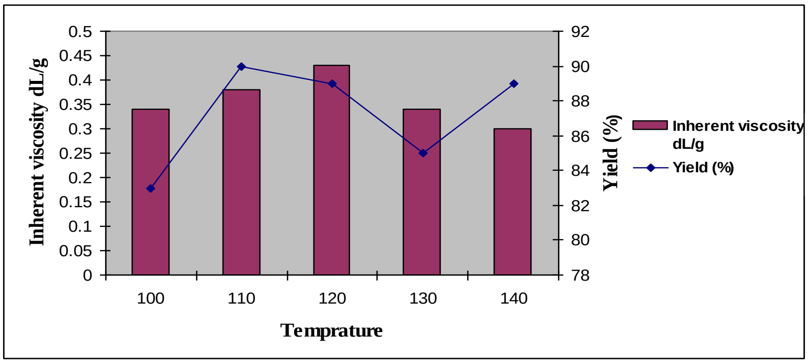


Fig. 3. Effect of temperature on the inherent viscosity and yield of **PE2a** for 2 h with an aging time of 30 min (for TsCl =1.0 mmol, diacid = 0.2 mmol, DMF = 1.4 mmol).

From this information an appropriate reaction time of 2 h is required to get **PE**s with high yield and inherent viscosity. The polycondensation reaction was also carried out at various temperatures and a suitable temperature of 120 °C was obtained (Fig. 3). The optimum conditions for the preparation of **PE**s are summerized in Table 1. The aforementioned optimization reactions were performed for the formation of PE2a and the optimized conditions were used for the preparation of other PEs in order to have unique conditions. The synthesis and some physical properties of these novel optically active **PE**s are listed in Table 2. The inherent viscosities of the resulting polymers under optimized condition were in the range 0.28-0.48 dL/g and the yields were 54–98%. **PE**s with low inherent viscosity of 0.28 dL/g was obtained from diol **2e** and with a high inherent viscosity of 0.48 dL/g from diol **2a**, this information clearly shows that **PE**s with a range of molecular weight and structure can be readily synthesized by this efficient method. The incorporation of a chiral unit into the polymer backbone was confirmed by measuring the specific rotations of polymers with different source lamps (Table 2). The specific rotation of polymers based on different diols showed random changes. These observations are the result of different polymer structures and inherent viscosities. As shown in Table 2 all of the polymers show a relatively high optical rotation and are therefore optically active polymers.

Tab. 1. The optimum conditions for the preparation of **PE**s.

Optimum Condition	
TsCl/Diacid (mol/mol)	5
Py/Diacid (mol/mol)	54
DMF/diacid (mol/mol)	7
Aging time (min)	30
Reaction time (h)	2

Tab. 2. Synthesis and some physical properties of **PE**s **2a–2h** prepared using TsCl/DMF/Py.

Polymer	Diols	Yield (%)	η (dL/g)[1]	$[\alpha]_{D}^{25,1}$	$[\alpha]_{Hg}^{25,1}$	Color[2]
PE2a	2a	98	0.48	-18.22	-29.10	W
PE2b	2b	95	0.41	-14.08	-16.64	W
PE2c	2c	79	0.30	-8.74	-14.93	B
PE2d	2d	84	0.35	-15.04	-33.76	W
PE2e	2e	72	0.28	-8.44	-14.48	W
PE2f	2f	96	0.43	-12.74	-25.58	W
PE2g	2g	93	0.41	-13.72	-20.38	OW
PE2h	2h	58	0.34	-10.74	-26.14	OW

[1] Measured at a concentration of 0.5 g/dL in DMF at 25 °C.

[2] W= White, OW = Off white, Y = Yellow, B = Brown

*Solubility of **PE**s*

Solubility of **PE2a-PE2h** at room temperature has been investigated in various solvents. All polymers were soluble in organic polar solvents such as *N*,*N*-dimethylacetamide (DMAc), DMF, and dimethyl sulfoxide and protic solvents. These polymers were insoluble in solvents such as chloroform, cyclohexane, and water. Higher solubility of **PE**s can be interpreted by the effects of flexible amide and imide groups in polymers side chain.

