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ПОЛИКОНДЕНСАЦИЯ

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NOVEL OPTICALLY ACTIVE POLY(AMIDE-IMIDE)S DERIVED FROM *L*-ASPARTIC ACID[1]

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Abstract—2,6-Bis-(2,5-dioxo-tetrahydro-N-(4-carboxyphenyl)pyrrol-3-yl)-pyrrolo[3,4-f]isoindole-1,3,5,7-teraone, a chiral diacid, was prepared from pyromellitic anhydride and *L*-aspartic acid in a three steps reaction pathway. The polycondensation reactions of the monomer with aromatic diamines were carried out in direct condensation reaction conditions. The synthesized poly(amide-imide)s had inherent viscosities in the range of 0.30–0.80 dl/g. Identification of all of the products were performed by conventional analytical techniques such as TLC, IR and ^{1}H NMR/^{13}C MR spectroscopy. Thermoanalytical techniques (TGA/DSC) showed useful levels of thermal stability, associated with relatively high glass transition temperatures and carbonized residues in excess of 40% at 600°C for the synthesized polymers. Amorphous morphology was obtained based on XRD patterns and DSC traces. The polymers were soluble in a variety of polar organic solvents and afforded transparent and relatively flexible to brittle films by solution casting.

INTRODUCTION

Optically active polymers (OAP) are principally synthesized by asymmetric polymerization in chain growth reactions or polycondensation of chiral functional monomers. They have found interesting attention and more applications because of their specific properties related to their special chiral structure [1, 2]. These polymers can establish different interactions with chiral molecules, resulted to applications such as creating chiral media at asymmetric synthesis for increasing stereoselectivity or obtaining stereospecificity [3–5], chiral stationary phase (CSP) or membrane counterparts in chromatographic separations of enantiomers [6–11]. They have also been used as chemosensors or responsive polymers in chiroptical materials [12–16].

Interning amino acid unites as naturally occurring precursors in monomer structure is one of the most important methods for the synthesis of optical active polymers. These building blocks can act both as an auxiliary in creating chirality and also as controlling some higher order conformational structures because of ability to intramolecular hydrogen bonding. In fact, amino acid residues in protein chains have the most important role in constructing their specific conformational structures which responsible for their special properties. It is an exciting challenging to mimic these protein-like abilities in synthetic polymers [17].

Amide and imide functional groups are polar organic units that can create strong dipolar and hydrogen bonding interactions between molecules. So, polyamides and polyimides are classified as chemically and physically stable materials due to many effective inter-chain interactions. The synthesis of polymers containing aliphatic moieties with these hard linkages can modify the properties of desired materials. Polymers derived from amino acids are located in this area. On the other hand, it can be accessed to suitable properties in all polymeric compounds using copolymerization processes. In this case, poly(amide-imide)s are the most interesting polymeric types which combine the structural properties of polyamides (PAs) and polyimides (PIs) such as the relative flexibility and ability to hydrogen bonding of the former compared to the rigid and planer nature of the later [18–20].

In continuing to our researches about optically active polymers [21–23], in the present study, we wish to report the synthesis and characterization of a series of optically active poly(amide-imide)s derived from *L*-aspartic acid. 4-Amino benzoic acid was used in monomer designing because of its aromatic character which is effective in direct polycondensation reactions by triphenylphosphate (TPP) [24]. Transformation of the amino acid as a cyclic and stable imide functionality is another feature of our synthesized monomer. The reactivity of desired compound was evaluated in a model reaction. All of polymerizations were performed using TPP as a condensing agent in the presence of $CaCl_2$ as an improver of polarity of the reaction media for better solubility of the components.

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[1] Статья печатается в представленном авторами виде.

EXPERIMENTAL

Materials and Equipments

The chemicals were purchased from Merck Chemical Co., Fluka Chemical Co., and Aldrich Chemical Co. All materials were purified according to the standard procedures. The reaction solvent, N,N'-Dimethyformamide (DMF) and N-Methylpyrrolidinone (NMP) was stored on 4 Å molecular sieves after drying with CaH_2 and vacuum distillation.

Infrared spectroscopic measurements were performed with a Buck Scientific IR Spectrometer using KBr as the sample diluent. Vibrational transition frequencies are reported in wave number (cm^{-1}). Band intensities are assigned as weak (w), medium (m) and strong (s). Proton and carbon nuclear magnetic resonance (^1H NMR and ^{13}C NMR) spectra were recorded with a Bruker MSL-400 (400 and 100 MHz) NMR spectrometer. Tetramethylsilane (TMS) was used as an internal reference. Multiplicities of proton resonances are designated as singlet (s), multiplet (m) and broad (br). Inherent viscosities were measured by a standard capillary procedure using a Cannon Fenske Routine Viscometer (Germany). The specific rotations ($[\alpha]_D$) were measured on a Kruss automatic digital polarimeter P3002 (Germany) with a sodium lamp as a light source (wavelength = 589 nm) at room temperature. Thermal Gravimetric Analysis (TGA) and Differential Scanning Calorimetric (DSC) data for the polymers were taken on TGA-PYRIS-1 and NETZSCH DSC 200 F3 instruments respectively under nitrogen atmosphere at a heating rate of 10°C/min. Wide angle X-ray diffractions were obtained on thin films with a D500 Siemens diffractometer with a nickel filter, a wavelength of 1.54 Å using copper radiation, a graphite monochromator, and the scanning was between the angles of 5–50 2θ. Elemental analyses were performed on a CHN-O-Rapid FOSS instrument (Elementar, Germany).

