

# Synthesis and properties of new transparent (co)polyimides based on adamantane-containing diamines and aromatic tetracarboxylic dianhydrides\*

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New (co)polyimides possessing good thermal and physicochemical characteristics, high hydrolytic stability, and transparency at the best world level were synthesized. It was shown that, depending on the natures of diamine and dianhydride used in the synthesis, the optical properties of polymers also change. These properties of (co)polyimide films correlate with the  $\Delta E$  value, which is defined as the difference between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energies of the polyimide repeating unit. It was shown that the use of 1,2-dichlorobenzene makes it possible to obtain high-molecular-weight (co)polyimides with a set of enhanced performance characteristics.

**Key words:** adamantane, 1,2-dichlorobenzene, aromatic acid dianhydrides, polycondensation, optical transparency.

Polyimides (PIs) occupy an important place among various classes of thermally stable polymers. Owing to excellent combination of thermal, electrical, and physico-mechanical properties, polyimide materials are widely used in various fields of technology, first of all, as heat-resistant dielectrics.<sup>1</sup> They are applied in microelectronics and electrical engineering, for the production of tapes for magnetic core winding, base films for flexible printed circuits, carrier tapes with self-gluing, magnetic tapes, shielding films with controlled temperature for satellite channels, etc.<sup>2–5</sup>

Fast development of optoelectronic engineering, especially portable smart devices, brought about high demand for the development of optical films with good thermal stability and high optical transmittance, which can be used as flexible substrates.

Traditional materials, such as ultra-thin glass, often do not possess the set of performance characteristics required for optoelectronic industry. Meanwhile, polyimide materials have excellent mechanical and dielectric properties and good chemical stability. However, the intense color and poor processability of many PIs are the key factors limiting their use as optical products. Most often, in the case of commercially manufactured polyimide films, their dark-brown or deep yellow color is due to the presence of electron-donating and electron-

withdrawing groups and related intramolecular and intermolecular charge transfer.<sup>6</sup>

In 2016, the Kolon company manufactured the world's first optically transparent polyimide film, which was considered to be a substitute for glass used in various displays.<sup>7</sup> It is noteworthy that a major challenge faced by the development of colorless transparent polyimide films is to find a balance between thermal, optical, mechanical, and other properties. There appeared the necessity of fabricating monomer structures that would, on the one hand, enhance the thermal stability and physicochemical characteristics of the obtained polymers and, on the other hand, possess relatively high optical transparency.<sup>8–10</sup>

## Results and Discussion

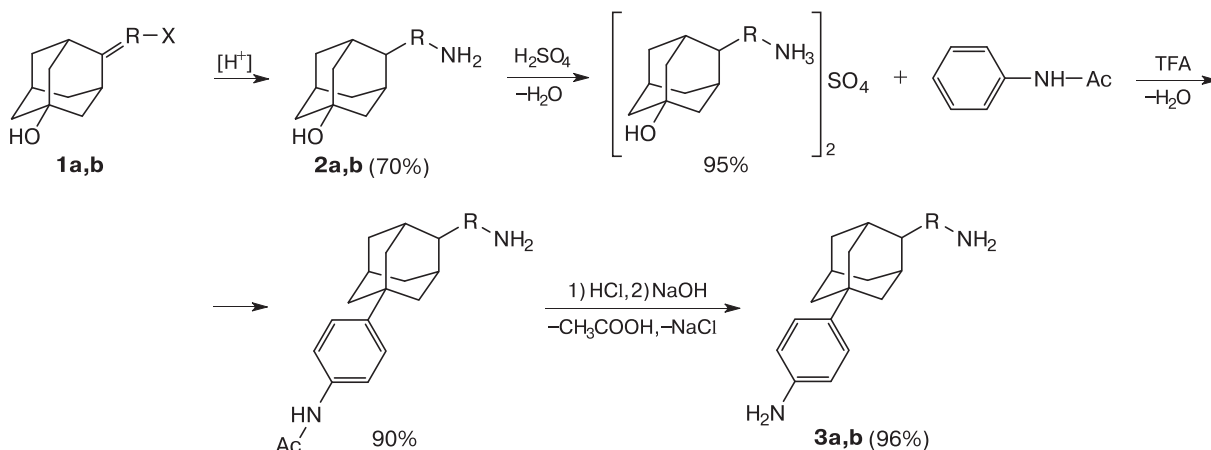
**Synthesis of monomers.** The monomers were synthesized as described in Scheme 1.

In the first step, compounds **1a,b** were reduced with lithium aluminum hydride<sup>11</sup> or Raney nickel<sup>12</sup> in 2-methyltetrahydrofuran (2-MeTHF) to give amines **2a,b**, which were then converted to salts. The reaction of the salts with acetanilide in the presence of trifluoroacetic acid (TFA) and subsequent hydrolysis of the resulting derivatives<sup>13</sup> afforded the corresponding diamines **3a,b** in good yield (96%) and with high purity (99%).

