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SYNTHESIS AND CHARACTERIZATION OF NEW THERMALLY STABLE POLY(AMIDE-IMIDE)S BASED ON BICYCLO[2,2,2]OCT-7-ENE-2,3,5,6-TETRACARBOXYLIC DIIMIDE AND AROMATIC DIAMINES[1]

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Abstract—N,N'-*bis*-(4-carboxyphenyl)bicyclo[2,2,2]oct-7-ene-2,3,5,6-tetracarboxylic diimide was prepared by reaction of bicyclo[2,2,2]oct-7-ene-2,3,5,6-tetra carboxylic dianhydride with *p*-aminobenzoic acid in a mixture of acetic acid and pyridine (3 : 2). Polycondensation of N,N'-*bis*-(4-carboxyphenyl)bicyclo[2,2,2]oct-7-ene-2,3,5,6-tetracarboxylic diimide with six different aromatic diamines produced a series of new poly(amide-imide)s (PAIs) in high yields with inherent viscosities between 0.49–0.95 dl/g. All PAIs were characterized by means of elemental analysis, viscosity measurement, solubility test, FTIR spectroscopy and ^{1}H-NMR spectroscopy. Dynamic TGA of PAIs shows 10% weight loss temperatures from 410 to 435°C under nitrogen.

INTRODUCTION

Polyimide are one of the most important class of thermally stable polymers [1, 2], which are well known for their high-performance properties but have one major disadvantage of typically being insoluble and unprocessable after conversion from the poly(amic acid) to the polyimide form. Replacement of polyimides by poly(amide-imide)s (PAIs) may be useful in modifying the intractable nature of polyimides [3, 4]. PAIs contain both amide and cyclic imide units along the polymer chain and hence constitute a polymer class with average properties between polyamides and polyimides. These class polymers seem to provide a favorable balance between processability and performance. On the other hand, polyimides derived from an alicyclic dianhydride, i.e., bicyclo[2,2,2]oct-7-ene-2,3,5,6-tetracarboxylic diimide, also offer solubility in organic solvents [5–11]. Alicyclic poly(amide-imide)s from bicyclo[2,2,2]oct-7-ene-2,3,5,6-tetracarboxylic acid dianhydride had been studied by Sumio and the coworkers [12]. These polyimides were soluble in organic solvents such as N-MP and DMF. Chun [13] reported the organosoluble optically transparent polyimides based on bicyclo segment. The results showed that the polyimides had thermal decomposition temperatures of 450°C in inert atmosphere.

PAIs usually have been synthesized through the three main routes. The first route goes through the amide-imide-forming reaction, by which trimellitic anhydride (TMA) react either with diisocyanate to produce poly(amide-imide) [14] or with thionyl chloride to synthesized TMA-chloride before the latter and diamine can produce poly(amide-imide) [15]. The second route goes through the imide-forming reaction, with amide-containing monomer diamine is polycondensed with dianhydride to provide the poly(amide-aminoacid), which is then dehydrated to obtain poly(amide-imide) [16–17]. The last route goes through the amide-forming reaction from imide-containing monomers such as dicarboxylic acids or diamines. Imide-containing dicarboxylic acids usually come from the thermal imidization products reaction of diamines and excess of TMA [18–26], from the condensation of dicarboxylic anhydride and amino acids [27, 28], or from the dehydration of aromatic amino acids and TMA [29–31]. Then, these resultant imide-containing dicarboxylic acids react with aromatic diamines to synthesize aromatic poly(amide-imide)s by polycondensation.

In this article, we describe synthesis and characterization a series of new polyamides **5a**–**f** containing rigid segments bicyclo[2,2,2]oct-7-ene-2,3,5,6-tetracarboxylic diimide in the main chain from the direct polycondensation of N,N'-*bis*-(4-carboxyphenyl)bicyclo[2,2,2]oct-7-ene-2,3,5,6-tetracarboxylic diimide **3** with six aromatic diamines such as 4,4′-diaminodiphenylether (**4a**), 4,4'-diaminodiphenylsulfone (**4b**), 3,3'-diaminodiphenylsulfone (**4c**), 1,4-diaminobenzene (**4d**), 1,5-diaminonaphthalene (**4e**), 2,6-diamino-6-chloropyrimidine (**4f**), in a medium consisting of N-methyl-2-pyrrolidone (N-MP), triphenyl phosphite (TPP), calcium chloride ($CaCl_2$) and pyridine (Py).

