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MACROMOLECULAR COMPOUNDS AND POLYMERIC MATERIALS

Films of Polyamides with Phenylpyridine Units in the Backbone

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Abstract—New polyamides derived from 2-(4-aminophenyl)-5-aminopyridine, 4,4-diaminodiphenyl ether, and 4,4'-terephthaloyloxybis(3-methoxybenzoic) acid dichloride were prepared. These polyamides are of interest as macromolecular ligands. The deformation–strength, thermomechanical, and thermal properties of films of polyamides with various content of phenylpyridine fragments were studied.

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The design, synthesis, and study of properties of new polymers containing heterorings are of much interest for both basic and applied chemistry, because such systems often exhibit unique properties: high strength and heat resistance in combination with the capability to form stable complexes with transition metals. Among such systems, researchers' attention has recently been attracted by polymers containing in the backbone [1] or pendant groups [2] 2-phenylpyridine (PP) fragments. Such polymers can act as macromolecular ligands in formation of electrically neutral metal–polymer complexes with Ir(III). These compounds exhibit a unique combination of chemical stability and luminescence and redox properties [3, 4]. Here we report on the synthesis and properties of a new series of polyamides (PAs) containing PP units in the backbone.

EXPERIMENTAL

Commercial solvents and chemicals were used without additional purification and drying.

2-(4-Aminophenyl)-5-aminopyridine was prepared in four steps. The first two steps have been implemented for the first time.

1,3-Bis(piperidinyl)trimethinium perchlorate I. To 1,1,3,3-tetramethoxypropane (14 ml, 0.085 mol), we added with stirring 8 ml of 57% perchloric acid and allowed the mixture to stand for 1 h at room temperature. Then piperidine (16.8 ml, 0.17 mol) was added dropwise with stirring and cooling on a water bath. The mixture was stirred for 20 min, after which 10 ml of 57% perchloric acid was added. In 20 min, the mixture was placed for 3 h in a refrigerator for complete precipitation of the product, after which the yellow precipitate was filtered off and washed with diethyl ether (2 × 5 ml). Yield 15.8 g (61%), mp 125–128°C. ^{1}H NMR spectrum, δ, ppm (300 MHz, DMSO-d_6): 7.67 d (J = 11.7 Hz, 2H, H^1 and H^3), 5.78 t (J = 11.7 Hz, 1H, H^2), 3.56 m (8H, $2CH_2NCH_2$), 1.60 m (12H, $2CH_2CH_2CH_2$).

2-Nitro-1,3-bis(piperidinyl)trimethinium perchlorate II. To a suspension of **I** (10.9 g, 0.036 mol) in acetic anhydride (12.5 ml), cooled to 0°C, we added dropwise with stirring nitric acid (3.0 ml, ρ = 1.4 g cm^{-3}), also cooled to 0°C, maintaining the reaction mixture temperature no higher than 3°C. The mixture was stirred on an ice bath for 1 h. Then 10 g of ice was added, and the pale yellow precipitate was filtered off and washed with ice-cold water (10 ml) and diethyl ether (2 × 5 ml). Yield 10.5 g (83%), mp 155–157°C (dec.). ^{1}H NMR spectrum, δ, ppm (300 MHz, $CDCl_3$): 8.42 s (2H, H^1 and H^3), 4.02–3.92 m (4H, $2CH_2N$), 3.76–3.66 m (4H,

$2CH_2N$), 2.00–1.73 m (12H, $2CH_2CH_2CH_2$).

The next two steps were performed by the procedure described in [1].

2-(4-Nitrophenyl)-5-nitropyridine III. A 100-ml three-necked round-bottomed flask equipped with a magnetic stirrer, an internal thermometer, a reflux condenser, and a dropping funnel was charged with a suspension of **II** (10.5 g, 0.03 mol) and *p*-nitroacetophenone (4.1 g, 0.025 mol) in acetonitrile (15 ml). The contents were cooled to 0°C, and triethylamine (7.5 ml, 0.054 mol) was added dropwise with the reaction mixture temperature maintained at approximately 5°C. The mixture was stirred at room temperature for 3 h. Then glacial acetic acid (8.6 ml) and ammonium acetate (11.5 g) were added, and the mixture was heated to 50°C and stirred for 5 h. After cooling, the grey-yellow precipitate was filtered off and washed with water, ethanol, and diethyl ether. Yield 3.7 g (80%), mp 210–213°C. ^1H NMR spectrum, δ, ppm (300 MHz, DMSO-d_6): 9.51 d (J = 3.0 Hz, 1H, 6-Py–H), 8.75 dd (J = 3.0 and 9.0 Hz, 1H, 4-Py–H), 8.50–8.30 m (5H, 3-Py–H and 4H–Ph).