This synthetic route furnishes the target and intermediate compounds with a purity of at least 98–99%, with

\* Dedicated to Academician of the Russian Academy of Sciences V. N. Charushin on the occasion of his 70th birthday.

Scheme 1



**1a:** R =  $-\text{CH}_2-$ , X =  $\text{NO}_2$ ; **1b:** R =  $-\text{C}_2\text{H}_4-$ , X = CN; **2a:** R =  $-\text{CH}_2-$ ; **2b:** R =  $-\text{C}_2\text{H}_4-$ ; **3a:** R =  $-\text{CH}_2-$ ; **3b:** R =  $-\text{C}_2\text{H}_4-$

the yields of products in each step being 70–96%. The structures of the intermediate and target compounds were confirmed by NMR and IR spectroscopy and the purity was checked by GC/MS analysis.

**Synthesis of polyimides and copolyimides.** New (co) polyimides (CPIs) were prepared by one-step high-temperature polycyclization in solution using adamantane-containing diamines **3a** or **3b**, 9,9-bis(4-aminophenyl)fluorene (**4**), and 3,4,3',4'-tetracarboxydiphenyl dianhydride (BPDA) or 5,5'-(1,1,1,3,3,3-hexafluoropropane-2,2-diyl)bis(2-benzofuran-1,3-dione) (dianhydride 6FDA) (Scheme 2).

Previously, *m*-cresol was used most often as the solvent for the one-step synthesis of PIs containing the adamantane moiety.<sup>14,15</sup> However, it was shown<sup>15</sup> that the synthesis in *m*-cresol may be accompanied by side reactions and, under certain conditions, the polycondensation can become reversible. Meanwhile, it was reported<sup>16</sup> that 1,2-dichlorobenzene (DCB) can be an efficient solvent for the one-step high-temperature synthesis of PIs. Using this solvent, it is possible to avoid the undesirable side reactions and, possibly, also to shift the polycondensation equilibrium towards the products. Therefore, (co)polymers based on adamantane-containing diamines were synthesized in DCB. It is noteworthy that with DCB being used as the solvent, the reduced viscosity of polyimides was markedly higher than in *m*-cresol (0.96–1.39 vs. 0.6–0.8, respectively).

The structures of PIs and CPIs were confirmed by IR spectroscopy. The IR spectra of all synthesized PIs and CPIs exhibit absorption bands at 750 and 1380  $\text{cm}^{-1}$ , characteristic of the imide ring, and bands at 1780 and 1740  $\text{cm}^{-1}$ , which correspond to C–N and C=O modes in the ring, respectively.

The dependence of the reduced viscosity ( $\eta_{\text{red}}$ ) of PIs and CPIs on the molar concentrations of the starting