Monomer Synthesis

2-[6-(1,2-Dicarboxy-ethyl)-1,3,5,7-tetraoxo-3,5,6,7-tetrahydro-1H-pyrrolo[3,4-f]isoindol-2-yl]-succinic acid (4)

In a round-bottomed flask equipped with a magnetic stirring bar, pyromellitic dianhydride (**1**) 1.000 g, (4.58×10^{-3} mol) and *L*-aspartic acid (**2**) 1.220 g, (9.17×10^{-2} mol) were suspended in 20 ml of the mixture of acetic acid and DMF (6 : 14). The mixture was stirred at room temperature for overnight, and then refluxed for 9 h. The solvent was removed under reduced pressure and the residue was poured into 50 ml of cooled acetone. The white precipitate was filtered off, washed with acetone and vacuum dried to give 2.050 g (quantitative yield) of tetra-acid (**4**). Mp: 245–248°C, dt: >300°C, $[\alpha]_D^{25} = +36.5°$ (0.050 g in 10 ml H_2O). IR(KBr): 3470 (m), 3360 (s, br), 1771 (m), 1720 (s), 1712 (s), 1595 (m), 1516 (m), 1462 (m), 1385 (s), 1305 (m), 1225 (m), 1185 (m), 1110 (m), 978 (w), 910 (m), 865 (m), 720 (m), 630 (m) cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6, TMS): δ 2.77 (dd, 2H, *J* = 5.0 Hz and *J* = 16.3 Hz), 3.55 (dd, 2H, *J* = 9.3 Hz and *J* = = 16.3 Hz), 4.95 (dd, 2H, *J* = 5.0 Hz and *J* = 9.3 Hz), 8.27 (s, 2H), 8.30–8.38 (s, br, 2H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6, TMS): δ 35.14, 49.91, 118.77, 137.69, 166.38, 170.58, 172.69 ppm. Elemental analysis calculated for $C_{18}H_{12}N_2O_{14}$: C, 48.22%; H, 2.68%; N, 6.25%; Found: C, 47.58%; H, 2.12%; N, 5.91%.

2,6-Bis-(2,5-dioxo-tetrahydrofuran-3-yl)-pyrrolo[3,4-f]isoindole-1,3,5,7-teraone (5)

Tetra-acid (**4**) 1.000 g, (2.23×10^{-3} mol) together with 10 ml of acetic anhydride was placed in a round-bottomed flask equipped with a magnetic stirring bar and drying tube. The mixture was stirred at 70°C for overnight, and then the excess of solvent was removed under reduced pressure. Cooled dichloromethane, 100 ml, was added to the residue to precipitate the white compound which was filtered off and vacuum dried to give 0.850 g (93.0%) of dianhydride (**5**). Mp: 216–219°C, $[\alpha]_D^{25} = +42.5°$ (0.050 g in 10 ml DMF). IR(KBr): 3650 (w), 3550 (w), 3110 (m), 3060 (m), 2950 (m), 1810 (s), 1780 (s), 1720 (s), 1490 (m), 1380 (s), 1275 (s), 1250 (s), 1170 (m), 1120 (s), 1000 (m), 910 (s), 860 (m), 700 (w), 645 (m), 635 (m) cm^{-1}.

2,6-Bis-(2,5-dioxo-tetrahydro-N-(4-carboxyphenyl)pyrrol-3-yl)-pyrrolo[3,4-f]isoindole-1,3,5,7-teraone (7)

1.000 g (2.43×10^{-3} mol) of dianhydride (**5**), 0.670 g (4.86×10^{-2} mol) of *p*-amino benzoic acid (**6**) and 15 ml of DMF were placed in a round-bottomed flask equipped with a magnetic stirring bar. The mixture was stirred at 70°C for 6 h, and then 10 fold molar acetic anhydride was added to the reaction mixture together with heating at 90°C for additional 3 h. The reaction mixture was poured into 100 ml of cooled water after concentrating in vacuum. The white precipitate was filtered off, washed well with water and dried in vacuum to give 1.550 g (95.0%) of diacid (**7**). Mp: 250–253°C, dt: >300°C, $[\alpha]_D^{25} = +29.7°$ (0.050 g in 10 ml DMF). IR(KBr): 3650–2560 (s, br), 2950 (m), 2920 (m, sh), 1780 (m), 1720 (s), 1675 (m), 1470 (w), 1380 (s), 1340 (w), 1250 (m), 1190 (m), 1170 (m), 1120 (m), 990 (w), 930 (w), 860 (m), 720 (m), 630 (w) cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6, TMS): δ 3.22 (dd, 2H, *J* = 5.0 Hz and *J* = 18.4 Hz), 3.34 (dd, 2H, *J* = = 9.6 Hz and *J* = 18.3 Hz), 5.54 (dd, 2H, *J* = 5.0 Hz and *J* = 9.6 Hz), 7.46 (d, 4H, *J* = 8.5 Hz), 8.11 (d, 4H, *J* = 8.5 Hz), 8.39 (s, 2H) ppm. ^{13}C MR (100 MHz, DMSO-d_6, TMS): δ 33.48, 47.43, 118.32, 126.63, 130.10, 135.50, 136.78, 139.55, 165.17, 166.51, 172.70, 173.47 ppm. Elemental analysis calculated for