Thermal properties

The thermal properties of some **PE**s were evaluated by means of thermal gravimetric analysis and differential thermal gravimetric TGA/DTG and differential scanning calorimetry (DSC) techniques in a nitrogen atmosphere at a heating rate of 10 °C/min. The temperature of 5% and 10% weight loss together with char yield at 800 ºC have been calculated by means of thermograms. Figures 4 and 5 show the TGA/DTG thermograms of **PE2a** and **PE2f**. The thermoanalyses data of these polymers are summarized in Table 3. Char yield can be used as criteria for evaluating limiting oxygen index (LOI) of the polymers in accordance with Van Krevelen and Hoftyzer equation [26]. LOI = 17.5 + 0.4 CR where CR = char yield. All of the polymers had LOI values calculated based on their char yield at 800 °C higher than 20. On the basis of LOI values, such macromolecules can be classified as self-extinguishing polymers. T_{10} (°C), char Yield and LOI of these polymers are in the range of 400-420, 9-19, 20-25, respectively. The obtained results showed that spacer containing polymers enjoyed higher thermal stabilities in comparison with no spacer ones [27].The T_gs of the **PE**s were determined by DSC and the results are given in Table 3. The DSC analyses for **PE**s show T_g around 200-240 °C. The above thermal properties were studied for two selected polymers (PE2a and PE2f) as representative, and the others would behave more or less the same.

Tab. 3. Thermal properties of **PE2a** and **PE2f**.

Polymer	Decomposition temperature (°C)		Char yield[c] (%)	T_g [d] (°C)	LOI
	T_5 [a]	T_{10} [b]			
PE2a	390	420	19	238	25.1
PE2f	376	404	9	200	20.3

[a] Temperature at which 5% weight loss was recorded by TGA at a heating rate of 10 °C/min in a nitrogen atmosphere.

[b] Temperature at which 10% weight loss was recorded by TGA at a heating rate of 10 °C/min in a nitrogen atmosphere.

[c] Percentage weight of material left undecomposed after TGA analysis at maximum temperature 800 °C in a nitrogen atmosphere.

[d] Glass-transition temperature recorded at a heating rate of 20 °C/min in a nitrogen atmosphere.

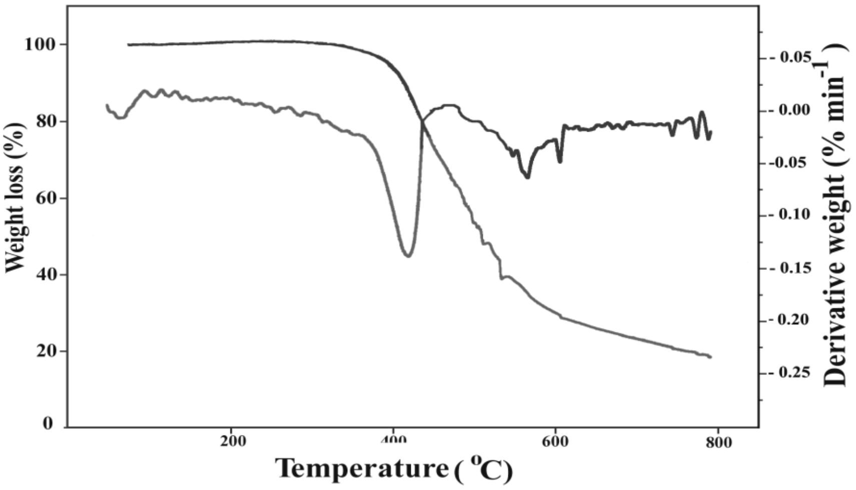


Fig. 4. TGA/DTG thermogram of **PE2a** under a nitrogen atmosphere at a heating rate of 10 °C/min.

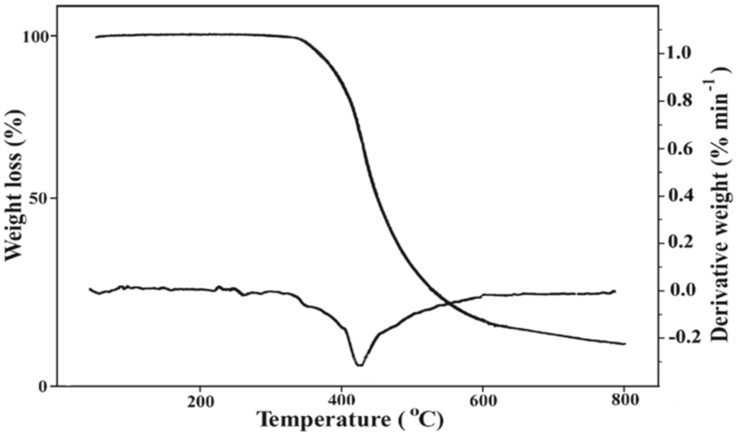


Fig. 5. TGA/DTG thermogram of **PE2f** under a nitrogen atmosphere at a heating rate of 10 °C/min.

