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ORGANIC SYNTHESIS AND INDUSTRIAL ORGANIC CHEMISTRY

Rearrangement of Polyarylene Benzimidates into Poly(*N*-arylenebenzamides)

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Abstract—The transformation of polyarylene benzimidates prepared by polycondensation of bisphenols with benzimidoyl chlorides in *N*-methyl-2-pyrrolidone into poly(*N*-arylenebenzamides) was studied.

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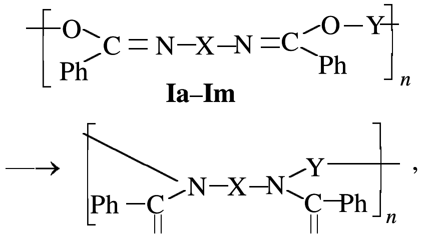
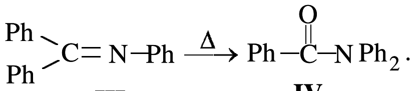
Polyarylene benzimidates (PBIs) prepared by polycondensation of imidoyl chlorides derived from aromatic mono- and dicarboxylic acids with bisphenols [1] exhibit high heat resistance and large interval between the decomposition onset and softening points. Specific features of the imidate bond and available data on its reactivity [2] allowed us to suggest the possibility of the following rearrangement in the polymer chain:



IIa–IIl

Ia, X = p-C_6H_4, Y = m-C_6H_4; **Ib**, X = p-C_6H_4, Y = $(p\text{-}C_6H_4)_2CMe_2$; **Ic**, X = p-C_6H_4, Y = $(p\text{-}C_6H_4)_2SO_2$; **Id**, X = m-C_6H_4, Y = p-C_6H_4; **Ie**, X = Y = m-C_6H_4; **If**, X = m-C_6H_4, Y = $(p\text{-}C_6H_4)_2CMe_2$; **Ig**, X = m-C_6H_4, Y = $(p\text{-}C_6H_4)_2SO_2$; **Ih**, X = $(p\text{-}C_6H_4)_2O$, Y = p-C_6H_4; **Ii**, X = $(p\text{-}C_6H_4)_2O$, Y = m-C_6H_4; **Ij**, X = $(p\text{-}C_6H_4)_2O$, Y = $(p\text{-}C_6H_4)_2SO_2$; **Ik**, X = $(p\text{-}C_6H_4)_2 \cdot CH_2$, Y = p-C_6H_4; **Il**, X = $(p\text{-}C_6H_4)_2CH_2$, Y = m-C_6H_4; **Im**, X = $(p\text{-}C_6H_4)_2CH_2$, Y = $(p\text{-}C_6H_4)_2CMe_2$; **IIa**, X = Y = m-C_6H_4; **IIb**, X = p-C_6H_4, Y = $(p\text{-}C_6H_4)_2CMe_2$; **IIc**, X = p-C_6H_4, Y = $(p\text{-}C_6H_4)_2SO_2$; **IId**, X = m-C_6H_4, Y = p-C_6H_4; **IIe**, X = Y = m-C_6H_4; **IIf**, X = m-C_6H_4, Y = $(p\text{-}C_6H_4)_2CMe_2$; **IIg**, X = $(p\text{-}C_6H_4)_2O$, Y = m-C_6H_4; **IIh**, X = $(p\text{-}C_6H_4)_2O$, Y = $(p\text{-}C_6H_4)_2SO_2$; **IIi**, X = $(p\text{-}C_6H_4)_2CH_2$, Y = p-C_6H_4; **IIj**, X = $(p\text{-}C_6H_4)_2CH_2$, Y = m-C_6H_4; **IIk**, X = $(p\text{-}C_6H_4)_2CH_2$, Y = $(p\text{-}C_6H_4)_2CMe_2$; **IIl**, X = $(p\text{-}C_6H_4)_2CH_2$, Y = $(p\text{-}C_6H_4)_2SO_2$.