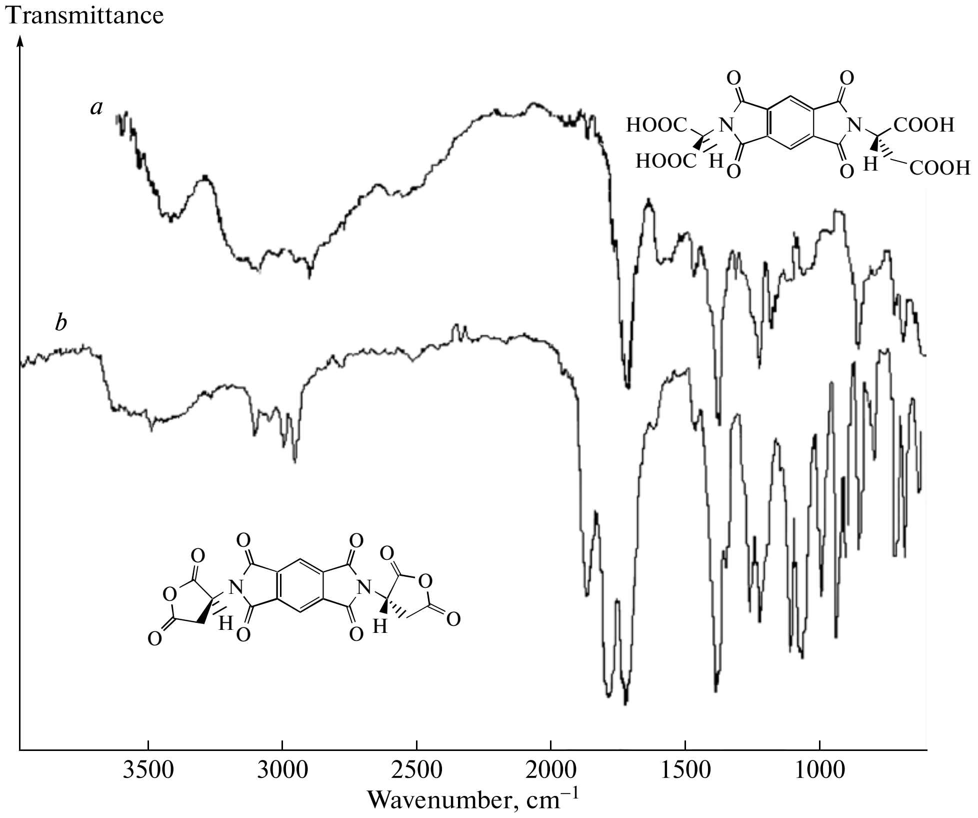


Fig. 1. IR (KBr) spectra of (*a*) tetra-acid (**4**), (*b*) dianhydride (**5**).

$C_{32}H_{18}N_4O_{12}$: C, 59.08%; H 2.79%; N, 8.61%; Found: C, 58.12%; H, 2.12%; N, 8.06%.

Model Reaction

A mixture of 0.270 g (4.15 × 10^{-4} mol) of diacid compound (**7**), 0.089 g (8.30 × 10^{-4} mol) of *p*-toluidine (**8**), 0.25 ml (9.60 × 10^{-4} mol) of triphenyl phosphite (TPP) and 0.035 g of $CaCl_2$ was placed in a round-bottomed flask equipped with a magnetic stirrer and a moisture protected condenser. NMP, 4.00 ml, together with 0.50 ml of pyridine was added to the reaction mixture and then was heated at 110°C for 5 h. The reaction mixture was worked up by pouring into 50 ml of methanol. The precipitate was filtered off, washed well with non-solvent and water. Model compound (**9**) was obtained after drying under vacuum (0.320 g, 93.0%). Dt: >300°C, $[\alpha]_D^{25}$ +32.4° (0.050 g in 10 ml DMF). IR(KBr): 3330 (m), 3079 (w), 2955 (w), 1775 (m), 1725 (s), 1651 (s), 1600 (m), 1515 (s), 1380 (s), 1320 (m), 1200 (m), 1180 (m), 1160 (m), 930 (w), 845 (w), 816 (m), 720 (m), 700 (m) cm^{-1}. Elemental analysis calculated for $C_{46}H_{32}N_6O_{10}$: C, 48.22%; H 2.68%; N, 6.25%; Found: C, 47.52%; H, 2.90%; N, 6.05%.

Polymer Synthesis

The polycondensation reactions were evaluated to optimize the reaction parameters. Typical procedure is as follows: a mixture of 0.500 g (7.69 × 10^{-4} mol) of diacid (**7**), 0.154 g (7.69 × 10^{-4} mol) of diamine (**10a**), 0.50 ml (1.91 × 10^{-3} mol) of TPP, 0.175 g of $CaCl_2$, 6.00 ml of NMP and 0.60 ml of pyridine was heated with stirring at 100°C for 6 h. The reaction mixture was worked up by pouring the viscose product into 100 ml of methanol with constant stirring, producing a stringy precipitate that was filtered off, washed thoroughly with non-solvent and water. The polymeric product **(PAI11a)** was obtained after drying under vacuum for 5 h (0.580 g, 94.0%, $[\alpha]_D^{25}$ = +26.8°, 0.050 g in 10 ml DMF). The inherent viscosity of the poly(amide-imide) was 0.52 dl/g, measured at concentration of 0.5 g/dl in DMF at 25°C. The other poly(amide-imide)s were prepared in the optimized conditions obtained for **PAI11a**.