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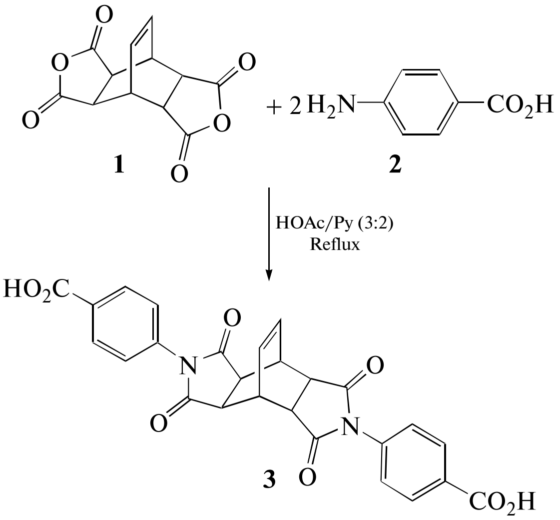
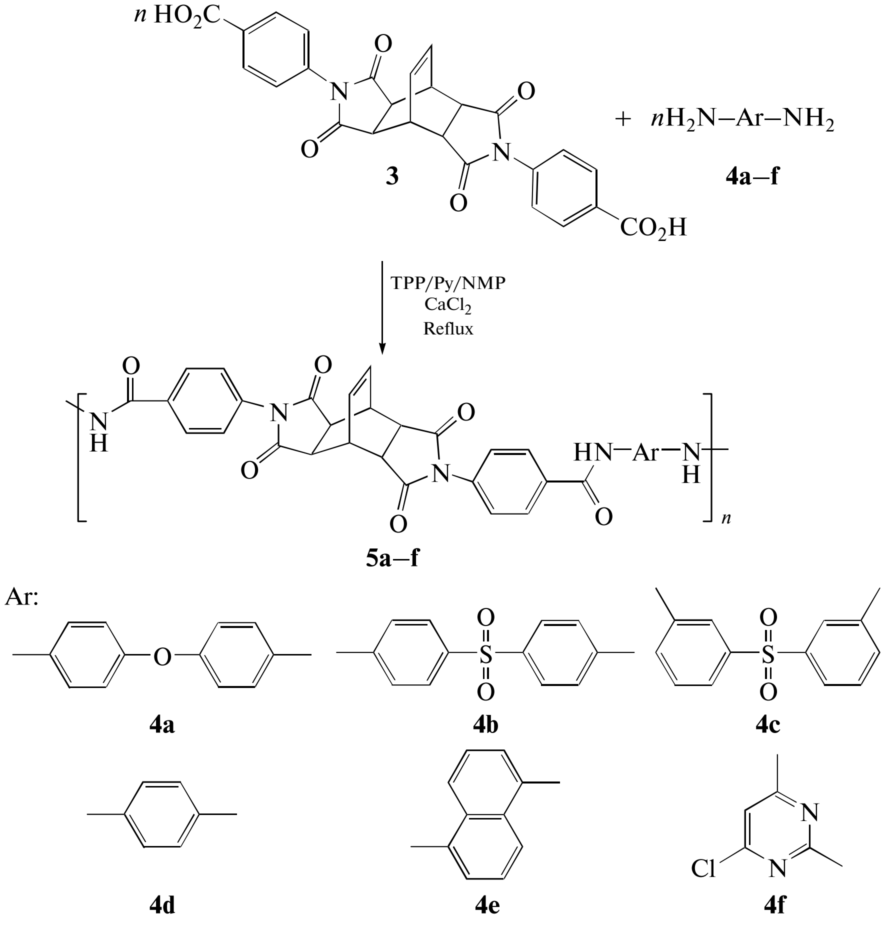
[1] Статья печатается в представленном авторами виде.