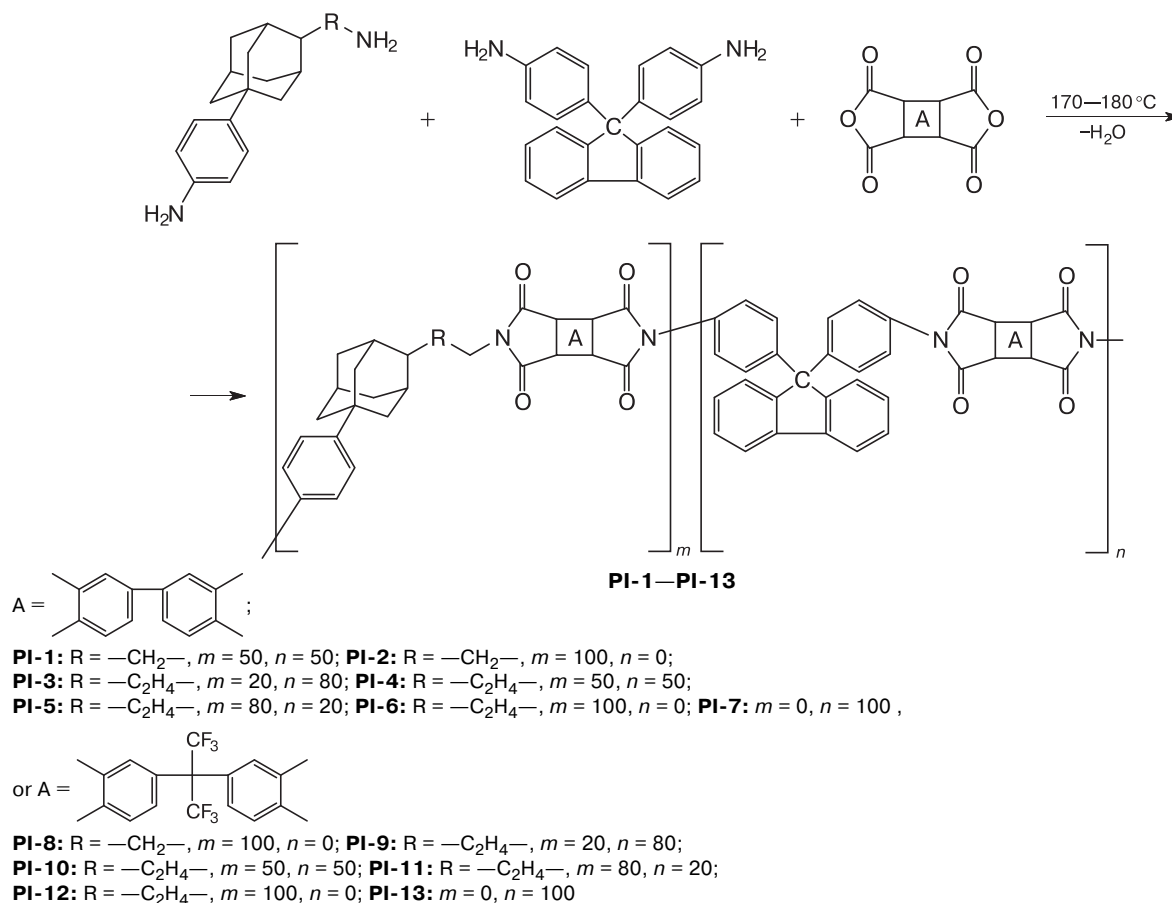
monomers in the reaction mixture was studied in relation to the sample **PI-6**. When *m*-cresol was used as the solvent, this dependence was nonmonotonic, with the viscosity maximum being attained at concentration of 0.3  $\text{mol L}^{-1}$ . In the case of DCB,  $\eta_{\text{red}}$  virtually did not depend on the initial reactant concentrations in the 0.2–0.4  $\text{mol L}^{-1}$  range. The unusual pattern of dependence observed in the case of DCB in the chosen range of monomer concentrations may be attributable to, first, the absence of side reactions with the solvent and, second, to the shift of reaction equilibrium towards the products. In addition,  $\eta_{\text{red}}$  and the yields after PI precipitation and reprecipitation were markedly higher for the products synthesized in DCB than for those synthesized in *m*-cresol (Table 1).

**Film preparation.** The films were prepared by casting of 13% solutions of specified PIs and CPIs in 2-MeTHF on a glass substrate. Note that the use of this solvent reduces the temperature and duration of film drying.

The cast films were dried *in vacuo* with stepwise temperature rise to 80 °C for 1 h to remove the solvent. The film thickness was 15–20  $\mu\text{m}$ .

**Optical properties.** The main factors considered to be responsible for coloring of polyimide films are the intramolecular charge transfer between the alternating electron-donating and electron-withdrawing moieties and the formation of intermolecular charge transfer complexes.<sup>6,16</sup> Since the formation of these complexes is directly related to the structure and geometry of molecular orbitals, we performed quantum chemical calculations for synthesized PIs. They included both preliminary geometry optimization for molecular structures of the polyimide moiety and the subsequent energy calculations. The calculations were performed by density functional theory using the B3LYP exchange correlation potential and the Gaussian basis set. Previously, it was shown<sup>16</sup> that the electron transition energy ( $\Delta E$ ) from the highest occupied molecular orbital

Scheme 2



(HOMO), located around the imide nitrogen atom, to the lowest unoccupied molecular orbital (LUMO), located around the carbonyl carbon atoms, is determined by the electron-donating properties of the diamine and electron-withdrawing properties of the dianhydride. Thus, the presence of highly basic alicyclic diamines **3a** and **3b** in the polyimide molecule leads to considerably higher  $\Delta E$  values.

Higher  $\Delta E$  values found for **PI-8** and **PI-12** compared to those for **PI-2** and **PI-6** are due to the presence of bulky

$\text{C}(\text{CF}_3)_2$  groups in their molecules; these groups considerably decrease the intermolecular interactions between the polymer chains due to steric hindrance and low polarizability of fluorinated groups. The dihedral angles between the imide and benzene rings in polyimides **PI-1**–**PI-12** vary from  $72^\circ$  to  $74^\circ$ . The calculation results are summarized in Table 2.

The optical characteristics of polyimide films are given in Figures 1–3 and in Table 2. All of the films were 15–20  $\mu\text{m}$  thick.

