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POLIMERY

MIESIĘCZNIK POŚWIĘCONY CHEMII, TECHNOLOGII i PRZETWÓRSTWU POLIMERÓW

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New aromatic polyesteramides: synthesis and properties

Summary — New aromatic polyesteramides with fairly high average molecular weight [(72—229) · 10^3] and rather narrow polydispersity in the range of 2.0—3.7 were prepared by polycondensation reaction of different aromatic diamines with a diacid chloride containing preformed ester groups. These polymers, easily soluble in *N*-methylpyrrolidinone, were cast into transparent, flexible films of various thickness (5—40 μm). The polymers showed high thermal stability with initial decomposition temperature above 340 °C and glass transition temperature in the range of 190—220 °C. The viscoelastic behavior of the new polyesteramides was investigated in the temperature range from -100 °C to 260 °C by dynamic mechanical analysis.

Keywords: polyesteramides, synthesis, chemical structure, thermal stability, viscoelastic properties.

NOWE AROMATYCZNE POLIESTROAMIDY: SYNTEZA I WŁAŚCIWOŚCI

Streszczenie — W wyniku polikondensacji 5 różnych diamin aromatycznych z chlorkiem kwasowym zawierającym grupy estrowe [dichlorkiem bis-3-oksybenzoilotereftaloilu o wzorze (I), schemat A], otrzymano szereg różniących się budową chemiczną nowych aromatycznych poliestroamidów (IIIa)—(IIIe) (schemat D, rys. 1 i 2). Produkty te charakteryzowały się dość dużym ciężarem cząsteczkowym [(72—229) · 10^3] oraz niewielką polidyspersyjnością mieszczącą się w przedziale 2,0—3,7 (metoda GPC, tabela 1). Ich dobra rozpuszczalność w *N*-metylopirolidynonie umożliwiła uzyskanie na ich podstawie wylewanych przezroczystych, giętkich folii grubości 5—40 μm. Przedstawiono wyniki badania poliestroamidów metodami analizy termograwimetrycznej (TGA, rys. 3) i różnicowej kalorymetrii skaningowej (DSC, tabela 2, rys. 4). Szczególnie dużo miejsca poświęcono interpretacji wyników uzyskanych metodami dynamicznej analizy mechanicznej w przedziale od -100 °C do +260 °C (rys. 5—9, tabela 2) oraz właściwościom cieplnym (rys. 3 i 4, tabela 2). Podkreślono przy tym, że badane polimery odznaczają się bardzo dobrą odpornością cieplną (początkowa temperatura rozkładu przekracza 340 °C). Ich temperatura zeszklenia mieści się — w zależności od budowy chemicznej — w przedziale 190—220 °C.

Słowa kluczowe: poliestroamidy, synteza, budowa chemiczna, odporność cieplna, właściwości lepkosprężyste.

Aromatic polyamides (polyaramids), similar as polyimides, belong to an important category of materials and represent now one of the key topics in polymer chemistry and physics. They are characterized by a high thermal stability and therefore are essential for various technical applications that require operation at increased temperatures, while maintaining their structural integrity as well as their physico-chemical and mechanical properties [1—4].

However, all of these polymers have a common impediment, namely, they are difficult to process owing to their infusibility and poor solubility in organic solvents. These undesired properties are caused by the strong interchain forces, inherent macromolecular rigidity or semicrystallinity. Therefore, much effort has been made to develop structurally modified polymers having increased solubility, hence processability, while maintaining a good thermal stability. The solubility of the polymers is often increased when flexible bonds, large pendant groups or polar substituents are incorporated into the polymer chain. Insertion of ester, ether or other flexible groups in the main chain has been found to be an effective approach towards improving processability, although with some negative effect on the thermal stability [5—8].

Alternating polyesteramides are regular copolymers which combine the good properties of both — the polyester and polyamide — such as high melting temperature, fast crystallization, good mechanical properties, good solvent resistance and low water absorption. They may be considered for application as engineering plastics, thermoplastic elastomers or biodegradable polymers [9—12].