Scheme 1. Synthesis route of diacid **3**.



Scheme 2. Synthesis of poly(amide-imide)s **5a–f**.

EXPERIMENTAL

Materials

Bicyclo[2,2,2]oct-7-ene-2,3,5,6-tetracarboxylic dianhydride **1** (from Aldrich), diamins **4a–4f** and *p*-aminobenzoic acid **2** (from Merck) were used without previous purification. Solvents were used as received. Commercially available calcium chloride (from Merck) was dried under vacuum at 150°C for 6 h.

Techniques

^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Bruker 300 MHz instrument (Germany). Fourier transform infrared (FTIR) spectra were recorded on Galaxy series FTIR 5000 spectrophotometer (England). Spectra of solid were performed by using KBr pellets. Band intensities were assigned as weak (w), medium (m), shoulder (sh), strong (s) and broad (br). Inherent viscosities were measured by a standard procedure by using a Technico Regd Trad Mark Viscometer. Thermal Gravimetric Analysis (TGA and DTG) data for polymers were taken on a Mettler TA4000 System under N_2 atmosphere at rate of 10 grad/min and differential scanning calorimeter (DSC) was conducted with a DSC Metller 110 (Switzerland) at a heating and heating rate of 10 grad/min in a nitrogen atmosphere. Elemental analyses were performed were performed by Vario EL equipment by Arak University.

Monomer Synthesis

Into a 250-ml, round-bottom flask, 1 g (4.03 mmol) of bicyclo[2,2,2]oct-7-ene-2,3,5,6-tetra carboxylic dianhydride **1**, 1.1 g (8.06 mmol) of *p*-aminobenzoic acid **2**, 80 ml of a mixture of acetic acid and pyridine (3 : 2) and a stirring bar were placed. The mixture was stirred at room temperature overnight and then was refluxed for 4 h. After this time the solvent was removed under reduced pressure, and the residue was dissolved in 100 ml of cold water; then, 5 ml of concentrated HCl was added. The solution was stirred until a white precipitate was formed, and then the precipitate was filtered off and purified by recrystallization from DMF–H_2O solution and dried in vacuum to give 1.76 g (90.2%) of compound **3**: $T_m > 380°C$, FT-IR(KBr), cm^{-1}: 2500–3400 (m, br), 1782 (w, sh), 1722 (s, br), 1606 (s), 1514 (m), 1427 (s), 1371 (s, br), 1284 (s, sh), 1176 (s, sh), 929 (m), 858 (m), 798 (m), 765 (m), 717 (m), 690 (w), 590 (w), 555 (w, sh), 503 (w). ^1H-NMR (300 MHz, DMSO-d_6, TMS): δ_H: 13.17 (br, 2H), 8.05 (d, 4H, $J = 8.4$ Hz), 7.33 (d, 4H, $J = 8.4$ Hz), 6.34 (t, 2H), 3.58 (s, 2H), 3.46 (s, 4H) ppm. ^{13}C-NMR (300 MHz, DMSO-d_6): δ_C: 176.87, 167.08, 136.24, 131.59, 131.072, 130.43, 127.22, 43.01, 34.49 ppm. Calc. for $C_{26}H_{18}N_2O_8$, %: C, 64.19; H, 3.70; N, 5.76; found, %: C, 64.02; H, 3.58; N, 5.68.

Polymer Synthesis

As a typical example, PAI **5a** was prepared as follows. Into a 50 ml round-bottom flask, 0.158 g (0.326 mmol) diimide-diacid **3**, 0.065 g (0.326 mmol) of 4,4'-diamino diphenyl ether **4a**, 0.5 g of calcium chloride, 1 ml of N-MP, 0.8 ml of triphenyl phophite and 0.3 ml of pyridine and a stirring bar were placed. The mixture was stirred at room temperature for 2 h and then was heated with stirring at 120–130°C for 8 h. At the end of the reaction, for quench growth polymer solution was slowly trickled in to stirred methanol, giving rise to a stringy precipitate, which was washed thoroughly with hot methanol, collectedly filtration and dried at 80°C for 12 h under vacuum to leave 0.20 g (94%) of solid polymer **5a**.