**Table 1.** Dependence of the reduced viscosity and yield of PIs based on dianhydride BPDA and diamine **3b** on the monomer concentration

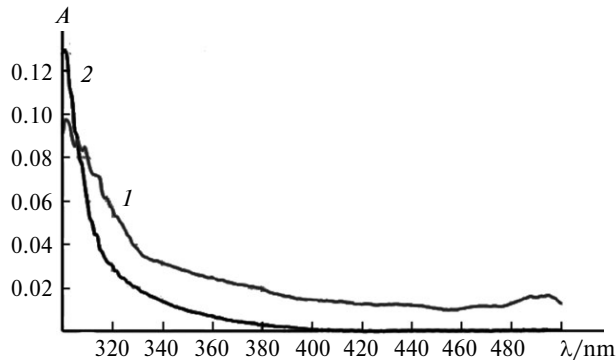
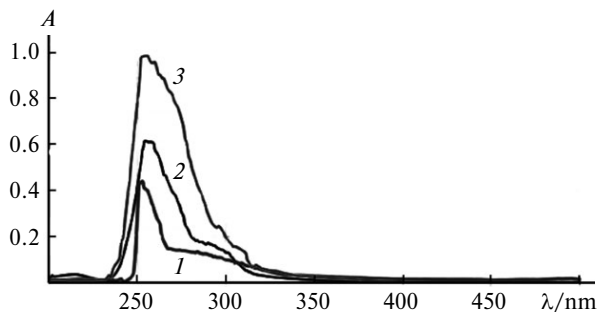
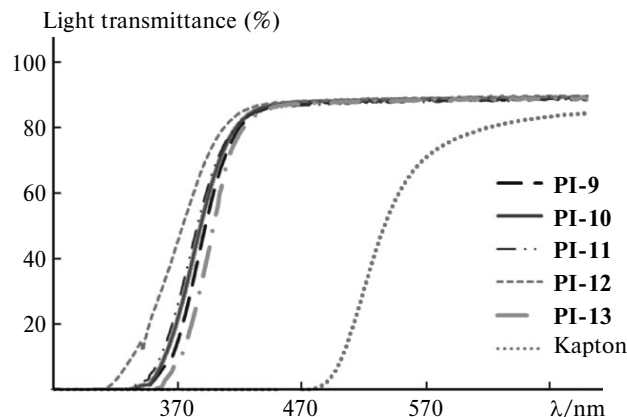
Monomer concentration/mol L <sup>-1</sup>	Solvent	$\eta_{\text{red}}/\text{dL g}^{-1}$	PI yield after reprecipitation (%)
0.1	<i>m</i> -Cresol	0.26	68
0.2	<i>m</i> -Cresol	0.31	76
0.3	<i>m</i> -Cresol	0.56	84
0.4	<i>m</i> -Cresol	0.38	70
0.1	1,2-Dichlorobenzene	1.00	98
0.2	1,2-Dichlorobenzene	1.03	Quantitative
0.3	1,2-Dichlorobenzene	1.06	Quantitative
0.4	1,2-Dichlorobenzene	1.06	Quantitative

**Table 2.** Calculated  $E_{\text{HOMO}}$ ,  $E_{\text{LUMO}}$ , and  $\Delta E$  (eV) for some of synthesized PIs

Polymer	$E_{\text{HOMO}}$	$E_{\text{LUMO}}$	$\Delta E$
PI-2	-4.980	-2.531	2.449
PI-6	-4.980	-2.531	2.449
PI-8	-6.014	-2.476	3.537
PI-12	-6.014	-2.476	3.537
PI-13	-5.660	-2.585	3.075

It is worth noting that the results of UV spectroscopic measurements of PI solutions (see Fig. 1) were in good agreement with calculation results. A solution of **PI-12** sample containing the 6FDA moiety, had a lower absorbance in the 300–360 nm range than BPDA-based **PI-6** sample. The **PI-12** sample, unlike BPDA-based PI (**PI-6**) did not absorb in the region above 400 nm.

Figure 2 shows the UV and visible spectra of 0.05% solutions of polyimides **PI-6**, **PI-12**, and **PI-13** in 2-MeTHF. Note that the **PI-6** and **PI-12** samples containing 100% alicyclic diamine units exhibit two absorption maxima, which is probably due to the presence of imide rings of different natures in the macromolecule. In the case of **PI-13**, the spectrum shows one broad peak, with the absorption maximum being shifted to longer wavelengths. It

**Fig. 1.** Absorption spectra of solutions of polyimides **PI-6** (1) and **PI-12** (2) in the UV and visible regions.**Fig. 2.** Absorption spectra of 0.05% solutions of polyimides **PI-6** (1), **PI-12** (2), and **PI-13** (3) in 2-MeTHF.**Fig. 3.** Transparency of the obtained polyimide films and commercial kapton film.

is also noteworthy that all solutions based on diamine **3b** and dianhydride 6FDA had no absorption bands in the region above 360 nm.

These results are in good agreement with the calculated  $\Delta E$  values (eV). Polyimides based on BPDA have much smaller  $\Delta E$  than PIs in which 6FDA was used as the monomer. The  $\Delta E$  value calculated for model PIs containing imide rings either only at aliphatic or only at aromatic moieties (see Table 1) accounts for the presence of two peaks in the UV spectrum of PIs based on diamine **3b**.

The transparency of polyimide films in the visible range was also studied by spectrophotometry (Fig. 3). The optical transmittance at 400, 420, and 450 nm, the average transmittance ( $T_{\text{av}}$ , %), and the yellowness index of the obtained samples are summarized in Table 3.

