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Macromolecular transformations of polyphenyl imidates into *N*-phenyl-substituted polyaramides and poly(*N*-benzoylamines)

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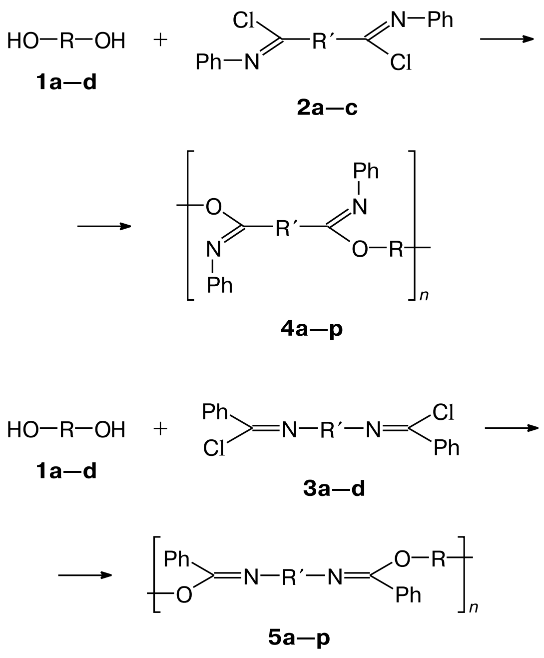
A possibility for the transformation of polyphenyl imidates, obtained by polycondensation of bisphenols with imidoyl chlorides of mono- and dicarboxylic acids, into *N*-phenyl-substituted aromatic polyamides and poly(*N*-benzoylamines) has been discovered. Such a rearrangement resulted from heating at 260—340 °C for 13—17 h, whereas in diphenyl ether solution at 240 °C for 10—14 h. The polymers synthesized are soluble in organic solvents and possess high stability against thermooxidative destruction.

Key words: polyphenyl imidates, imidoyl chlorides, imidates, phenols, polyamides, the Chapman rearrangement.

Earlier,[1] we have shown a possibility for the synthesis of polyphenyl imidates (PPID) on the basis of the reaction of bisphenols **1** with imidoyl chlorides **2** or **3** (Scheme 1).

Scheme 1

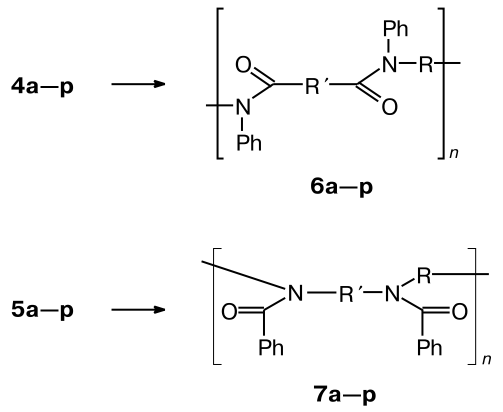


R = *m*-C_6H_4 (**1a**, **4a—d**, **5a—d**), *p*-C_6H_4 (**1b**, **4e—h**, **5e—h**), $(p\text{-}C_6H_4)_2O$ (**1c**, **4i—l**, **5i—l**), $(p\text{-}C_6H_4)_2CMe_2$ (**1d**, **4m—p**, **5m—p**); R´ = *m*-C_6H_4 (**2a**, **3a**, **4a,e,i,m**, **5a,e,i,m**), *p*-C_6H_4 (**2b**, **3b**, **4b,f,j,n**, **5b,f,j,n**), $(p\text{-}C_6H_4)_2O$ (**2c**, **3c**, **4c,g,k,o**, **5c,g,k,o**), $(p\text{-}C_6H_4)_2CH_2$ (**2d**, **3d**, **4d,h,l,p**, **5d,h,l,p**)

The polymers synthesized possess good solubility, high thermal stability, and wide range between starting points of decomposition and softening.