RESULTS AND DISCUSSION

Monomer Synthesis

N,N'-*Bis*-(4-carboxyphenyl)bicyclo[2,2,2]oct-7-ene-2,3,5,6-tetracarboxylic diimide **3** was prepared in one-step as shown in Scheme 1. The chemical structure and purities of diimide-diacid **3** were also analyzed by elemental analysis, ^1H-NMR, ^{13}C-NMR and FTIR spectroscopy.

The measured results in elemental analyses closely corresponded to the calculated ones, demonstrating that the expected compound was obtained. Figure 1a displays FTIR spectrum of diimide-diacid **3**. Peaks appearing at 2500–3400 cm^{-1} (acid O–H stretching), 1782 (imide, asymmetric C=O stretching), 1722 cm^{-1} a broad peak (acid C=O and symmetric imide stretching), 1606 cm^{-1} (C=C), 1371 and 798 cm^{-1} (imide characteristic ring vibration) confirmed the presence of imide ring and carboxylic groups in this compound. The ^1H-NMR spectrum of diimide-diacid **3** showed in Fig. 1b. The protons H(a) relevant to O–H carboxylic groups and protons H(b) and H(c) relevant to aromatic protons. H(d) protons relevant to bicyclic olefin in compound **3**. The ^{13}C-NMR spectrum of diimide-diacid **3** showed 9 signals, including C(a) and C(b) in carbonyl imide ring and carboxylic acid and 4 signals of carbon atoms at 127–131 ppm relevant to aromatic rings (Fig. 1c). This peaks in ^{13}C-NMR spectrum along with elemental analyses data confirmed the proposal structure of compound **3**.

Polymer Synthesis

The direct polycondensation of a dicarboxylic acid and diamine is one of the well-known methods for PAI synthesis. In this article, we synthesized PAIs **5a–f** by direct polycondensation reactions of an equimolar mixture of monomer **3** with six different derivative of aromatic diamines **4a–f** in a medium consisting of N-methyl-2-pyrrolidone (N-MP), triphenyl phosphite (TPP), calcium chloride ($CaCl_2$) and pyridine (Py), as shown in Scheme 2.

The yield and some physical properties of these new PAIs **5a–f** are given in Table 1. The entire polycondensation reaction readily proceeds in a homogeneous solution, tough and stringy precipitates formed when the viscous PAIs solution was obtained in good yields. Also the resulting polymers have a range of color between white and pale yellow.

Polymer Characterization

The structure of polymers was confirmed as PAIs by means of FTIR spectroscopy and elemental analy-