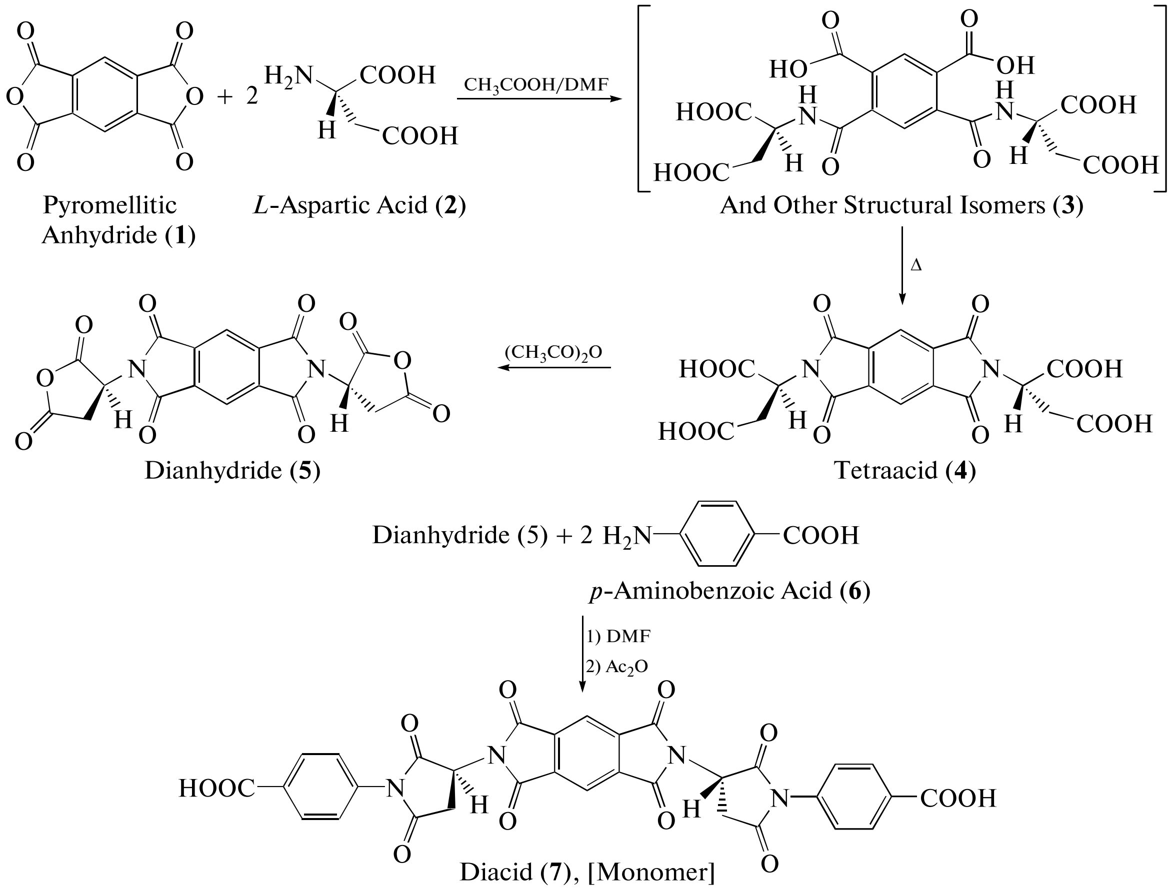
Preparation of Polymer Films

A solution of 0.20 g of the polymer in 2 ml of DMF was made to afford an approximate 10 wt% solution. After the polymer was dissolved completely, the solution was poured into a petri dish, which was placed in ambient temperature overnight and then at 50°C vacuum oven to remove the most of solvent. The semi-dried polymer film was stripped off from the glass surface by immersing in water and then further dried in a vacuum oven at 100°C for 8 h. The obtained films had about 0.08 mm in thickness and were used for X-ray diffraction measurements, solubility tests and thermal analysis.

RESULTS AND DISCUSSION

Monomer Synthesis

Compound (**7**) as a diacid monomer was prepared by a three-step reaction pathway as shown in Scheme 1. Pyromellitic anhydride (**1**) was reacted with two equimolar of *L*-Aspartic acid to produce tetra-acid (**4**) after exerting dehydration conditions. According to our earlier works [21–23], the reaction was investigated in different solvents, such as HOAc, HOAc/Py, Toluene/TEA, DMF, and HOAc/DMF under heating. The best result achieved in the later case. The amic-acid intermediate, a mixture of three structural isomers, (**3**) was converted to tetra-acid (**4**) without isolation.



Scheme 1

In the next step, the last compound was dehydrated to dianhydride (**5**) using acetic anhydride as a suitable dehydrating agent and then the monomer (**7**) was produced upon the reaction of compound (**5**) with *p*-aminobenzoic acid. The following of the second reaction by TLC technique was difficult, because of the low solubility of the reactants. So, the traditional infrared spectroscopy was confirmed us the conversion of tetra-acid to dianhydride (**5**).

The chemical structure, purity and optical activity of all resulting compounds were approved using IR, NMR spectroscopy, optical rotation measurement and elemental analysis techniques. The IR spectrum of compound (**4**), Fig. 1a, depicts the characteristic peaks of imidic functions at 1718 and 1770 cm^{-1} for carbonyl stretching's and at 1380 and 720 cm^{-1} for imide ring vibrations. Carboxyl groups showed a broad and strong peak in the range of 3360–2440 cm^{-1}.

The ^{1}H MR (400 MHz) spectrum of tetra-acid (**4**) has the expected pattern. The compound has a C_2

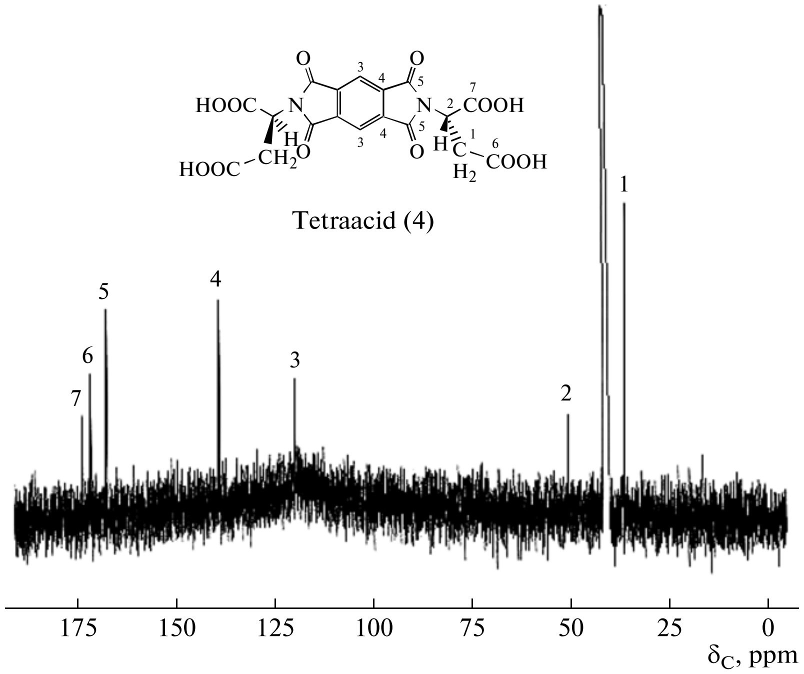
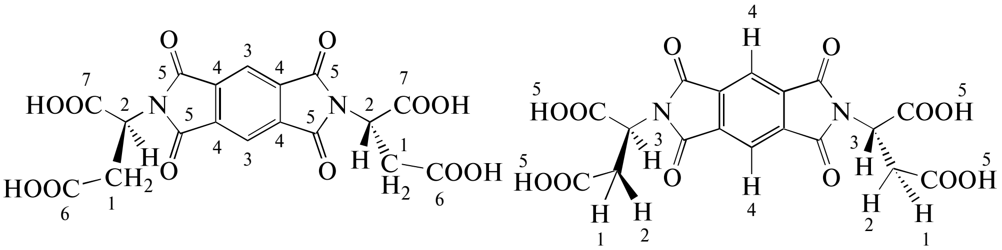


Fig. 2. ^{13}C NMR (DMSO-d_6 100 MHz) spectrum of tetra-acid (**4**).

symmetry axis which simplifies the appearance of the spectrum. There is a clear diastereotopic relation between the methylene hydrogens (**1** and **2**) which results to a geminal coupling. So we see a doublet of doublet pattern for each of the desired hydrogens. In ^{13}C NMR spectrum (100 MHz) of the compound, Fig. 2, it is identified seven distinct peaks for seven types of carbon atoms. It is noted that only one signal is observed for all imide carbonyl groups. Apparently, chirality has not affected the chemical shift of carbonyl carbons. Descriptions for NMR assignments are shown in Scheme 2.