Note that the PIs consisting of adamantane-based diamine and dianhydride 6FDA moieties demonstrated much better optical properties ( $\lambda_{\text{cut-off}} = 305\text{--}337$  nm,  $T_{\text{av}} = 89\%$ ) than the commercial Kapton film ( $\lambda_{\text{cut-off}} = 470$  nm,  $T_{\text{av}} = 69\%$ ). As the amount of alicyclic diamine in the monomer increased, the transmittance of polyimide films increased and the yellowness index decreased (see Table 3). Indeed, the polyimide films **PI-6** and **PI-12**, containing 100% diamines **3a** and **3b** in the molecules, respectively, have the lowest  $\lambda_{\text{cut-off}}$  values (305–306 nm) and the highest transmittance at 400 nm wavelength (75–76%).

Polyimide films based on adamantane-containing diamines and dianhydride 6FDA also have relatively low yellowness indices. For example, for **PI-12**, containing 100% diamine **3b**,  $T_{\text{av}} = 89\%$ , and the yellowness index is 1.76, while for the commercial Kapton film,  $T_{\text{av}} = 69\%$  and the yellowness index is 93 (see Table 3).

It was found that  $\lambda_{\text{cut-off}}$  for **PI-8–PI-12** are markedly lower than that for **PI-13**, which contains diamine component **4**.

It is known that  $\Delta E$  approximately coincides, in the order of magnitude, with the energy of quantum corre-

**Table 3.** Optical properties of PI and CPI films based on diamines **3a**, **b**, and **4** and dianhydride 6FDA

Polymer	$d^a$ / $\mu\text{m}$	$\lambda^b_{\text{cut-off}}$ /nm	Transmittance <sup>c</sup> (%)				Yellowness index
			$T_{400}$	$T_{420}$	$T_{450}$	$T^d_{\text{av}}$	
<b>PI-8</b>	20	305	75	82	86	89	2.80
<b>PI-9</b>	20	337	62	80	86	88	2.84
<b>PI-10</b>	20	329	66	81	87	88	2.74
<b>PI-11</b>	20	319	67	80	87	88	2.48
<b>PI-12</b>	20	306	76	84	87	89	1.76
<b>PI-13</b>	20	348	60	80	86	87	2.89
Kolon Industries PI <sup>e</sup>	25	300–320	31–70	41–77	80–87	84–88	1.82–9.7
Kapton <sup>f</sup>	60	470	0	0	0	69	93

<sup>a</sup> Film thickness;<sup>b</sup> cut-off wavelength;<sup>c</sup> transmittance at 400, 420, 450 nm;<sup>d</sup> average transmittance in the visible region (400–780 nm);<sup>e</sup> published data;<sup>f</sup> the properties of commercial PI film Kapton are given for comparison.

sponding to the absorption edge wavelength ( $\lambda_E$ ) in the UV/Vis spectra ( $\lambda_E$  is the wavelength corresponding to the point of intersection of two tangent lines to the absorption curve). All of the polyimide films, except for commercial Kapton film, virtually did not absorb in the region above 370 nm. It was found that  $\lambda_E$  values for PIs decrease in the order **PI-13** > **PI-9** > **PI-10** > **PI-11**  $\approx$  **PI-8** > **PI-12**, which is consistent with the calculated  $\Delta E$  values. Thus, the results confirm that the structures of proposed diamines provide increased transparency and decreased yellowness indices for PIs based on them.

**Thermal and mechanical properties.** Usually, the presence of bulky substituents and aliphatic moieties in the chain has an adverse effect on the thermal properties of PIs. In particular, 5% weight loss temperature ( $T_{5\%}$ ), important for the application of polymers, somewhat decreases.<sup>17</sup>

Note that the thermal oxidative stability of alicyclic-containing PIs is somewhat lower than that of fully aromatic ones, but it still remains fairly high. Indeed, 5% weight loss for PI based on diamine **3b** and 6FDA was observed at a temperature of 470 °C. The results of studying the thermal oxidative stability of PIs are summarized in Table 4. Generally, the synthesized PIs possess relatively high thermal oxidative stability; the  $T_{5\%}$  and  $T_{10\%}$  are higher for polymers based on dianhydride 6FDA than for those based on BPDA (see Table 4). Furthermore, they considerably exceed these values for the previously obtained PIs based on adamantane-containing diamines and 3,4,3',4'-tetracarboxydiphenyl oxide dianhydride (ODPA) ( $T_{5\%} = 380$  °C),<sup>17</sup> although they are somewhat lower than those of fully aromatic **PI-7** and **PI-13**.

Generally, the physicomechanical characteristics of the synthesized films are relatively high (see Table 4), although some of them are lower than those of Kapton

films. For example, the tensile strength of the films we obtained was 70–79 MPa, while the tensile elongation was 5–7%.