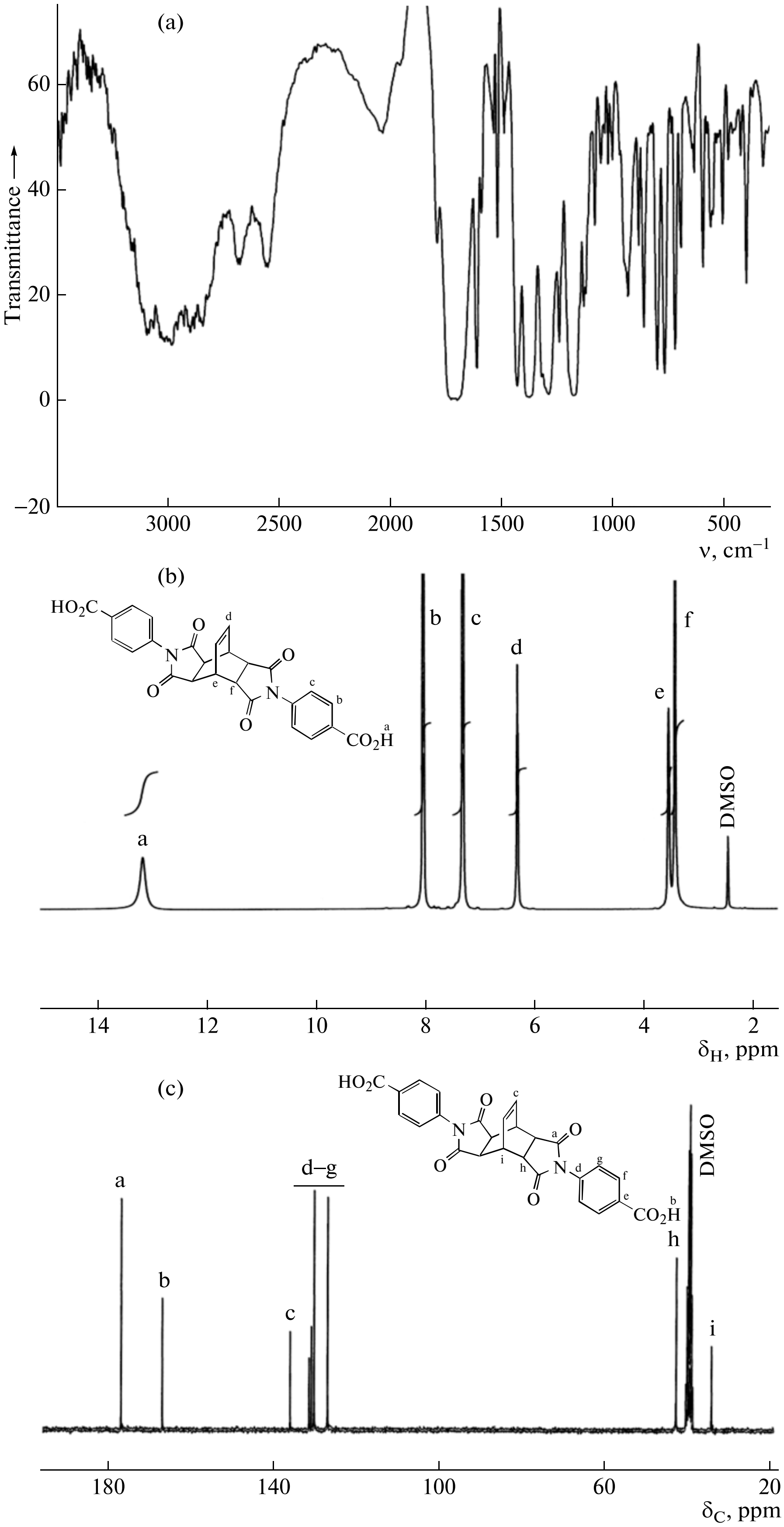


Fig. 1. FTIR (a), ^{1}H-NMR (b) and ^{13}C-NMR (c) spectra of diimide-diacid **3**.