Particularities of chemical structure of the imidate bond, some data on its chemical transformations,[2] and preliminary experimental data[3] allowed us to suggest a possibility of rearrangement of PPID of the type **4** into *N*-phenyl-substituted aromatic polyamides (PAPA) **6** and PPID **5** into poly(*N*-benzoylamines) (PBA) **7** (Scheme 2).

Scheme 2



R = *m*-C_6H_4 (**6a—d**, **7a—d**), *p*-C_6H_4 (**6e—h**, **7e—h**), $(p\text{-}C_6H_4)_2O$ (**6i—l**, **7i—l**), $(p\text{-}C_6H_4)_2CMe_2$ (**6m—p**, **7m—p**); R´ = *m*-C_6H_4 (**6a,e,i,m**, **7a,e,i,m**), *p*-C_6H_4 (**6b,f,j,n**, **7b,f,j,n**), $(p\text{-}C_6H_4)_2O$ (**6c,g,k,o**, **7c,g,k,o**), $(p\text{-}C_6H_4)_2CH_2$ (**6d,h,l,p**, **7d,h,l,p**)

In this connection, the aim of the present work consisted in the study of a possibility of transformation of PPID into PAPA and PBA.

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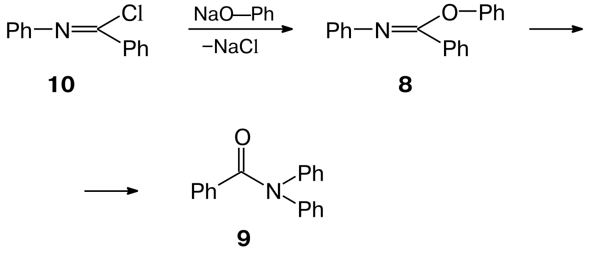
First, we studied the rearrangement of a model compound, phenyl *N*-phenylbenzenecarboximidoate (**8**), into *N*,*N*-diphenylbenzamide (**9**), which is known as the Chapman rearrangement**4** (Scheme 3).

Scheme 3



Imino ester **8** was obtained by the condensation of suspended in dioxane phenylbenzimidoyl chloride (**10**) and sodium phenoxide. The reaction proceeds readily, with a degree of conversion (γ) at room temperature in argon atmosphere being 87%. The model compound **8** after recrystallization looks like a pale yellow powder with m.p. 103.1—103.9 °C. The substance is soluble in amide solvents and in chloroform at room temperature and in diphenyl ether (DPE) under heating.

The structure of compound **8** was confirmed by the elemental analysis and IR spectroscopic data. In the IR spectrum (Fig. 1), there are characteristic absorption bands at 1651 (C=N) and 1210 cm^{-1} (C—O) corresponding to the imidate group.

The heating of compound **8** at 250 °C for 13 h or in DPE at 240 °C for 12 h is accompanied by a complete change of its IR spectrum, showing formation of the same product **9** in both cases. The yield of compound **9** reaches 99%. In the IR spectrum of compound **9** (see Fig. 1), a characteristic band at 1657 cm^{-1} (C=O) is present, whereas a band at 1210 cm^{-1} (C—O) is virtually absent. Thus, a decrease in intensity of the absorption band related to the C—O vibrations can be used for the monitoring of conversion of the model compound and imidate polymers **4** and **5**.

In the ^{13}C NMR spectrum (DMSO-d$_6$) of compound **9**, a characteristic signal at δ 170.53 corresponding to the C atom of the amide group is present.

The results obtained during the study of the model reaction allowed us to start a research on similar rearrangement in related polymers.

A possibility for the rearrangement of polymers was studied with the use of PPID **4m** in solution, in film, in the fused state, and in the glass-like state. A degree of conversion during the rearrangement was evaluated from the IR spectra by comparison of absorption intensities of the imidate group.