Initially we studied the rearrangement of a model compound, phenyl *N*-phenylbenzimidate **III**, into *N*,*N*-diphenylbenzamide **IV**, known as Chapman rearrangement [3]:



III **IV**

We found that heating of **III** at 250°C for 13 h leads to its complete transformation into **IV**. The structure of the product was proved by IR and ^{13}C NMR spectroscopy. The IR spectrum of **IV** contains a C=O absorption band at 1657 cm^{-1}, whereas the C–O band at 1210 cm^{-1} is absent. In the ^{13}C NMR spectrum of **IV**, a carbonyl carbon signal appears at 170.53 ppm.

Having obtained the positive result in the model reaction, we examined the possibility of the similar rearrangement in PBIs.

The possibility of thermal rearrangement of the polymers was checked with **Ie** as example (Fig. 1). The first evidences of the transformation in the melt appear in 3 h, after which the reaction accelerates and is complete in 18 h at 86% conversion. The rearrangement in a film and in the glassy state involves a long induction period and therefore takes more than 30 h. The rearrangement of **Ie**, according to viscosity measurements, is not accompanied by significant changes in the molecular weight. The conversion was estimated from the IR spectra (absorption of the imido ester bond).

Figure 1 shows the conversion curves of **If** in nitrobenzene (NB) and diphenyl ether (DPE). The behavior of **If** in these solvents was different. In NB, compound **If** dissolved immediately without swelling, whereas in DPE the dissolution occurred only on heating above 150°C. Nevertheless, at equal other conditions, the rearrangement in DPE was faster.

We found that the molecular weight of PBI did not noticeably affect the kinetic parameters of the reaction.

Our results show that the rearrangement of PBIs into poly(*N*-arylenebenzamides) (PBAs) occurred considerably more readily in the melt and in DPE at 240°C. The conditions for preparing some PBAs are given in Table 1.

For more flexible PBIs **Ie**, **If**, **Il**, and **Im**, the transformation occurs to a greater extent in DPE, and for more rigid PBIs, in the melt.

The structures of PBAs were confirmed by IR spectroscopy: The C=N absorption band in PBIs at 1658 cm^{-1} shifted to 1672 cm^{-1}, and the C–O band at 1220 cm^{-1} virtually disappeared. The most convincing proof is furnished by ^{13}C NMR spectroscopy: In the spectra of PBAs, a signal of the carbonyl carbon atom appears at 174.7 ppm.

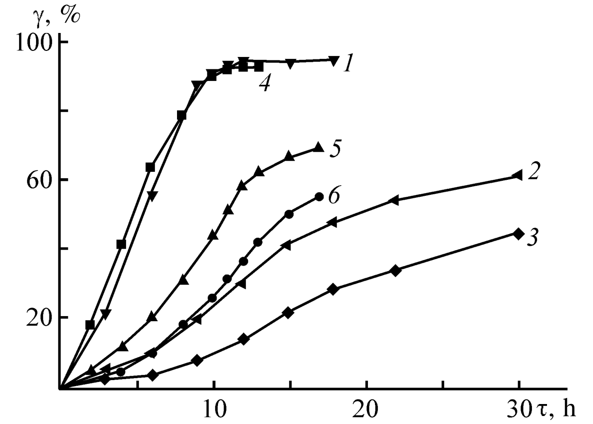
The PBAs obtained, like the starting PBIs, are soluble in DMF, *N*,*N*-dimethylacetamide, DMSO, *m*-cresol, and pyridine, but, in contrast to the starting polymers, dissolve in chloroform only on heating.

The glass transition point of the polymers changes insignificantly upon PBI → PBA rearrangement: from 275–318 to 210–252°C, respectively. The PBAs prepared significantly surpass the PIDs in the heat resistance: The 10% weight loss (TGA in air, 5 deg min^{-1}) is observed at 454–487°C (for the starting PIDs, at 360–415°C).

The PBAs obtained exhibit good film-forming properties; the physicomechanical characteristics of the films are given in Table 2. The properties of the press materials prepared by pressing PBA powders at 70–75 MPa/250–350°C are also given in Table 2.

EXPERIMENTAL

The IR spectra were recorded on Specord IR-75 and UR-20 spectrophotometers (4000–400 cm^{-1}) in KBr. The ^{13}C NMR spectra were taken on a Varian VXR-500S spectrometer (400.0 MHz for ^1H) in DMSO-d_6, internal reference TMS.