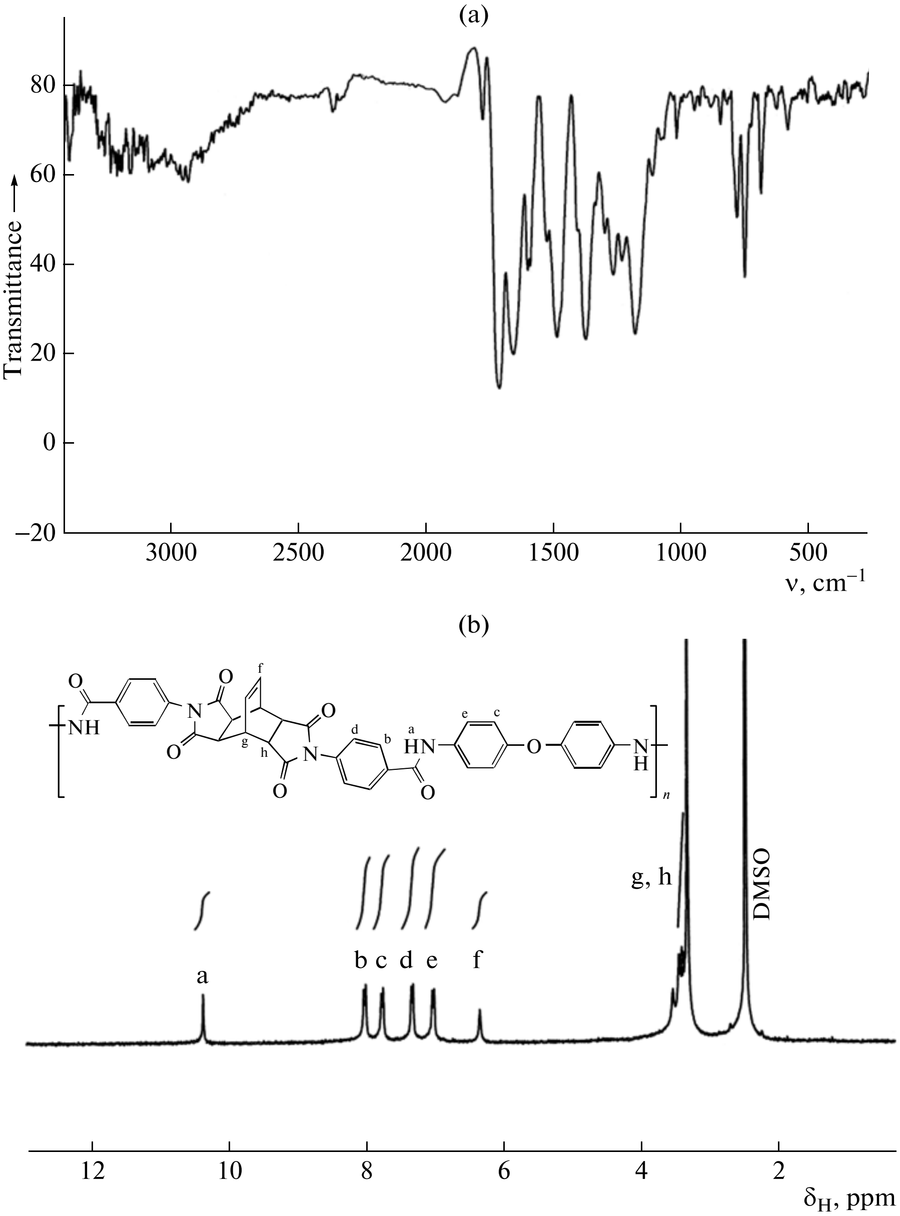


Fig. 2. FTIR spectrum of PAI **5e** (a) and ^{1}H-NMR spectrum of PAI **5a** (b).

ses the representative FTIR spectrum of PAI **5e** was shown in Fig. 2a. The polymer exhibited characteristic absorption bands at 1712–1780 cm^{-1} for the imide ring (asymmetric and symmetric C=O stretching vibration), 1377cm^{-1} (C–N stretching vibration), 1182 and 756 cm^{-1} (imide ring deformation). The absorption bands of amide groups appeared at 3161 cm^{-1} (N–H stretching) and 1656 cm^{-1} (C=O stretching). FTIR spectroscopy data for all PAIs **5a–f** are analogical.

The ^{1}H-NMR spectrum of polymer **5a** showed peaks that confirm its chemical structure (Fig. 2b). The aromatic protons appeared in the region of 7.02–8.04 ppm. The peaks in the region of 10.38 ppm are assigned for NH of the amide groups in the polymer backbone. Also the elemental analyses of the resulting PAIs **5a–f** were in good agreement with the calculated values for the proposed structure.