2-(4-Aminophenyl)-5-aminopyridine IV. A 1-l round-bottomed flask equipped with a magnetic stirrer, a reflux condenser, and a tube for feeding argon was charged with a solution of **III** (3.5 g, 0.019 mol) in tetrahydrofuran (500 ml) and 1.22 g of 10% Pd/C as catalyst. The reaction was performed in an argon atmosphere. The mixture was heated to boil, and 18.4 ml of hydrazine hydrate (90%) was slowly added dropwise. Refluxing under argon was continued for an additional 3.5 h. TLC analysis (silica gel, eluent methylene chloride–methanol, 6 : 1) showed that the reaction was complete. The catalyst was filtered off through a dense paper filter. The filtrate was evaporated to dryness at reduced pressure and vacuum-dried at 61°C for 1 h. Yellow product, yield 2.33 g (99%), mp 195–196°C. ^1H NMR spectrum, δ, ppm (300 MHz, DMSO-d_6): 7.93 d (J = 3.0 Hz, 1H, H^2), 7.59 d (J = 9.0 Hz, 2H, 2,6-Ph–H), 7.41 d (J = 9.0 Hz, 1H, 3-Py–H), 6.93 dd (J = 3.0 and 9.0 Hz, 1H, 4-Py–H), 6.57 d (J = 9.0 Hz, 2H, 3,5-Ph–H), 5.19 s (2H, Py–NH_2), 5.10 s (2H, Py–NH_2).

To prepare the copolyamide, a two-necked round-bottomed flask was charged with a mixture of 2-(4-aminophenyl)-5-aminopyridine (0.057 g, 3 mmol) and diaminodiphenyl ether (0.348 g, 17.4 mmol) in *N*-methyl-2-pyrrolidone (N-MP) (3.64 ml) in 0.1 : 0.9 molar ratio. The mixture was stirred until the components fully dissolved. To the solution cooled to –12°C we added 4,4'-terephthaloyloxybis(3-methoxybenzoic) acid dichloride (0.258 g). The suspension was stirred at this temperature for 1 h, allowed to warm up to room temperature, and stirred at room temperature for an additional 1 h. Then several drops of propylene oxide were added, and the mixture was stirred for 3 h more. The resulting viscous solution of the copolyamide in N-MP was filtered through a glass frit.

The ^1H NMR spectra of 1% solutions of substances were recorded with an Avance-400 spectrometer (Bruker, Germany) operating at 400 MHz, with Me_4Si as internal reference.

The copolyamide films were prepared by casting from polymer solutions onto glass supports using a template. The formed solution layers were vacuum-dried to constant weight (8 h) at 80°C. The film thickness was 20–25 μm.

The mechanical characteristics and transition temperatures were determined using films with the working area size of 20 × 2 mm.

Mechanical tests of the films were performed with a UTS 10 universal installation (UTStestsysteme, Germany) in the uniaxial extension mode. In the course of tests, we determined the elastic modulus E, plastic limit σ_p, tensile strength σ_t, and elongation at break ε_b.