PBI conversion γ as a function of time τ in (*1*) melt, (*2*) glassy state, (*3*) film, (*4*) DPE at 240°C, (*5*) DPE at 200°C, and (*6*) NB at 200°C.

Dynamic thermogravimetric analysis was performed with a Q-1000 derivatograph in air at a heating rate of 5 deg min^{-1}, with Al_2O_3 as reference. The thermomechanical analysis was performed with a Tsetlin device at a constant load of 0.08 MPa and a heating rate of 100 deg h^{-1}.

Film materials were obtained by casting an 18–20% solution of a polymer in DMF onto a glass support. Physicomechanical tests of film samples were performed according to GOST (State Standard) 14236–81 (COMECON Standard 1490–79), and those of press materials, according to GOSTs 4647–80 and 4648–71.

Phenyl *N*-phenylbenzimidate. A flask equipped with tubes for argon inlet and outlet was charged with

Table 1. Conditions for the rearrangement of PBIs and conversions γ

PBI	In melt			In solution	
	T, °C	τ, h	γ, %	τ, h	γ, %
Ia	340	17	89.7	14	79.2
Ib	290	17	88.3	14	87.1
Ic	320	16	90.2	14	78.8
Id	350	17	89.1	13	87.9
Ie	330	18	86.3	14	89.4
If	260	16	89.6	11	92.8
Ig	290	16	92.0	13	89.6
Ih	340	16	87.4	12	80.2
Ii	340	16	90.5	11	84.5
Ij	300	17	91.3	12	90.3
Ik	320	17	86.7	13	80.5
Il	290	17	90.8	11	94.0
Im	250	17	92.2	10	97.8

Table 2. Physicomechanical properties of PBA films and press materials*

PBA	Films		Press materials	
	σ_t, MPa	ε_b, %	σ_t, MPa	*a*, MPa
IIa	60.7	3.0	60.4	8.2
IIb	39.2	4.6	–	–
IIc	–	–	58.8	6.9
IId	–	–	59.2	6.6
IIe	55.6	3.8	57.5	6.8
IIf	40.8	4.9	–	–
IIg	–	–	62.6	7.3
IIh	42.6	5.5	–	–
IIi	–	–	60.7	8.4
IIj	41.8	4.8	–	–
IIk	39.1	5.0	–	–
IIl	–	–	59.1	7.1

* (σ_t) Breaking tensile stress, (ε_b) relative break elongation, and (*a*) specific impact resilience.

250 ml of absolute ethanol and 0.3 mol of phenol; 0.25 mol of Na was added in small portions while purging with Ar. After the reaction completion, a solution of 0.25 mol of *N*-phenylbenzimidoyl chloride in dioxane was slowly added. After stirring for 15 h, the mixture was poured onto 300 ml of ice and placed in a freezing chamber for 10 h, after which it was allowed to warm up to room temperature. The precipitate was filtered off and recrystallized from absolute ethanol; yield 87.4%.

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** was prepared by rearrangement of phenyl *N*-phenylbenzimidate in an inert atmosphere at 250°C for 13 h; mp 179.5–179.8°C (cf. 179.6°C [4]).

Polyarylene benzimidates were prepared in a 50-ml three-necked flask equipped with a stirrer and with tubes for argon inlet and outlet. A mixture of 0.01 mol of bisphenol with *N*-methyl-2-pyrrolidone was added while purging with argon, and the mixture was homogenized. Then 0.02 mol of triethylamine and 0.01 mol of appropriate imidoyl chloride were added with vigorous stirring. The homogenized reaction mixture was heated to 170–180°C for 17–18 h, after which the product was precipitated by pouring the mixture into 2% aqueous ammonia, filtered off, washed with a 1% solution of sodium bisulfite in water and with water, and dried in a vacuum at 60–70°C to constant weight.

Poly(*N*-arylenebenzamides) were prepared by rearrangement of the corresponding PBIs under Ar in the melt and in DPE (Table 1).

CONCLUSION

Film-forming poly(*N*-arylenebenzamides) were prepared by rearrangement of polyarylene benzimidates in the melt and in diphenyl ether at 240°C. The polymers obtained exhibit good solubility, high resistance to thermal oxidative degradation, and relatively low softening points.

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