Scheme 2

The disappearance of strong-broad carboxylic acid hydroxyl peak and appearance of new peaks in carbonyl absorption area, 1780–1720 cm^{-1}, in the IR spectrum of dianhydride (**5**), Fig. 1b, confirmed a complete conversion of tetra-acid (**4**) to the product.

Finely compound (**7**) could be recognized using its infrared and NMR spectra. In the ^{1}H MR (400 MHz) and ^{13}C MR (100 MHz) spectra we can see the similar pattern of couplings relative to the spectrum of tetra-acid (**4**). Figure 3 illustrates the ^{1}H MR spectrum of diacid monomer. It should be noted that the signals of diastereotopic hydrogens, H_1 and H_2, appear as doublet of doublet included in water signal.

In order to elucidate the retention of chirality in reaction conditions, polarimetric measurements were utilized which showed optical rotation in all three synthesized compounds **4**, **5**, and **7**.

Model Reaction

A model reaction, Scheme 3, between monomer and *p*-toluidine (**8**) was conducted to investigate the reactivity of desired compound as a monomer toward aromatic amines in polycondensation reaction conditions. The model compound (**9**) can be used as a reference for structural characterization of corresponding

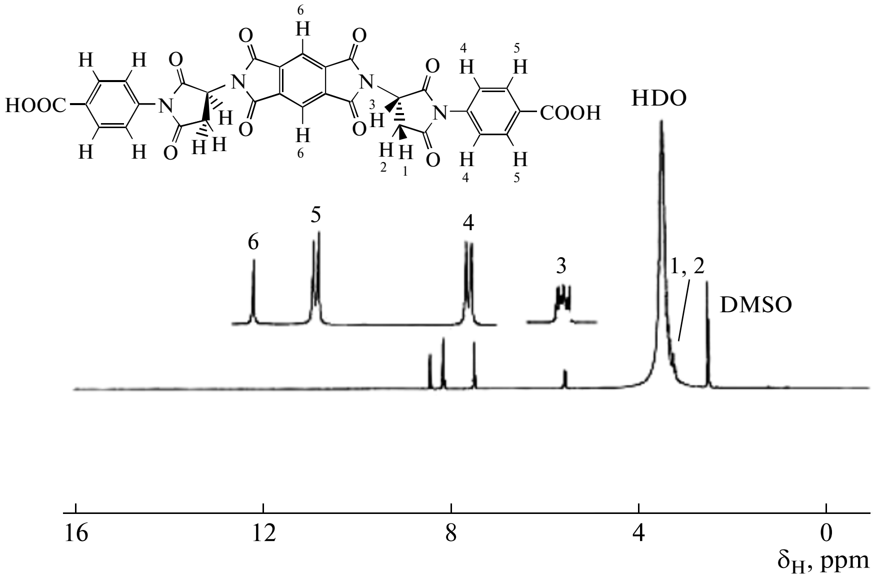
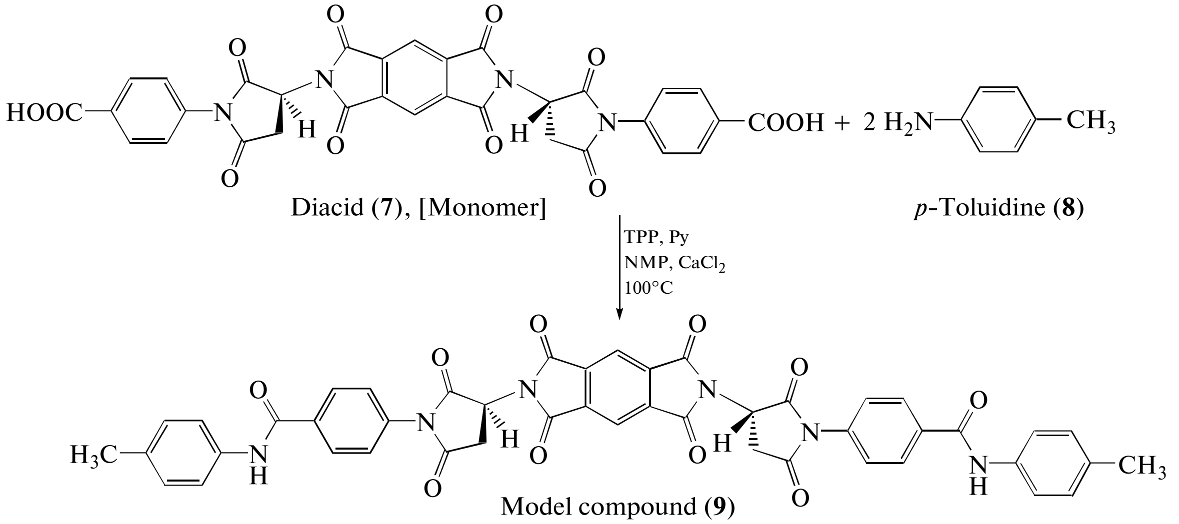


Fig. 3. ^{1}H MR (DMSO-d_6 400 MHz) spectrum of monomer (**7**).

polymers and illustration of retention of chirality under polymerization conditions. Characterization of model product was achieved by TLC technique, IR and optical rotation measurements.