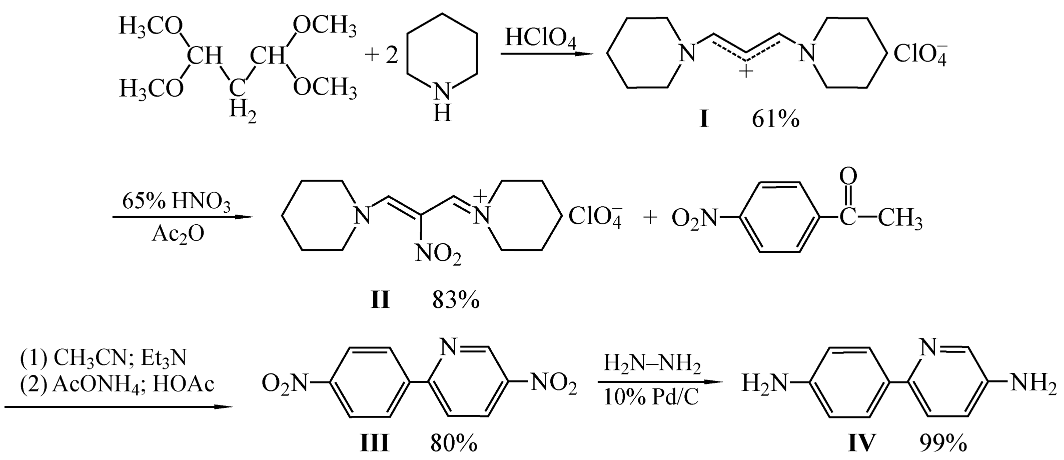
The temperatures of transitions occurring in the course of heating of copolyamide films were determined by thermomechanical analysis with a UMIV-3 device (Tochpribor, Ivanovo, Russia) in the course of sample heating at a rate of 5 deg min^{-1} under a constant tensile load $\sigma \le 0.5$ MPa.

Thermal gravimetric analysis (TGA) of films was performed with a laboratory thermal balance in the self-generated atmosphere at a heating rate of 5 deg min^{-1}. From the TGA data we determined the heat resistance parameters of the copolyamide films: τ_1, τ_5, and τ_{10} (temperatures corresponding to 1, 5, and 10% weight loss of the polymer in the course of heating, respectively).

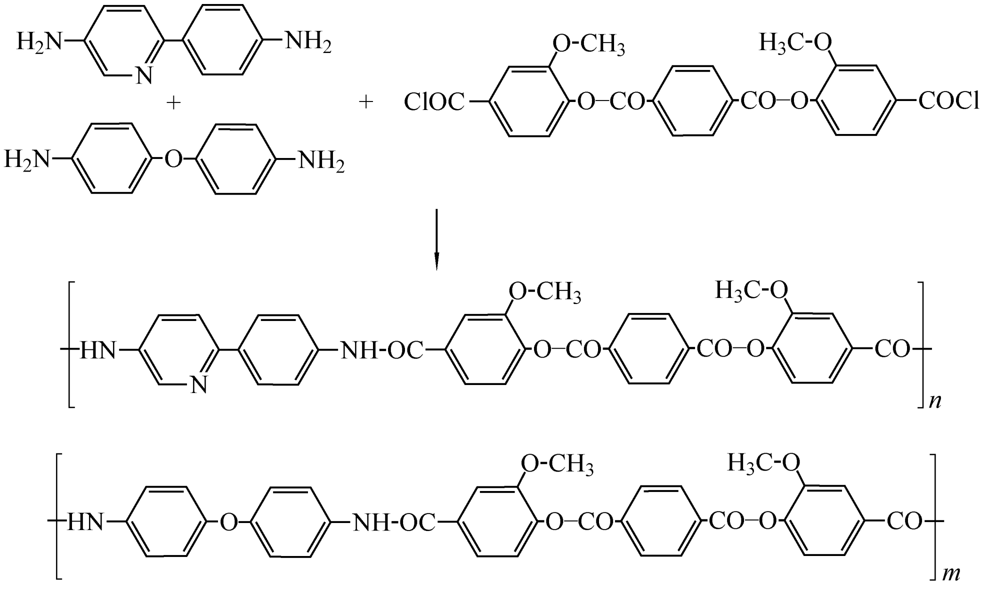
As a monomer used in the synthesis of the polymers with 2-phenylpyridine units we chose 2-(4-aminophenyl)-5-aminopyridine. The scheme of its synthesis is given in Scheme 1.

From the monomer obtained and 4,4'-diaminodiphenyl ether, we prepared by low-temperature polycondensation a series of polyamides with different content of 2-phenylpyridine units. As chloride component we

Scheme 1.



Scheme 2.



$n = 0, 10, 20, 30, 40$ mol%

used 4,4'-terephthaloyloxybis(3-methoxybenzoic) acid dichloride ensuring formation of highly strong, heat-resistant polymers exhibiting high intrinsic viscosity [5] (Scheme 2):

The maximal content of 2-phenylpyridine units n in the copolyamide was 40 mol %. Synthesis of polymers with $n > 40$ mol % was accompanied by intense gelation in solutions.