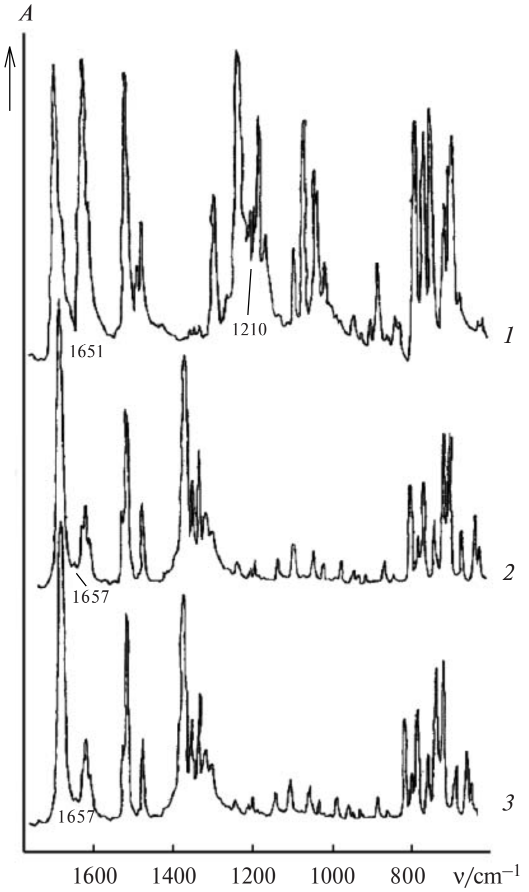


Fig. 1. IR spectra of phenyl *N*-phenylbenzenecarboximidoate (**8**) (*1*) and *N*,*N*-phenylbenzamide (**9**) obtained by the rearrangement in solution (*2*) and in the fused state (*3*).

Kinetic curves of the transformation of PPID are given in Fig. 2. The thermal rearrangements of PPID in the fused state (curve *1*) and in DPE at 240 °C (curve *2*) proceed at comparable rates and stop after 12 h reaching a conversion higher than 90%. The reactions in nitroben-

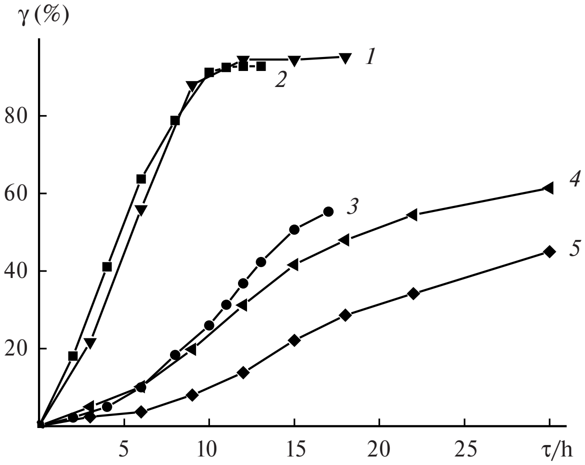


Fig. 2. Curves of transformation of PPID **4m** in the fused state (*1*) and in DPE at 240 °C (*2*), in nitrobenzene at 200 °C (*3*), in the glass-like state (*4*), and in the film (*5*).

zene at 200 °C (curve *3*), in the glass-like state (*4*), and in film (*5*) proceed significantly slower. Molecular weight of PPID does not influence the rate of the interaction.

Solubility properties of the polymers should be mentioned: in nitrobenzene PPID dissolves readily, whereas in DPE only under heating above 150 °C.

Conditions for the synthesis of some PAPA and PBA in the fused state and in DPE at 240 °C and in the concentration less than 20 wt % are given in Table 1.

The rearrangement of PID in DPE proceeds faster in the case of more flexible polymers, whereas rigid polymers are better to transform in the fused state.

From Table 1, it can be also seen that PAPA are formed significantly faster than PBA. Obviously, such a phenomenon confirmes the mechanism of the Chapman rearrangement.

The PPID **4i** and the product of its rearrangement, PAPA **6i**, were studied to determine the mechanism of the reaction of PPID by gel permeation chromatography (GPC) (Fig. 3). The GPC curve of PPID has a bimodal molecular weight distribution, which after the reaction already for the polyamide is virtually the same. Moreover, it was found that polymers PPID and polyamide have similar M_w (29120 and 28970, respectively), as well as M_n (16850 and 16300).