Diacid (**7**), [Monomer]

p-Toluidine (**8**)

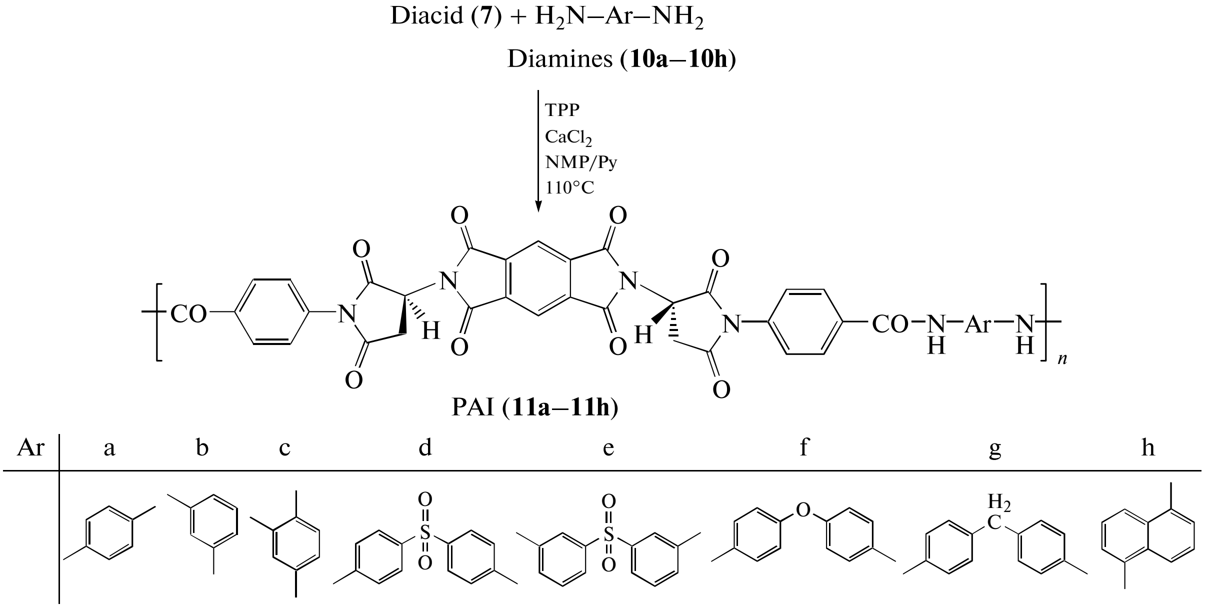
Model compound (**9**)

Scheme 3

The appearance of a relatively sharp peak at 3330 cm^{-1} due to amide band together with disappearance of carboxylic hydrogen bonding peak clearly confirmed the formation of the model compound. It possessed optical rotation, demonstrated the retention of chirality under the reaction conditions. Model reaction was performed to optimize the process conditions for high yield, low reaction time and temperature without over heating.

Polycondensation Reactions

Based on the results of the model reaction, a typical polycondensation was performed under phosphorylation reaction conditions of an equimolar mixture of diacid monomer (**7**) and aromatic diamine (**10a**), Scheme 4.



Scheme 4

Inorganic salts such as $CaCl_2$ and LiCl improve the polarity of the reaction solvent and solubility of macromolecules, needed to continuing chain growth. The polymerization reactions proceeded homogenously and transparent as a viscose solution, and the resulting products were isolated as stringy or powder form.

Table 1 represents the results of some polymerizations performed with different reaction parameters for PAI-**11a**. Good yield and viscosity as criterions of polymer growing have obtained for 10% (w/v). In long reaction time or at high temperature, the obtained products showed low solubility in polar organic solvents such as DMF, DMAc or their 5% $CaCl_2$ solutions.

Some of the physical properties of all synthesized PAIs associated with polycondensation yields are shown in Table 2.

Polymer Characterization

Characterizing the amide formation in the polycondensation process was performed by means of IR spectroscopy. The most distinctive features of the infrared spectra of all polymers are the characteristic bands of amide groups appeared around 3350 cm^{-1} (N–H), an overlapped peak at 1700 cm^{-1} (C=O stret.) and NH bending frequency at 1590 cm^{-1}, which are apparently demonstrated from the IR spectra of model compound (**9**). All of other absorption peaks were those expected for imide ring and other functional groups. Figure 4 shows a typical IR spectrum. On the other hand, elemental analysis values of the resulting PAIs showed a little inconsistency between the calculated and found data. This may be due to the moisture and solvent intakes in the hydrophilic PAIs, which is identified in their thermograms.

Optical rotation measurements of the synthesized PAIs in DMF using D-line of sodium lamp clarified

Table 1. Reaction results for PAI-**11a** synthesis in different reaction conditions

No	Solvent Volume[a], ml	Time, h	T, °C	Yield, %	η_{inh}[b], dl/g
1	0.5 (20)	6	100	85.6	0.25
2	1.0 (10)	6	100	94.0	0.52
3	1.5 (6.7)	6	100	86.4	0.40
4	1.0 (10)	6	115	90.4	–[c]
5	1.0 (10)	6	135	92.0	–[c]
6	1.0 (10)	4	100	86.4	0.40
7	1.0 (10)	4	120	88.0	0.47

[a] Numbers in parentheses are monomer concentration (w/v).
[b] Measured at a concentration of 0.5 g/dl in DMF at 25°C.
[c] Partially-soluble in DMF, DMAc or their 5% $CaCl_2$ solutions.

Table 2. Reaction results and some physical properties of PAIs(**11a–11h**)