In our study we evaluated the mechanical properties, determined the characteristics of physical transitions, and performed thermal gravimetric tests of films of the synthesized copolyamides in relation to the content of phenylpyridine fragments in polymer chains.

With an increase in the concentration of PP rings in elementary units, quite definite and regular changes in the mechanical behavior of films are observed (Table 1, Fig. 1). First and foremost, a regular increase in the elastic modulus of films with an increase in the content of these rings should be noted. This effect reflects enhancement of intermolecular interactions in the material, which can be associated both with a certain increase in the degree of ordering of the supramolecular structure of

Table 1. Mechanical characteristics of copolyamide films with various concentrations of phenylpyridine rings Concentration of units with PP, %

E, GPa	σ_p, MPa	σ_t, MPa	ε_b, %	ε_p, %
0	4.31 ± 0.07	132 ± 3	181 ± 8	34 ± 2
10	4.27 ± 0.06	133 ± 4	179 ± 6	33 ± 3
20	4.29 ± 0.09	134 ± 2	191 ± 6	38 ± 3
30	4.56 ± 0.19	132 ± 5	181 ± 5	41 ± 3
40	4.62 ± 0.11	129 ± 3	162 ± 4	51 ± 3

the film (increase in the concentration of bonds without changes in their type) and with formation of new intermolecular hydrogen bonds involving nitrogen atoms of the phenylpyridine ring [6]. Apparently, enhancement of intermolecular interactions takes place already in the polymer solution, as judged from the tendency to gelation, observed in the copolyamide solutions at increased (up to 40%) concentrations of PP in polymer chains.

In the region of high strains (when the plastic limit is exceeded), the character of variation of the deformation behavior of films with an increase in the concentration of PP rings becomes different: The material demonstrates more and more pronounced plastic behavior. Whereas the deformation process observed with samples containing no PP rings (Fig. 1, curve *1*) is typical of polymer films with prevalent induced highly elastic deformation behavior, with an increase in the concentration of PP units to 40% (Fig. 1, going to curve *5*) a well-defined maximum, "plasticity tooth," appears in the extension diagram at approximately 6% strain, which is followed by more and more pronounced necking.

After passing to the section of deformation strengthening, the current modulus of the material regularly decreases with an increase in the concentration of PP rings (regular decrease in the slope of curves in this deformation range, observed in going from the homopolyamide to the copolyamide containing 40% PP units), i.e., with an increase in the PP concentration the material deformation in this range occurs with decreasing energy consumption. Because in this portion of the extension diagram the film deformation occurs mainly at the expense of conformational rearrangement of macrochains, it can be concluded that incorporation of PP rings into the polymer chain leads to a decrease in the mean energy of transitions from rolled-up to straightened conformations of macrochains.

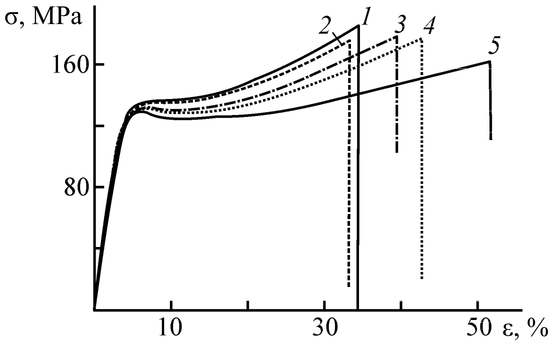


Fig. 1. Extension diagrams of copolyamide films. (σ) Stress and (ε) strain. Content of units with PP rings in the chains, %: (*1*) 0, (*2*) 10, (*3*) 20, (*4*) 30, and (*5*) 40.

Finally, a regular increase in the elongation at break of films with an increase in the content of units with PP rings in copolyamide chains can be noted: an increase in the concentration of these units from 0 to 40% leads to an increase in ε_b of the film by a factor of 1.5. As already noted, this increase is mainly due to the fact that a more and more extended segment in which the plastic mechanism of material deformation prevails becomes involved in the deformation process, and this is followed by transition to the range where deformations due to conformational transitions in the chains become prevalent.