**Solubility and hydrolytic stability of the powders.** High solubility expands the scope of applicability of PIs, may facilitate their processing, and, in addition, it is useful for more extensive studies of PIs.

The solubility of the obtained PIs was studied by considering their ability to form stable 5% solutions at room temperature or on heating (Table 5). The presence of bulky moieties and asymmetric molecules in the PI structure is known to increase the polymer solubility.<sup>18</sup> It was found that the **PI-8**–**PI-13** samples were soluble not only in bipolar aprotic solvents with high dielectric constants, such as *N,N*-dimethylformamide (DMF,  $\epsilon = 36.71$ ), *N,N*-dimethylacetamide (DMA,  $\epsilon = 37.78$ ), dimethyl sulfoxide (DMSO,  $\epsilon = 46.45$ ), and *N*-methylpyrrolidone (NMP,  $\epsilon = 32.2$ ), but also in solvents with low dielectric constants such as  $\text{CHCl}_3$  ( $\epsilon = 4.89$ ),  $\text{CH}_2\text{Cl}_2$  ( $\epsilon = 8.93$ ), tetrahydro-

**Table 4.** Thermal and physicomechanical characteristics of CPI films based on adamantane-containing diamine **3b**, diamine **4**, and 6FDA

Polymer	$T_{5\%}/^\circ\text{C}$	$T_{10\%}/^\circ\text{C}$	$\sigma/\text{MPa}$	$\epsilon$ (%)
<b>PI-8</b>	470	510	70	5
<b>PI-9</b>	470	510	72	5
<b>PI-10</b>	480	520	78	7
<b>PI-11</b>	500	530	75	6
<b>PI-12</b>	510	550	79	7
<b>PI-13</b> <sup>a</sup>	520	550	78	8
Kolon Industries PI <sup>b</sup>	350–530	400–570	70–112	5–12

<sup>a</sup> Data for fully aromatic polyimide are given for comparison;<sup>b</sup> published data.

**Table 5.** Solubility of PIs and CPIs

Polymer	$\eta_{\text{red}}$ /dL g <sup>-1</sup>	Solvent								
		<i>m</i> -Cresol	CHCl <sub>3</sub>	CH <sub>2</sub> Cl <sub>2</sub>	NMP	DMA	DMSO	DMF	2-Me-THF	THF
PI-1	1.10	+	—	—	+ <sup>a</sup>	+	+	+	—	—
PI-2	1.05	+	—	—	+ <sup>a</sup>	+	+	+	—	—
PI-3	0.99	+	—	—	+ <sup>a</sup>	+	+	+	—	—
PI-4	1.23	+	—	—	+ <sup>a</sup>	+	+	+	—	—
PI-5	1.39	+	—	—	+ <sup>a</sup>	+	+	+	—	—
PI-6	1.03	+	—	—	+ <sup>a</sup>	+	+	+	—	—
PI-7 <sup>b</sup>	0.96	+	—	+	+ <sup>a</sup>	+	+	+	—	—
PI-8	1.10	+	+	+	+	+	+	+	+	+
PI-9	1.06	+	+	+	+	+	+	+	+	+
PI-10	1.23	+	+	+	+	+	+	+	+	+
PI-11	1.10	+	+	+	+	+	+	+	+	+
PI-12	1.15	+	+	+	+	+	+	+	+	+
PI-13 <sup>b</sup>	1.20	+	+	+	+	+	+	+	+	+

<sup>a</sup> Polymers are dissolved on heating.<sup>b</sup> Data for fully aromatic polyimide are given for comparison.

furan (THF,  $\epsilon = 7.58$ ), and 2-methyltetrahydrofuran (2-MeTHF,  $\epsilon = 6.97$ ). The excellent solubility of these PIs is attributable to the presence of both fluorine-containing and methyl groups in the chain. This leads to decreasing intermolecular interactions and prevents the formation of coplanar structures; consequently, the packing density of PIs decreases. Meanwhile, BPDA-based PIs were much less soluble. Polyimides based on 6FDA and diamine **3b** were soluble in a very broad range of solvents, while polymers based on the same diamine and BPDA were insoluble in THF or 2-MeTHF and poorly soluble in NMP.

A drawback of aromatic PIs is the reduced stability to the action of alkalis, which restricts some applications of polyimide films with good optical properties. Previously, it was shown<sup>17</sup> that PIs based on adamantane-containing diamines and dianhydride ODPa possess relatively high hydrolytic stability. However, the thermal oxidative stability of these polymers was insufficiently high in comparison with PIs based on the same dianhydride and aromatic diamines. Therefore, we studied the hydrolytic stability and thermal properties of **PI-1**–**PI-7** based on alicyclic diamines and BPDA. The absence of a pivotal atom in the BPDA molecule may result, in our opinion, in a considerable increase in the thermal oxidative stability, with the relatively high level of hydrolytic properties being retained.