Polymer Code	Yield, %	η_{inh}[a], dl/g	T_D[b], °C	Film[c]	$[\alpha]_D^{25}$	Characteristic IR absorptions, cm^{-1}
PAI-**11a**	94.0	0.52	323	No shattered, Flexible	–26.8	3380 (m), 3360 (s), 1798 (m), 1720 (s), 1659 (s), 1599 (m), 1490 (s), 1370 (s), 1213 (s), 1104 (m), 827 (m), 742 (m)
PAI-**11b**	98.0	0.80	340	No shattered, Flexible	–35.2	3382 (m), 3355 (s), 1780 (m), 1717 (s), 1662 (s), 1600 (m), 1495 (s), 1435 (m), 1376 (s), 1155 (s), 1100 (m), 725 (s)
PAI-**11c**	91.0	0.60	305	Shattered, Flexible	–41.4	3375 (m), 3320 (s), 1780 (m), 1722 (s), 1690 (s), 1510 (m), 1500 (m), 1470 (m), 1375 (s), 1310 (m), 1180 (m)
PAI-**11d**	93.0	0.40	298	Shattered, Brittle	–37.2	3370 (m), 3320 (s), 1784 (m), 1720 (s), 1693 (s), 1520 (s), 1450 (m), 1374 (s), 1300 (m), 1101 (m), 766 (m)
PAI-**11e**	95.0	0.53	310	Shattered, Flexible	–31.8	3387 (m), 3350 (s), 1777 (m), 1720 (s), 1684 (s), 1590 (s), 1520 (s), 1450 (m), 1380 (s), 1320 (m), 1295 (m), 1100 (m)
PAI-**11f**	92.0	0.34	300	Shattered, Brittle	–31.6	3381 (m), 3350 (s), 1764 (m), 1715 (s), 1685 (s), 1587 (s), 1505 (s), 1496 (s), 1359 (s), 1320 (s), 1143 (s), 1107 (s)
PAI-**11g**	94.0	0.30	292	Shattered, Brittle	–40.0	3385 (m), 3345 (s), 1770 (m), 1720 (s), 1695 (s), 1580 (s), 1500 (s), 1490 (s), 1355 (s), 1323 (s), 1150 (s), 1100 (s)
PAI-**11h**	0.40	0.40	288	Shattered, Brittle	–23.0	3380 (m), 3350 (s), 1774 (m), 1720 (s), 1685 (s), 1585 (s), 1500 (s), 1495 (s), 1350 (s), 1420 (m), 1243 (m), 1107 (m)

[a] Measured in dimethylformamide (DMF) at a concentration of 0.5 g/dl at 25°C.
[b] Onset decomposition temperature measured by melting point apparatus.
[c] Solution casting film (10% w/v in DMF), ability with or without shattering and quality.

Table 3. Solubility behavior of PAIs(**11a–11h**)

Solvents[a]	PAI-**11a**	PAI-**11b**	PAI-**11c**	PAI-**11d**	PAI-**11e**	PAI-**11f**	PAI-**11g**	PAI-**11h**
DMAc	± (+)	± (+)	± (+)	± (+)	+ (+)	+ (+)	+ (+)	± (+)
DMF	± (+)	± (+)	± (+)	± (+)	+ (+)	+ (+)	+ (+)	± (+)
NMP	+ (+)	+ (+)	+ (+)	+ (+)	+ (+)	+ (+)	+ (+)	+ (+)
DMSO	– (±)	– (±)	– (±)	– (±)	– (±)	± (+)	± (+)	– (±)
THF	– (–)	– (–)	– (–)	– (–)	– (–)	– (–)	– (–)	– (–)
H_2SO_4	+ (+)	+ (+)	+ (+)	+ (+)	+ (+)	+ (+)	+ (+)	+ (+)

[a] Solubility concentration: 5 mg/ml; ±, partially-soluble; –, insoluble; +, soluble; symbol out of parenthesis is at room temperature; symbol into the parenthesis is on heating at 70°C; DMAc, N,N-dimethylacetamide; DMF, N,N-dimethylformamide; DMSO, dimethylsulfoxide; NMP, N-methyl-2-pyrrolidone; THF, tetrahydrofuran.

the optical activity characteristic of the polymers. There is not any meaningful difference between the specific rotations of the model compound and PAIs(**11a–11h**), so there is no probable helix like and stable conformation for the polymers [25, 26].

Polymer Properties

The solubility of poly(amide-imide)s was evaluated in polar organic and traditional solvents which summarized in Table 3. Limited solubility of the **PAI**s is principally due to more polar cyclic imide and hydrogen bonded functionalities in the main chain of polymers associated with rigid structure. This characteristic may be expected to influence the other physical properties such as glass and decomposition temperatures. It seems that they can be used as insoluble membranes in chiral separations.

All of the **PAI**s were cast onto a glass plate, dried in a low humidity air environment at ambient tempera-

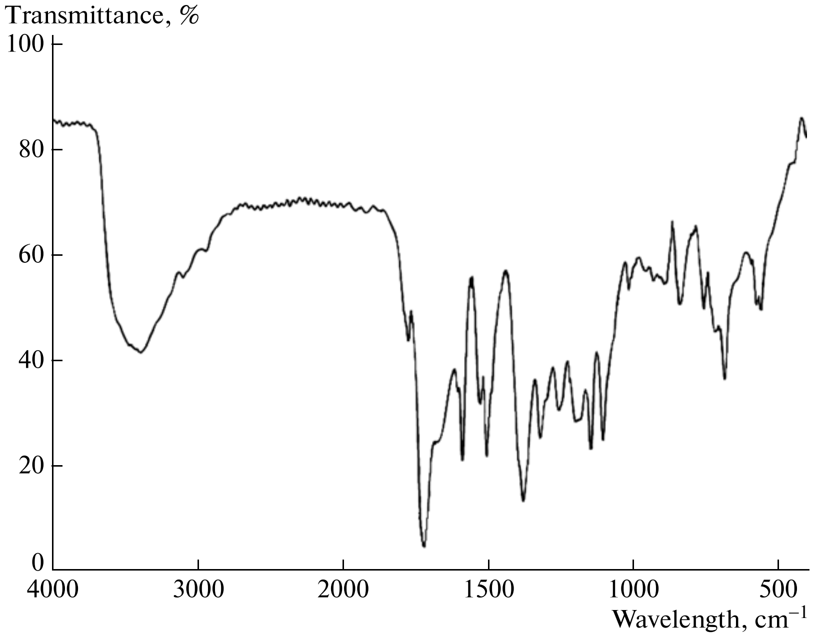


Fig. 4. FT-IR (KBr) spectrum of PAI-**11a**.

ture for 12 h, and then in vacuumed oven at 50°C. The resulting polymer films were transparent and exhibited various degrees of integrity. As presented in Table 2, PAI-**11a** and **11b** showed good film forming ability and film flexibility, but the other films shattered into small flexible or brittle pieces. It seems that the high reactivity of diamines such as **10a**, **10b**, **10c** and **10e** can result to high molecular weight polymers, which together with bond flexibility in the case of the first two diamines results to good film forming properties in the polymers.