In thermomechanical tests, we obtained curves of the temperature dependence of the sample strain at a constant extending load (Fig. 2). In all the curves (characterizing films with different PP content), there are two regions of sharp increase in the ductility: at 200–225 and 300–310°C (Table 2). The first of these transitions is apparently devitrification, whereas the second, high-temperature, transition is associated with rearrangements on the chemical level. Indeed, in attempts of multiple recording of this transition with sample heating in each measurement cycle to the temperature exceeding by 10°C the transition temperature, followed by cooling before the next measurement cycle, we observed a noticeable decrease in the intensity of the defrosting of the mobility from cycle to cycle and a gradual shift of the transition toward higher temperatures. This transition is observed at essentially the same temperature as the onset of material degradation in the TGA curves (its temperature practically coincides with the τ_1 point in the TGA curves, Table 2).

Finally, with the films containing PP rings, we recorded one more transition, a low-temperature

Table 2. Transition temperatures and parameters of heat resistance of copolyamide films with various concentrations of phenylpyridine rings

Concentration of units with PP, %	$T_{\text{transition}}$	τ_1	τ_5	τ_{10}
	°C			
0	226, 309	310	351	367
10	108, 216, 311	310	350	364
20	117, 211, 306	305	344	359
40	128, 198, 304	295	336	350

process (in the interval 110–130°C) of very low intensity (Table 2). With the film of the homopolyamide containing no PP rings, this process was not detected. Presumably, it reflects activation of short-scale mobility associated specifically with the PP rings in the polymer chains.

As seen from the TGA data (Fig. 3, Table 2), the release of volatiles from the examined films is multistep. In the first step, at temperatures of up to 120°C, the sorbed water is removed. Its content in the films is on the level of 1–3%. Further heating to 220–230°C is accompanied by the removal of the residual solvent in which the synthesis was performed, N-MP, and only on heating to approximately 300°C the polymer itself starts to degrade. The degradation, in turn, occurs in two steps readily discernible in the TGA curves, especially in the differential curves (Fig. 3b). The first step with the maximal weight loss intensity in the range 370–385°C is complete at 400–420°C, and the second, high-temperature, step of the degradation occurs at temperatures above 460–470°C.

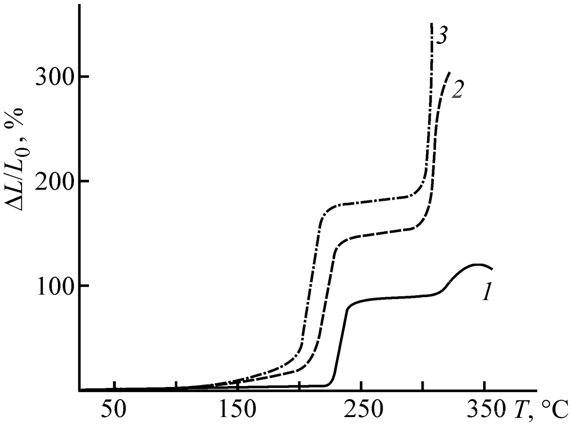


Fig. 2. Thermomechanical curves of copolyamide films. ($\Delta L/L_0$) Relative elongation and (T) temperature. Content of units with PP rings in the chains, %: (*1*) 0, (*2*) 20, and (*3*) 40; the same for Fig. 3.

It should be noted that, in the first step of the polymer degradation, significant release of volatiles is observed: from 24% (of the polymer weight) for the homopolyamide to 20% for the copolyamide containing 40% units with PP.

As the concentration of units with PP in copolyamide chains is increased, all the parameters of the heat resistance of the film regularly decrease: both steps of thermal degradation are shifted toward lower temperatures.