In this context the goal of this article is the synthesis and characterization of new polyesteramides with substantially improved solubility (particularly in *N*-methylpyrrolidinone) and processability into thin flexible films. These polymers were synthesized by the polycondensation reaction of different aromatic diamines with a diacid chloride containing preformed esters groups, namely terephthaloyl-bis(2-oxybenzoyl chloride). Their properties, such as solubility, thermal stability, glass transition temperature and average molecular weight, have been evaluated with respect to their chemical structure. Dynamic mechanical analysis was used to explore the viscoelastic properties in term of the storage modulus and tan δ as a function of temperature.

EXPERIMENTAL

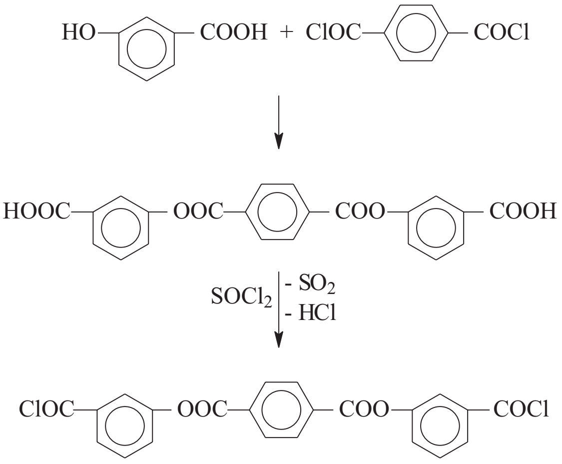
Materials

N-methylpyrrolidinone (NMP) (Merck) was dried over phosphorous pentoxide and distilled under reduced pressure. Thionyl chloride (Riedel de Haen) was freshly distilled before use. 3-Hydroxybenzoic acid (Merck) and 1,4-bis-(*p*-aminophenoxy-phenyl)-2,2-isopropane (Hoechst Celanese) were used as received. 2,6-Dichlorobenzonitrile, *p*-aminophenol, terephthalic and isophthalic acid, sodium hydroxide, hydrochloric acid, pyridine were provided by various commercial suppliers and used as received.

Synthesis of substrates for polycondensation

Diacid chloride with ester groups

Terephthaloyl-bis(3-oxybenzoyl-chloride) (I), was prepared by treating with thionyl chloride the corresponding diester-dicarboxylic acid, previously obtained from the reaction of 3-hydroxybenzoic acid with therephthaloyl chloride, according to a procedure described elsewhere (Scheme A) [13—16]. After recrystallization from chloroform, the melting point (m.p.) corresponds to the one reported in the literature: m.p. I: 239—241 °C. ^{1}H NMR (DMSO-d_6, ppm): 8.35 aromatic protons *para* substituted benzene (d, 4H); 7.92 aromatic protons *meta* to COCl (t, 2H); 7.90 aromatic protons *ortho* to COCl (s, 2H); 7.64 aromatic protons *ortho* and *para* to COCl (dd, 4 H) [17]. Elemental analysis: calcd. for $C_{22}H_{12}O_6Cl_2$: C — 59.62 %; H — 2.73 %; Cl — 16 %; found: C — 59.72 %; H — 2.70 %; Cl — 15.84 %.



(I)

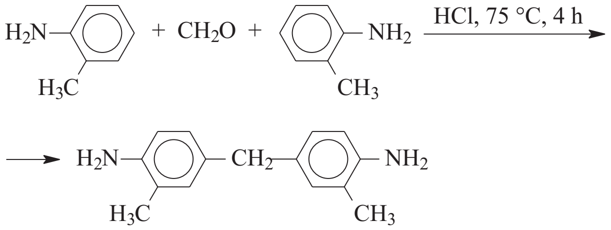
Scheme A. Synthesis of the diester-diacid chloride (I)

Aromatic diamines

— 4,4′-Diaminodiphenylmethane (IIa) (Fluka) was recrystallized from ethanol; m.p. = 90—92 °C.