Conclusions

In this study, we have successfully synthesized a series of new organosoluble thermally stable optically active aromatic **PE**s by the direct polycondensation from compound **1** with various aromatic diols using TsCl/DMF/Py as a condensing agent. Flexible pendant groups of these polymers disturbed the strong interchain forces and inherent macromolecular rigidity. The results presented herein also clearly demonstrate that incorporating the phthalimide group into the polymer side chain as well as combination of the wholly aromatic backbone and aliphatic pendant group in the presence of several functional groups remarkably enhanced the solubility while maintaining good thermal stability of the new polymers. From the chemical point of view the ester group imparts to the polymer's main chain increased sensibility to hydrolysis that can cause chain breaking.

Experimental

Materials and Equipments

All chemicals were purchased from Fluka chemical CO. (Buchs, Switzerland), Aldrich chemical CO. (Milwaukee, WI). Riedel-deHaen AG (Seelze, Germany) and Merck chemical CO. *p*-aminobenzoic acid and 5-aminoisophthalic acid were recrystallized from H_2O and H_2O/DMF (4/1) mixture, respectively. DMAc and tetrahydrofuran (THF) were dried over BaO, and sodium metal, followed by fractional distillation, respectively. Bisphenol-A was purified by recrystallization from acetic acid-water. The other diols were used as obtained without further purification.

Proton nuclear magnetic resonance (^{1}H-NMR, 500 MHz) spectra were recorded in DMSO-d_6 solution using a Bruker (Germany) Avance 500 instrument at Sharif University of Technology, Tehran, Iran. FT-IR spectra were recorded on a spectrophotometer (Jasco-680, Japan). The spectra of solids were obtained using KBr pellets. The vibrational transition frequencies are reported in wave numbers (cm^{-1}). Band intensities were assigned as weak (w), medium (m), strong (s) and broad (br). Inherent viscosities were measured by using a Cannon-Fenske Routine Viscometer (Germany) at the concentration of 0.5 g/dL at 25 °C. Specific rotations were measured by a Jasco Polarimeter (Japan). TGA data for polymers were taken on a Perkin Elmer instrument in a nitrogen atmosphere at a rate of 10 °C/min, and

DSC data were recorded on a rate of 20 °C at shahreza azad university, Iran. Elemental analyses were performed by the Iran Polymer and Petrochemical Research Institute, Tehran, Iran. Glass transition temperatures (T_g) were read at the middle of the transition in the heat capacity taken from the heating DSC traces.

Polymer synthesis and characterization

The **PE**s were prepared by the following procedure: For synthesis of **PE2a**, a Py (0.20mL, 2.4×10^{-3} mol) solution of TsCl 0.19 g (1.0×10^{-3} mol), after 30 min stirring at room temperature, was treated with DMF 0.07 g (9.57×10^{-4} mol) for 30 min and the resulting solution was added dropwise to a solution of diacid 9, 0.10 g (1.99×10^{-4} mol) in Py (0.50 mL). The mixture was maintained at room temperature for 30 min and then to this mixture, a solution of bisphenol-A (10a) 0.04 g (1.99×10^{-4} mol) in Py (0.20 mL) was added dropwise and the whole solution was stirred at room temperature for 30 min and at 120 °C for 2 h. As the reaction proceeded, the solution became viscous. Then the viscous liquid was precipitated in 15 mL of methanol to give 0.14 g (98%) of **PE2a**. The other **PE**s (**2b-2h**) were prepared by a similar procedure. The structures of some polymers were confirmed as **PE**s with elemental analysis and FT-IR and ^{1}H-NMR spectroscopy techniques. Elemental analysis data of the resulting polymers are listed in Table 4. FT-IR spectra of all polymers indicate the characteristic absorption peaks for the imide ring at 1384 and 720 cm^{-1} because of the symmetrical and asymmetrical carbonyl stretching vibrations. The ^{1}H-NMR spectra of **PE2a** and **PE2f** are given in Figures 6 and 7. The pattern of the spectra is similar to those of monomer **1** and the corresponding diols.