Identical molecular weights and a degree of polydispersion of polymers before and after the interaction attest that the molecular weight of the polymer does not change during the course of the reaction, *i.e.,* destructive processes, a sewing together, and depolymerization do not implement.

The rearrangement of a mixture of PPID **4f** and **5a** (1 : 1) was conducted in DPE for 20 h at 240 °C. The product was subjected to the thermomechanical analysis (TMA) (Fig. 4). On the TMA curve, two transitions into the viscously-liquid state were established. The shape of the TMA curve for the authentic mixture of rearrangement products was virtually the same.

Table 1. Rearrangement conditions and degree of conversion of PPID

PPID	[η]/dL g^{-1} (DMF)	In the fused state			In solution*	
		T/°C	τ/h	γ (%)	τ/h	γ (%)
4a	0.40	340	14	95.5	11	76.1
4f	0.30	340	14	92.4	12	76.6
4i	0.34	320	13	92.7	11	84.7
4h	0.36	310	14	90.3	11	84.0
4o	0.43	260	13	90.5	10	96.8
5c	0.33	340	16	90.5	13	84.5
5e	0.31	350	17	89.1	13	73.9
5f	0.29	340	17	90.1	14	73.9
5h	0.33	320	17	86.7	13	80.5
5m	0.40	260	16	89.6	12	95.8
5o	0.37	250	17	92.2	11	97.8

* At *T* = 240 °C.

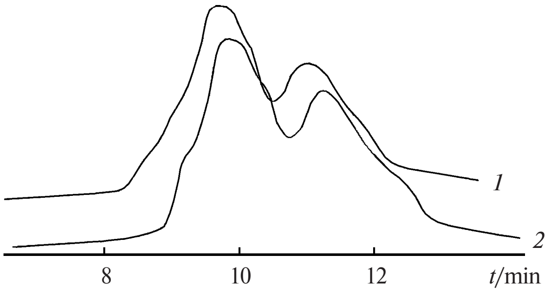


Fig. 3. Gel chromatograms of PPID **4** (*1*) and the corresponding polyamide (*2*).

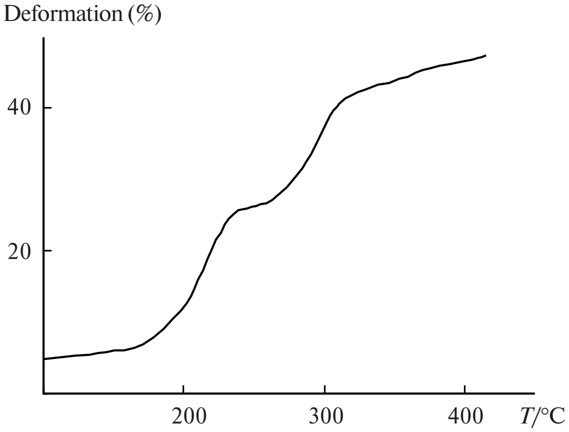


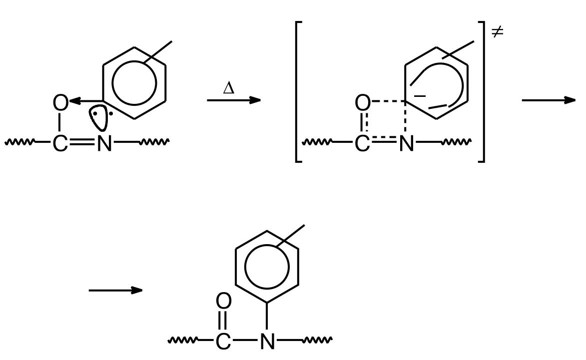
Fig. 4. TMA curve of the rearrangement products of PPID **4b,f** and **5d,g**.