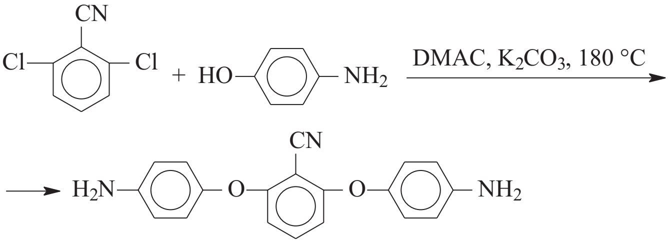
— 4,4′-Diamino-3,3′-dimethyl-diphenylmethane (IIb) was synthesized according to a previously reported method (Scheme B) [18], m.p. = 155—157 °C. ^{1}H NMR (DMSO-d_6): 2.11 (s, 6H, CH_3); 3.41 (s, 4H, NH_2); 3.72 (s, 2H, CH_2); 6.58 aromatic protons *ortho* to NH_2 (d, 2H), 6.83 aromatic protons *para* to CH_3 (d, 2H); 6.86 aromatic protons *ortho* to CH_3 (s, 2H). Elemental analysis: calcd. for $C_{15}H_{18}N_2$: C — 79.61 %, H — 8.02 %, N — 12.38 %; found: C — 79.52 %, H — 7.95 %, N — 12.14 %.

— 1,4-Bis-(*p*-aminophenoxy-phenyl)-2,2-isopropane (IIc) (from Aldrich) was used as received, m.p. 128—130 °C.



Scheme B. Synthesis of 4,4′-diamino-3,3′-dimethyldiphenylmethane (IIb)

— 2,6-Bis(*p*-aminophenoxy)-benzonitrile (IId) and 2,6-bis(*m*-aminophenoxy)-benzonitrile (IIe) were obtained by the reaction of 2,6-dichlorobenzonitrile with *p*-aminophenol or *m*-aminophenol, respectively, by using potassium carbonate (as catalyst) and dimethylacetamide (DMAc) as solvent, by following a procedure previously reported (Scheme C) [19, 20]. After recrystallization from a mixture of dimethylformamide and water the melting point of (IId) was identical to that found in the literature, namely 210—213 °C; m.p. (IIe) = 122—125 °C. ^{1}H NMR (DMSO-d_6) of (IId): 5.14 (s, 4H, NH_2); 6.31 aromatic proton *meta* to CN (d, 2H); 6.65 aromatic protons *meta* to NH_2 (d, 4H); 6.88 aromatic protons *ortho* to NH_2 (d, 4H) and 7.45 ppm aromatic protons *para* to CN (t, 1H); ^{1}H NMR (DMSO-d_6) of (IIe): 5.38 (s, 4H, NH_2); 6.28 and 6.32 aromatic protons *ortho* to NH_2 (d, 2H and s, 2H, respectively); 6.45 aromatic protons *para* to NH_2 (2H); 6.62 aromatic protons *meta* to CN (2H); 7.07 aromatic protons *meta* to NH_2 (2H) and 7.55 ppm aromatic protons *para* to CN (1H). Elemental analysis: calcd. for $C_{19}H_{15}O_2N_3$: C — 71.91 %; H — 4.76 %; N — 13.24 %. Found (IId): C — 72 %, H — 4.65 %, N — 13.1 %, found (IIe): C — 71.8 %, H — 4.6 %, N — 13.0 %.