The thermal properties of the poly(amide-imide)s were investigated by differential scanning calorimetry and thermogravimetric analysis. The thermograms of PAIs(**11a**, **11b** and **11c**), shown in Figs. 5 and 6, respectively, for DSC and TGA, illustrate the typical behavior exhibited by some of the homologues prepared in this research. DSC measurements were performed as a first heating from room temperature to 200°C for removing the residual of moisture and solvents entrapped in polymer matrix after precipitation and drying [27]. Apparently, the synthesized PAIs retain water and polar organic solvents because of many polar hydrophilic groups. This is appeared as initial weigh loss up to 10% in TGA thermograms. Cooling of heated polymer to room temperature was take placed without any transition representing crystallization or other thermal phenomena. It can be deduced that the glass transition temperature be greater than 200°C. The

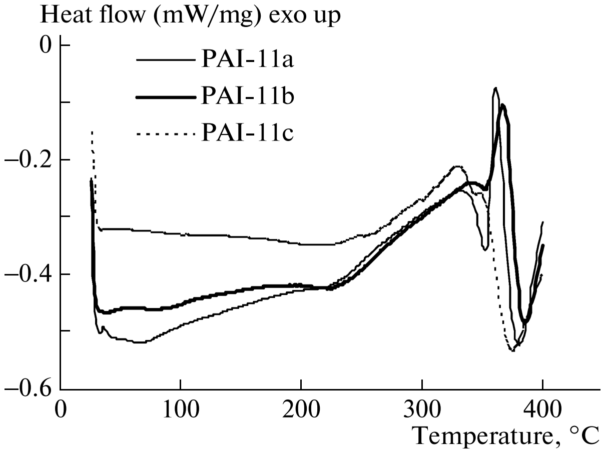


Fig. 5. DSC traces of PAIs-**11a**, **11b** and **11c**.

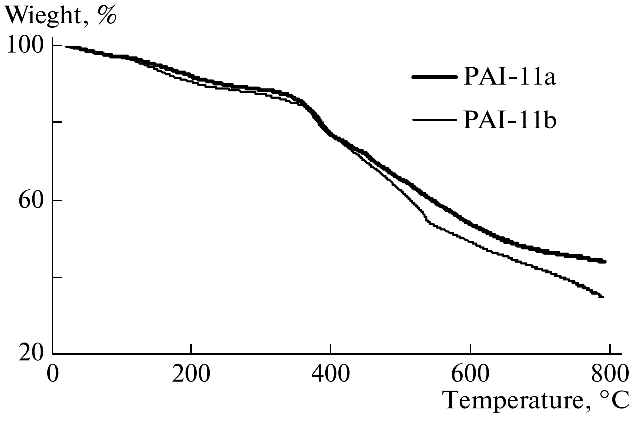


Fig. 6. TGA thermograms of PAIs-**11a** and **11b**.

Table 4. Thermal data of the PAIs-**11a**, **11b** and **11c**

Polymer Code	$T_g{}^a$, °C	$T_C{}^b$, °C	$T_m{}^c$, °C	$T_d{}^d$, °C	$T_d{}^e$, °C	Char Yield[f], %
PAI-**11a**	–	226	352	380	361	46
PAI-**11b**	209	230	355	386	368	42
PAI-**11c**	185	228	345	378	–	–

[a] Glass transition.
[b] Temperature of induced crystallization.
[c] Melting process.
[d] Proposed thermal decomposition all measured by DSC in second heating.
[e] Onset of thermal decomposition temperature at which the weight loss began to dip.
[f] Carbonized residue in 600°C, both gained from TGA.

second heating process has a similar pattern for all polymers. PAI-**11a** do not show detectable second order endotherm related to glass transition, since PAIs-**11b** and **11c** illustrate mild endotherms at 209 and 185°C, respectively. The three polymers reveal a smooth and expand exothermic inflections after softening region, beginning in temperatures 226, 230 and 228°C, respectively, for PAI-**11a**, **11b** and **11c,** due to probable chain reorientations. Following these induced crystallizations, a mild endotherm assigned to melting process was seen in all thermograms. The second endo peak in DSC traces certifies a chemical decomposition which is confirmed by weight lose in TG analysis. The decomposition process promotes smoothly resulted to retaining high carbonized residue at elevated temperatures which can be emanated from aromatic and rigid nature of repeating unites. The values of thermal information for the PAIs are given in Table 4.

The morphology of the synthesized PAIs was investigated by means of X-ray diffraction patterns. The examined polymers showed a broad peak at $2\theta = 19°$, which is the characteristic of diffraction by the amorphous regions of a polymer. The similarity of diffraction patterns and their intensity show similar morphology irrespective to different diamine segments. Probably, the structural unit of the synthesized diacid monomer is the principle controlling segment of the polymer structure. The similarity of thermograms in view of transition and decomposition temperatures can be a confirming evidence for this description.

The similar pattern of thermal and diffraction properties of the treated poly(amide-imide)s together with film forming ability illustrate the structure property relationship. The aliphatic and soft segments of the PAIs are the major constituent of the polymer chains, so are determinant in thermal stability and amorphous structure of the polymers. On the other hand, it seems that active diamines specially **10a** and **10b** can result to high molecular weight polycondensation which may be a controlling factor in film flexibility or brittleness [28]. A well distinguished and sensibly clear T_g was not observed in DSC thermograms, we proposed this uncertainty because of entrapped solvent in polymer matrix. It can cause to chain separation which after first scanning to the temperature lower than required to segmental motion, remains unchanged and so a distinguished transition is not observed.

CONCLUSIONS

A series of novel optically active aromatic poly(amide-imide)s containing *L*-aspartic acid residue were synthesized using triphenylphosphite as the activating agent in direct solution polycondensation. Relative reactivity of the synthesized diacid monomer toward amines was examined in a model reaction. The polycondensation reactions had high yield produced poly(amide-imide)s with inherent viscosities in the range of 0.30–0.80 dl/g and optical rotations in the range of –23°...–41.4°. In order to rationalize the structure-property relationships, film forming capability together with thermal and morphological properties of the polymers were evaluated. Films cast from DMF for PAIs-**11a**, **11b**, **11c** and **11e** were flexible without shattering for the first two whereas the others break to brittle pieces. All of the considered PAIs exhibited a mild glass transition, chain crystallization, melt and decomposition processes in the second DSC scans and hold high carbonized residue in the TG analysis. Wide-angle X-ray measurements showed the PAIs are amorphous.

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