The solubility of PAIs **5a–f** was investigated as 0.01 g of polymeric sample in 2 ml of solvent. Due to present bicyclo[2,2,2]oct-7-ene-2,3,5,6-tetracarboxylic diimide moiety and amide groups in the polymer backbone, these poly(amide-imide)s have good solubility in organic solvents. All of the polymers are soluble in organic solvents such as DMF, DMSO, N-MP and DMAc in room temperature and are insoluble in sol-

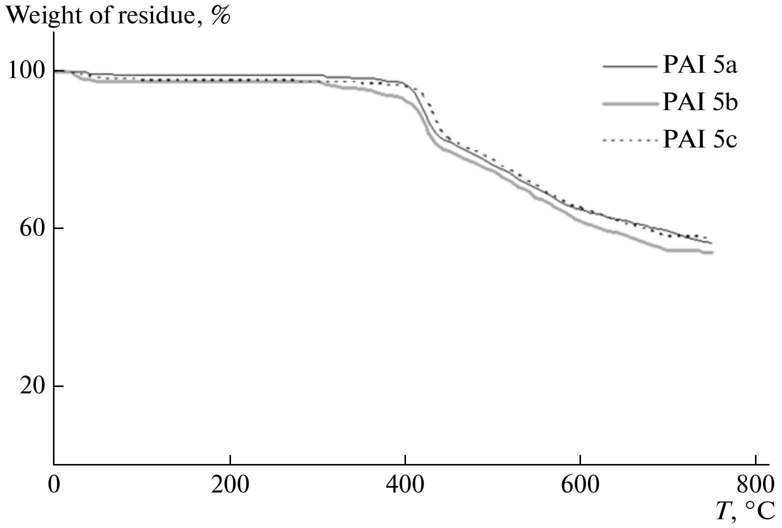


Fig. 3. TGA curves of PAIs **5a**, **5b** and **5c**.

vents such as chloroform, acetone, methanol and ethanol even in high temperature.

The thermal properties of PAIs **5a**, **5b** and **5c** were investigated by TGA and DTG in a nitrogen atmosphere at a heating a rate of 10 grad/min (Fig. 3). All of these polymers showed similar decomposition behavior. Initial decomposition temperature, 5 and 10% weight loss temperature (T_5, T_{10}), and char yields at 600°C for these PAIs **5a**, **5b** and **5c** were summarized in Table 2. These polymers exhibited good resistance to thermal decomposition up to 345–415°C in nitrogen and began to decompose gradually above that temperature. The temperatures of 5% weight loss for all the polymers ranged from 350 to 420°C, and the residual weight at 600°C ranged from 61.6 to 65.5% in nitrogen. Also the DSC analyses for PAIs **5a**, **5b** and **5c** showed T_g around 188–205°C.

A new series of PAIs **5a**–**f** containing bicyclo[2,2,2]oct-7-ene-2,3,5,6-tetracarboxylic diimide was synthesized by direct polycondensation reaction of an equimolar mixture of monomer **3** with six different aromatic diamines **4a**–**f**. Due to the presence of bicyclotetracarboxylic diimide and amide groups into the backbone, these polymers showed excellent thermal stability. On the other hand, these poly(amide-imide)s have good solubility in organic solvents [5]. Also these polymers have good inherent viscosity of 0.49–0.95 dl/g. These properties could make these PAIs attractive for practical applications such as processable high-performance engineering plastics.

Table 1. Yield and inherent viscosity of PAIs **5a–f**

Aromatic diamine	Polymer	Yield, %	η_{inh}, dl/g^a	Color
4a	**5a**	94	0.95	White
4b	**5b**	89	0.55	White
4c	**5c**	92	0.56	White
4d	**5d**	94	0.72	Pale yellow
4e	**5e**	95	0.67	White
4f	**5f**	80	0.49	Pale yellow

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

Table 2. Thermal properties of PAIs **5a**, **5b** and **5c**

Polymer	T_g^a	T_5, °C^b	T_{10}, °C^b	Char yield^c
5a	195	410–415	420–425	65.0
5b	188	345–350	410–415	61.6
5c	205	415–420	425–430	65.5

[a] Glass transition temperature was recorded at a heating rate of 10 grad/min in a nitrogen atmosphere.

[b] Temperature at which 5 or 10% weight loss was recorded TGA at a heating rate of 10 grad/min in N_2.

[c] Weight percentage of material left after TGA analysis maximum temperature 600°C in N_2.

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