It could be assumed that in this case, the two transitions on the TMA curve correspond to the glass-transition temperature of two polymers, rather than to the block-copolymer.[5,6] Formation of the block-copolymer suggested alternation of the PBA and PAPA units, which can appear in the case of intermolecular interaction of these polymers. In such an approach, the similarity of the molecular weights before and after the reaction can not be observed. Moreover, in the intermolecular interaction, the formation of a statistical copolymer is the most probable. Were this the case, only one glass-transition temperature would have been observed on the TMA curve.[5]

To summarize the data obtained, it could be suggested that the rearrangement proceeds intramolecularly without cleavage of the polymeric chain, the mechanisms of transformations of the low-molecular weight and high-molecular weight compounds are similar and consist in the attack of the lone electron pair of the nitrogen atom at the aromatic moiety (Scheme 4).

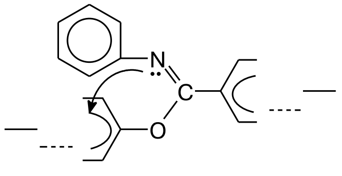
The migration of the latter occurs through the formation of the intramolecular four-membered transition complex, and the reaction proceeds as the nucleophilic substitution in the aromatic ring.

Scheme 4



It is obvious that for the fast and deep proceeding of the reaction, a high flexibility of the polymeric chain and compactness of the rearranging fragment are necessary.

The compactness of the rearranging fragment, in our view, is one of the principal reasons resulting in the slower rearrangement of PPID **5** relatively to PPID **4**. The major difference in them consists in the conformation of the rearranging fragment, which is caused by the particularities of the polymeric chain. The PPID **5** transforms slower since its fragment of the rearrangement is stretched along the polymeric chain, whereas in the PPID **4**, it is more compact. In addition, in PPID **4**, the reacting fragment is located in the side group, which significantly facilitates proceeding of the reaction.[7]



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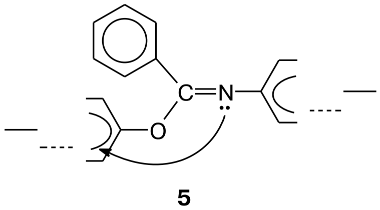

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The structures of PAPA and PBA were confirmed by the IR spectroscopy data (Fig. 5): a characteristic absorption in the region 1672 cm^{-1} (C=O) is recorded, whereas at 1210 cm^{-1} (C—O), the absorption is not found. In the ^{13}C NMR spectrum (DMSO-d$_6$), the signal at δ 165.8 corresponding to the amide functional group is present, at the same time, the signal of the imidoester carbon atom (δ 155.7) is absent. It should be noted that the elemental compositions of the starting PPID and the products of their rearrangement are identical.

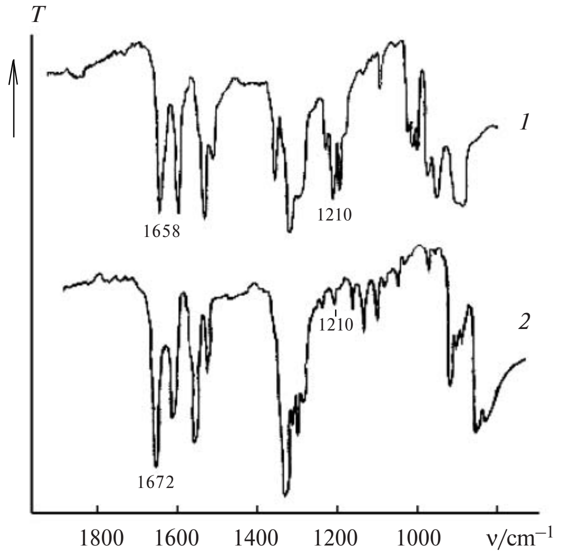

Fig. 5. IR spectra of PPID (*1*) and PAPA (*2*); *T* — transmission.

The polymers synthesized, similarly to the corresponding PPID, are soluble in DMF, DMAA, DMSO, *m*-cresol, pyridine, but, in contrast to the starting PPID, they dissolve in chloroform only under heating.