PE2a: white solid; FT-IR (KBr): 3369 (m, br), 2967 (m), 1779 (w), 1716 (s), 1600 (s), 1506 (s), 1450 (m), 1422 (m), 1385 (s), 1337 (m), 1278 (m), 1200 (s), 1169 (s), 1096 (m) 1078 (m), 721 (m) cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 1.61 (d, 3H, CH_3, J = 7.14 Hz), 1.71 (s, 6H, $2CH_3$), 4.98-5.03 (m, 1H, CH), 7.04 (s, 4H, Ar-H), 7.26-7.35 (s, 4H, Ar-H), 7.73 (s, 2H, Ar-H), 7.87-7.95 (d, 4H, Ar-H, J = 8.20 Hz), 8.01 (s, 2H, Ar-H), 8.48 (s, 1H, Ar-H), 8.95-9.02 (s, 1H, Ar-H), 10.19 (s, 1H, N-H), 10.67 (s, 1H, N-H).

PE2b: white solid; FT-IR (KBr): 3400 (m, br), 1779 (m), 1716 (m), 1600 (s), 1507 (s), 1451 (m), 1385 (s), 1338 (m), 1278 (m), 1200 (s), 1169 (m), 721 (m) cm^{-1}.

PE2c: Brown solid; FT-IR (KBr): 3362 (m, br), 1715 (s), 1598 (s), 1527 (s), 1489 (m), 1451 (m), 1423 (m), 1386 (s), 1321 (m), 1293(m), 1192 (s), 1151(s), 1105 (s) 721 (m) cm^{-1}.

PE2d: off white solid; FT-IR (KBr): 3359 (s, br), 2967 (w), 1779 (w), 1716 (s), 1600 (s), 1506 (s), 1451 (m), 1422 (m), 1385 (s), 1337 (s), 1277 (m), 1200 (s), 1169 (s), 1016 (s) 721 (w) cm^{-1}.

PE2e: white solid; FT-IR (KBr): 3328 (m, br), 3068 (m), 1778 (m), 1716 (s), 1600 (s), 1530 (s), 1473 (m), 1449 (m), 1386 (s), 1336 (s), 1184 (s), 1120 (s), 749 (s), 721 (s) cm^{-1}.

PE2f: white solid; FT-IR (KBr): 3360 (s, br), 1714 (s), 1597 (s), 1524 (s), 1489 (w), 1191 (s), 1151 (s), 1105 (s), 720 (w) cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 1.61 (s, 3H, CH_3), 4.98-5.01(m, 1H, CH), 7.59-7.61 (d, 4H, Ar-H, J = 8.15 Hz), 7.65-7.66 (d, 4H, Ar-H, J = 8.15 Hz), 7.91-7.92 (d, 2H, Ar-H, J = 8.20 Hz), 7.98-7.99 (d, 2H, Ar-H, J = 8.20 Hz), 8.01 (s, 2H, Ar-H), 8.15 (s, 2H, Ar-H), 8.41 (s, 1H, Ar-H), 8.95 (s, 2H, Ar-H), 10.19 (s, 1H, N-H), 10.58 (s, 1H, N-H).

PE2g: off white; FT-IR (KBr): 3362 (s, br), 1778 (m), 1714 (s), 1559 (s), 1526 (s), 1486 (s), 1415 (m), 1423 (m), 1386 (s), 1336 (m), 1193 (s), 1163 (m), 1080 (m), 721 (m) cm^{-1}.

PE2h: off white; FT-IR (KBr): 3265 (s, br), 3069 (m), 1778 (m), 1714 (s), 1664(s), 1599 (s), 1386 (s), 1208 (s), 1168 (s), 721 (m) cm^{-1}.

Tab. 4. Elemental Analysis of **PEs 2a** and **2f**.