Such character of the thermal behavior of the synthesized polymers becomes clear if we take into account that thermal degradation of polyamides derived from 4,4'-terephthaloyloxybis(3-methoxybenzoic) acid dichloride and aromatic diamines is accompanied by partial cross-linking. It was shown previously [7] that the heat resistance of such systems and their degradation rate are primarily determined by the structure of the diamine fragment. Studies of the mechanical properties of the copolyamides with various contents of 2-phenylpyridine units showed that, at high strains when the processes are

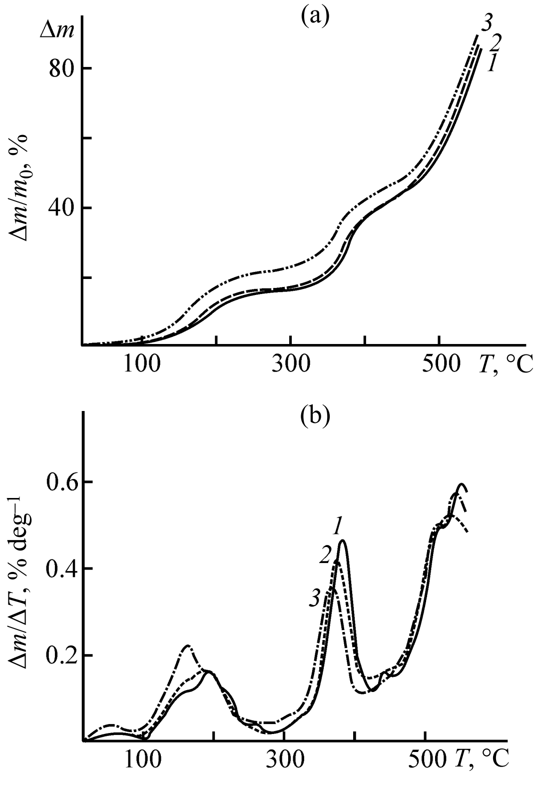


Fig. 3. TGA curves of copolyamide films. (T) Temperature; (a) integral ($\Delta m/m_0$) and (b) differential ($\Delta m/\Delta T$) weight loss curves.

determined by conformational transitions, introduction of these units leads to a decrease in the rigidity of the polymer chain. This, in turn, leads to a certain decrease in the heat resistance of the polymers in the range 350–400°C, namely, to increased intensity of the release of volatiles on heating the films in this temperature range. In the same temperature range, the nitrogen-containing heterorings start to degrade, which is accompanied by formation of partially cross-linked structures. Their degradation corresponds to the high-temperature step starting at 460–470°C.

Thus, a study of the behavior of the copolyamide films on heating shows that the upper limit of the admissible operation temperature of these films is determined by the glass transition point, which is equal to 200–225°C and slightly decreases with an increase in the content of units with PP in the chains.

CONCLUSIONS

(1) The developed synthesis procedure allowed preparation of strong elastic films of the copolyamides containing up to 40% units with phenylpyridine heterorings in the chains.

(2) A relaxation transition at 200–225°C, associated with the material devitrification, and a high-temperature transition at 305–310°C, accompanied by the onset of thermal degradation, were recorded.

(3) Thermal degradation of the polymers occurs in two steps: at 300–400 and above 460–470°C.

(4) An increase in the concentration of units with phenylpyridine rings leads to an increase in the elastic modulus and elongation at break of the films, and also to the shift of the relaxation transition temperatures and heat resistance parameters toward lower temperatures.

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REFERENCES

1. Aixiang Xia, Guanghua Lu, Xuepeng Qiu, et al., *J. Appl. Polym. Sci.,* 2006, vol. 102, no. 2, pp. 1844–1851.
2. Jae-Suk Lee, Nam-Goo Kang, Young-Sun Cho, et al., *Polym. Prepr*., 2001, vol. 42, no. 2, pp. 448–449.
3. Bolletta, F. and Balzani, V., *Inorg. Chem. Acta*, 1982, vol. 62, pp. 207–213.
4. Peng, Z. and Gharavi, A.R., *J. Am. Chem. Soc*., 1997, vol. 119, no. 20, pp. 4622–4632.
5. Goikhman, M.Ya., Podeshvo, I.V., and Mikhailov, G.M., *Zh. Prikl. Khim*., 1997, vol. 70, no. 2, pp. 312–326.
6. Artem'eva, V.N., Borovik, V.P., Denisov, V.M., et al., *Izv. Akad. Nauk SSSR, Ser. Khim*., 1988, no. 2, pp. 405–409.
7. Sazanov, Yu.N., Podeshvo, I.V., Mikhailov, G.M., et al., *Zh. Prikl. Khim*., 2002, vol. 75, no. 5, pp. 795–798.