Thermal stability of the PAPA and PBA obtained changes insignificantly in comparison to the starting PPID: the glass-transition temperatures are 275—318 and 210—252 °C, respectively. The polyamides and polyamines synthesized significantly exceed PPID in their thermal stability: according to the TGA data, a 10% loss in weight is observed at 454—487 °C, which is much higher than for the corresponding starting PPID (360—415 °C).

Flexible and durable film materials with σ = 60.4—33.9 MPa and ε = 6.6—3.1% were obtained on the basis of PAPA and PBA.

In conclusion, a possibility for the synthesis of the well soluble, thermally stable, and film-forming poly(*N*-benzoylamines) and *N*-phenyl-substituted aromatic polyamides resulting from the transformation of polyphenyl imidates by the Chapman rearrangement has been demonstrated.

Experimental

Phenyl *N*-phenylbenzenecarboximidoate (**8**) was obtained in the reaction flask equipped with the inlet and outlet for argon. Anhydrous ethanol (250 mL) and phenol (0.3 mol) were placed into the flask, Na (0.25 mol) was added in small portions under argon. After dissolution of sodium, *N*-phenylbenzimidoyl chloride (0.25 mol) dissolved in dioxane (150 mL) was added slowly. After 15 h, the content of the flask was poured in ice and kept for 10 h at −18 °C. After defreezing, a precipitate was filtered off and recrystallized from anhydrous ethanol. Found (%): C, 83.18; H, 5.90; N, 4.95. $C_{19}H_{15}NO$. Calculated (%): C, 83.52; H, 5.49; N, 5.13.

***N*,*N*-Diphenylbenzamide (9)** was synthesized by the rearrangement of benzanyl imino ester under argon, the reaction time 13 h, m.p. 179.5—179.8 °C (*cf.* data in Ref. 8: m.p. 179.6 °C).

Starting PPID **4** and **5** were obtained in a three-neck flask (50 mL) equipped with a stirrer, inlet and outlet for argon. Bisphenol **1** (0.01 mol) and *N*-methyl-2-pyrrolidone (20 mL) were placed into it sequentially in the flow of argon, and the mixture was homogenized. Then, triethylamine (0.02 mol) and imidoyl chloride **2** or **3** (0.01 mol) (see Ref. 1) were added with vigorous stirring. The homogenized reaction mixture was placed into the heating bath and the temperature was raised to 170—180 °C. After 17—18 h, the mixture was poured into 2% aqueous ammonia, a precipitate was filtered off, gradually washed with 1% aq. sodium bisulfite and water, and dried in a vacuum oven at 60—70 °C until the weight is constant.

Polymers PAPA **6** and PBA **7** were synthesized by the rearrangement of the corresponding PPID under argon at the temperatures and reaction times given in Table 1.

Polymers **6** and **7** were obtained also under argon by the rearrangement of 10—15% solutions of the corresponding PPID in DPE. The temperatures and reaction times are given in Table 1.

IR spectra were recorded on a Specord IR-75 and Specord UR-20 spectrophotometers in the range of wave numbers 4000—400 cm^{-1}. The samples were prepared in KBr pellets. ^{13}C NMR spectra were recorded on a Varian VXR-500S spectrometer (400 MHz) in DMSO-d$_6$ with the concentrations of 10—15 wt %, Me$_4$Si was used as the internal standard.

Dynamic thermogravimetric analysis was carried out on a MOM Q-1000 derivatograph (Hungary) in air at the rate of heating 5 deg min^{-1}, Al$_2$O$_3$ was used as the comparison substance. Thermomechanical analysis was performed on a Tsetlin apparatus at the constant load of 0.08 MPa and the rate of heating 100 deg h^{-1}. Gel permeation chromatography of polymers was carried out on a Waters chromatograph with U-Styragel Linear as the column packing, refractometer detector, THF was used as the solvent, T = 20 °C, the rate of the flow 0.3 mL min^{-1}; the Maxima system was used for the data processing, polystyrene standards were used for the calibration.

Film materials were obtained by the pouring of 18—20% solutions of a polymer in DMF on the glass support.

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