The hydrolytic stability of the polymers was studied by their degradation under the action of superheated steam under heterogeneous conditions and was estimated as the relative change in the reduced viscosity ( $\eta_{\text{red}}$ ) of the samples. The thermal stability was evaluated from the 5 and 10% weight loss temperatures for polymer samples (Table 6).

The alicyclic structures present in PIs increase the hydrolytic stability, which is probably attributable to shielding of the sterically poorly accessible reaction centers

with bulky hydrophobic groups. One more possible cause is that highly basic amino groups of the adamantane-containing diamine decrease the electrophilicity of the carbonyl carbon atoms of the imide rings.

Thus, we synthesized new (co)polyimides possessing good thermal and physicochemical characteristics and high hydrolytic stability in comparison with the fully aromatic polyimide **PI-7**. It was shown that the adamantane moiety present in PI molecules provides very good optical properties of the PI-based polymer films in comparison with commercial Kapton films. These properties are fully correlated with the  $\Delta E$  value, which is defined as the energy difference between the HOMO and LUMO of the repeating unit. The use of 1,2-dichlorobenzene as the solvent provides the synthesis of polyimides with relatively high reduced viscosities in comparison with the same polymers

**Table 6.** Resistance to hydrolysis and thermal properties of PIs and CPIs based on adamantane-containing diamines, diamine **3**, and BPDA

Polymer	<i>m</i>	$\eta_{\text{red}}/\eta_{\text{red init}}^a$		$T_{5\%}$	$T_{10\%}$
		6 h	12 h		
PI-1	50	0.93	0.78	470	480
PI-2	100	1	1	440	460
PI-3	20	0.87	0.70	470	500
PI-4	50	0.94	0.80	460	490
PI-5	80	0.97	0.84	450	480
PI-6	100	1	1	430	470
PI-7 <sup>b</sup>	0	0.80	0.57	500	520

<sup>a</sup> The measurements were carried out in *symm*-tetrachloroethane at  $T = 25 \pm 0.1$  °C; hydrolysis was conducted at 180 °C in glass tubes.<sup>b</sup> Data for fully aromatic polyimide are given for comparison.

obtained in *m*-cresol. We developed a convenient synthetic route to 1,4-adamantane-containing diamines, comprising less steps than the previously known methods of synthesis of this type of compounds and giving the target diamines in high yields and with high purity.

### Experimental

Mass spectra were recorded on a Saturn-2100 gas chromatograph/mass spectrometer.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were measured on a Mercury 300 plus BB Varian instrument (internal HMDS,  $\text{CDCl}_3$ ,  $\text{CCl}_4$ ). IR spectra were measured on a Nicolet 6700 FTIR spectrometer (attenuated total reflectance (ATR) mode). The film transparency in the visible range and the yellowness index were determined using an SF-56 spectrophotometer with software and mathematical data processing function. The absorption spectra of polymer solutions were recorded on an Agilent spectrophotometer.

Quantum chemical calculations were performed by the GAMESS software (US). Density functional theory with the B3LYP hybrid functional and 6-31G(d) basis set was used. Preliminary geometry optimization was done by semiempirical PM3 quantum chemical method.

The viscosity of dilute solutions of PIs was measured using a VPZh-2 viscometer at  $25 \pm 0.1$  °C in *symm*-tetrachloroethane. The capillary diameter was 0.56 mm.

The dynamic thermogravimetric analysis of polymer samples was carried out on a Q-1000 derivatograph (MOM); the heating rate was  $10$  °C  $\text{min}^{-1}$ ; the sample weight was 70–100 mg.

The hydrolytic stability of the polymers was studied by their degradation on treatment with superheated steam under heterogeneous conditions and estimated as the relative change in the reduced viscosity ( $\eta_{\text{red}}$ ) of the polymers. A polymer powder (0.1 g) with known  $\eta_{\text{red}}$  and distilled water (10 mL) were placed into a  $30 \text{ cm}^3$  heat resistant glass tube. The tube was sealed and kept at a constant temperature in a thermostat for a specified period of time. Then the tube was broken, the polymer was separated on a filter, washed with acetone, and dried, and the  $\eta_{\text{red}}$  value of the sample after hydrolysis was determined in *symm*-tetrachloroethane.

The physicomechanical testing of PI and CPI films was carried out on a Tinius Olsen tensile machine. The speed of the lower grip was  $5 \text{ mm min}^{-1}$ . The basic film length was 20 mm, the width was 8.1 mm, and thickness was 15–20  $\mu\text{m}$ . Testing was performed at a tensile speed of  $5 \text{ mm s}^{-1}$  and a load of  $10^4 \text{ N}$ .