			Elemental Analysis (%)		
Polymer	Formula		**C**	**H**	**N**
PE2a	$(C_{41}H_{31}N_3O_8)_n$	Calcd.	70.99	4.50	6.06
	$(693.7)_n$	Found	69.45	4.62	5.90
PE2f	$(C_{38}H_{25}N_3O_{10}S)_n$	Calcd.	63.70	3.52	6.87
	$(683.69)_n$	Found	61.82	3.53	5.90

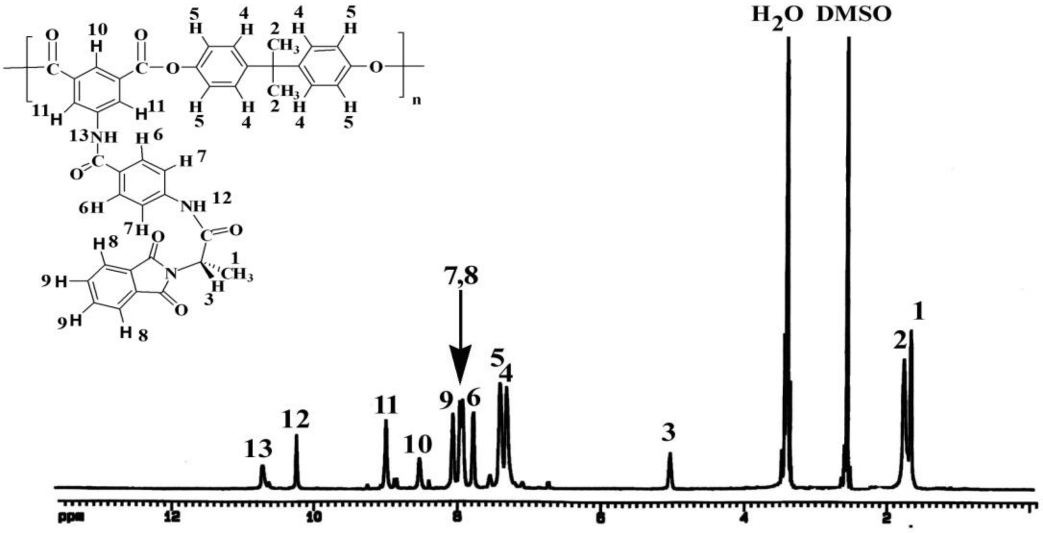


Fig. 6. ^{1}H-NMR (500 MHz) spectrum of **PE2a** in DMSO-d_6 at RT.

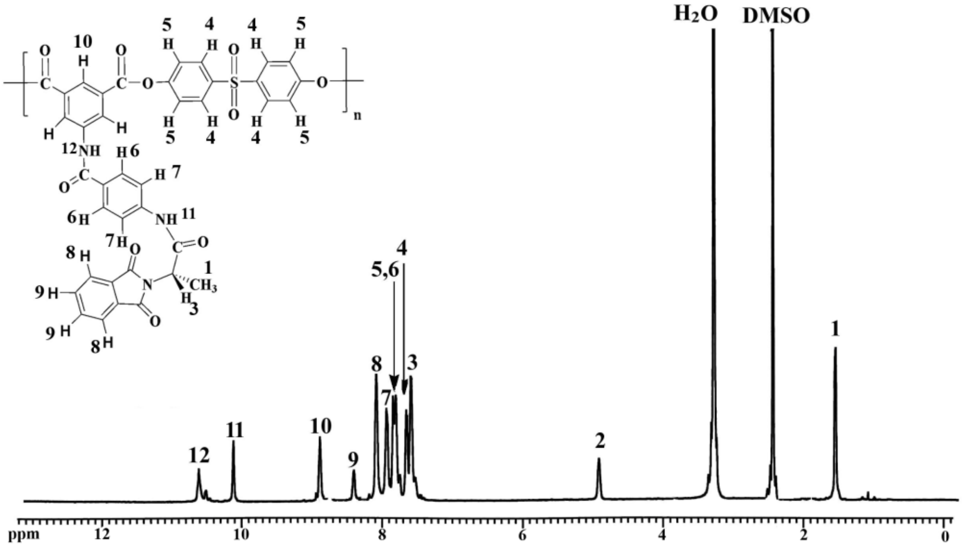


Fig. 7. ^{1}H-NMR (500 MHz) spectrum of **PE2f** in DMSO-d_6 at RT.

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