The following commercial chemicals were used: 9,9-bis(4-aminophenyl)fluorene (**4**, BLDpharm), 3,4,3',4'-tetracarboxy-diphenyl dianhydride (BPDA, Aldrich) and 5,5'-(1,1,1,3,3,3-hexafluoropropane-2,2-diyl)bis(2-benzofuran-1,3-dione) (6FDA, J&K). Dianhydrides were preheated in air for 1 h at a bath temperature of 200 °C. All dianhydrides and diamines were purified by sublimation at a reduced pressure (4 Torr). *m*-Cresol, 1,2-dichlorobenzene, NMP, DMAC, DMSO, and DMF were distilled preliminarily under vacuum of a water jet pump; 2-MeTHF, THF,  $\text{CHCl}_3$ , and  $\text{CH}_2\text{Cl}_2$  were purified by distillation. The other commercial chemicals were used as received.

**4-(Aminomethyl)tricyclo[3.3.1.1<sup>3,7</sup>]decan-1-ol (2a)** was synthesized by a previously reported procedure.<sup>12</sup>

**4-(2-Aminoethyl)tricyclo[3.3.1.1<sup>3,7</sup>]decan-1-ol (2b)** was synthesized by a previously reported procedure.<sup>11</sup>

**4-[4-Aminomethyl]tricyclo[3.3.1.1<sup>3,7</sup>]dec-1-yl]aniline (3a)** was synthesized by a known procedure,<sup>13</sup> except that 8.8 g of 4-(2-amino)methyladamantan-2-ol sulfate was used. The yield was 92% and the purity was 99%, m.p. 91–93 °C. IR,  $\nu/\text{cm}^{-1}$ : 3373 ( $\text{NH}_2$ ); 2900, 2851 (CH); 1672 ( $\text{NH}_2$ ); 1615 (C–C–Ar); 1451 ( $\text{CH}_2$ ); 1313, 1139, 1009, 961, 838, 744, 722. MS (EI, 70 eV),  $m/z$  ( $I_{\text{rel}}$  (%)): 257 [ $\text{M} + 1$ ] (31.7), 256 [ $\text{M}$ ]<sup>+</sup> (100), 239 [ $\text{M} - \text{NH}_3$ ] (62.8), 213 [ $\text{M} - \text{CH} - \text{NH}_3$ ] (4.4); 169 [ $\text{M} - \text{CH}_2 - \text{CH}_3(\text{Ad}) - \text{CH} - \text{NH}_3$ ] (3.2); 156 [ $\text{M} - \text{CH}_3 - \text{C}_2\text{H}_5 - \text{CH}_3(\text{Ad}) - \text{CH} - \text{NH}_3$ ] (9.8), 133 (disubstituted Ad) (20), 106 (16.1), 77 (3.5).  $^1\text{H}$  NMR (300 MHz,  $\text{CCl}_4$ ,  $\delta$ ): 0.78 (s, 2 H,  $\text{AdCH}_2\text{NH}_2$ ); 1.20 (m, 2 H,  $\text{AdCH}_2\text{NH}_2$ ); 1.43–2.00 (m, 14 H, H (Ad)); 2.40 (t, 2 H,  $\text{AdCH}_2\text{NH}_2$ ,  $J = 7.1 \text{ Hz}$ ,  $J = 0.9 \text{ Hz}$ ); 3.68 (s, 2 H, Ar,  $\text{NH}_2$ ); 6.70 (m, 2 H, H(2,6)); 7.02 (m, 2 H, H(3,5)).

**4-[4-(2-Aminoethyl)tricyclo[3.3.1.1<sup>3,7</sup>]dec-1-yl]aniline (3b)** was synthesized according to the previously reported procedure.<sup>13</sup>

**Synthesis of (co)polyimides PI-1–PI-13 (general procedure).** Diamine **3a** or **3b** (0.01 mol), dianhydride BPDA or 6FDA (0.01 mol), and DCB (33 mL) were charged into a reactor equipped with an inlet for inert gas and a hydraulic lock. The reactant concentration was  $0.30 \text{ mol L}^{-1}$ . The reaction mixture was heated for 1 h from 20 to 175 °C with continuous purging of inert gas to remove the reaction water and kept under these conditions for additional 12 h. Then, after cooling, the reaction mixture was dissolved in chloroform and poured into acetone. The precipitated polyimide was collected on a filter, washed with acetone, and reprecipitated from chloroform. The yield of the polymer was 97–98% of the theoretical yield,  $\eta_{\text{red}} = 1.20\text{--}1.40 \text{ dL g}^{-1}$ .

(Co)polyimides with different unit ratios ( $m : n$ ) were prepared in a similar way using appropriate amounts of the components.

Polyimide films were obtained by casting of a filtered 13% solution of a polymer in 2-MeTHF on a glass substrate followed by stepwise heating to 80 °C for 1 h and conditioning at this temperature in a vacuum chamber for 1 h. Then the film was heated to 150 °C and kept under these conditions in a vacuum chamber for 1 h.

The study was carried out using equipment of the Center for Collective Use "Physicochemical Investigation Methods" of the Volgograd State Technical University.

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