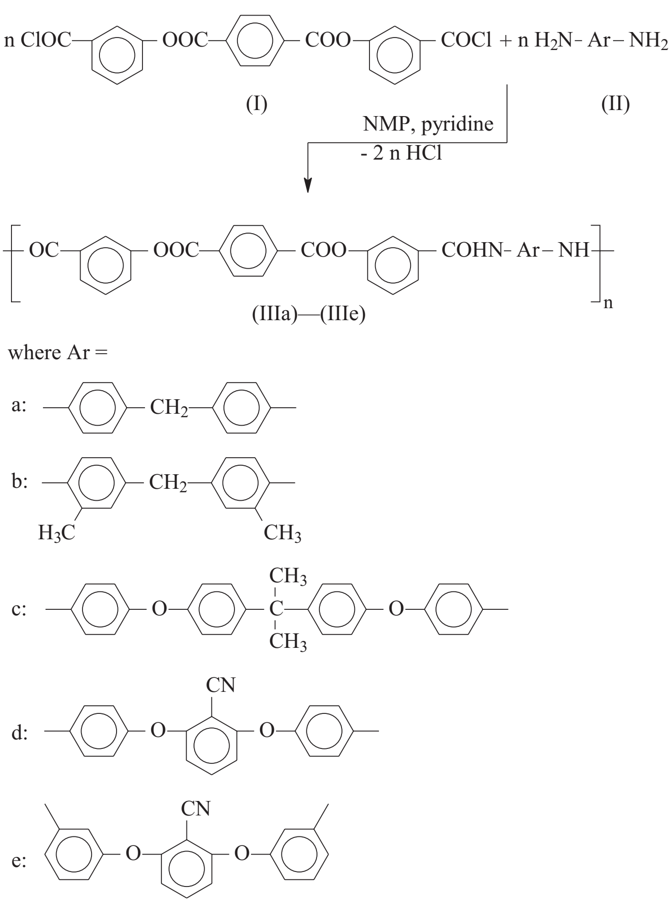
(IId) (IIe)

Scheme C. Synthesis of 2,6-bis(p-aminophenoxy)-benzonitrile (IId), (IIe)

Polycondensation

Low temperature solution polycondensation reaction of equimolar amounts of diacid chloride (I) which contains preformed ester groups with aromatic diamines (II) was carried out in NMP using pyridine as acid acceptor to obtain the polyesteramides [(IIIa)—(IIIe)] as shown in Scheme D.

A general procedure is as follows in this example: in a three-necked flask equipped with mechanical stirrer and N_2-inlet and outlet, 0.396 g (0.002 mol) of diamine (IIa), 16 ml NMP and 0.5 ml pyridine were placed, and the mixture was stirred under N_2. The solution was cooled to -5 °C and then 0.886 g (0.002 mol) of diacid chloride (I) was added, as a fine powder, under rapid stirring. The concentration of the solutions, after the addition of the diacid chloride, was 8.0 % solids. The flask content was kept below 0 °C for 30 min, then the cooling bath was removed and the reaction mixture was allowed to reach the room temperature and stirred for further 4 h. Approximately half of the polymer solution was used to prepare thin films. The other half was poured into water in order to precipitate the polymer. The resulting solid was filtered, washed twice with water and once with ethanol, and dried in vacuum at 105 °C for 2—3 h.



Scheme D. Synthesis of the polymers (IIIa)—(IIIe)

Preparation of thin polymer films

Approximately 8 ml of first half of polymer solution obtained from the polycondensation reaction were cast onto glass plates (100 mm × 100 mm) and dried gradually in an oven for 1 h at each of the following temperatures: 80 °C, 120 °C, 160 °C and 220 °C. The resulting films were stripped off the plates by immersion in water, followed by drying in a vacuum oven at 105 °C. Films of various thicknesse (ranging from 5 to 40 μm) were thus prepared and were used afterwards for measurements.

Measurements

— Inherent viscosities were determined at 20 °C for solutions of polymers (0.5 g/dl) in NMP, using an Ubbelohde viscometer.

— The IR spectra were recorded on a Perkin-Elmer spectrometer using polymer films of 2—5 μm thickness or KBr pellets.

— Thermogravimetric analysis (TGA) was performed on a MOM-type Derivatograph made in Budapest, Hungary, operating in air at a heating rate of 12 °C/min.

— The glass transition temperature (T_g) was measured on a Mettler DSC 12E apparatus in nitrogen with a heating rate of 20 °C/min. Approximately 7 to 10 mg of the polymers were crimped in Al pans and run in nitrogen purge of 50 ml/min with a heat-cool-heat profile from 30 °C to 320 °C at 20 °C/min, with 3 min isothermal stabilization times at the temperature extremes. The mid-point of the inflection curve resulting from the typical second heating cycle was assigned as the T_g of polymers.

— Model molecules for a polymer fragment were obtained through molecular mechanics (MM+) using the Hyperchem program, Version 7.5 [21]. The same program was used to visualise the structures obtained after energy minimisation. The calculations were carried out with full geometry optimisation (bond lengths, bond angles and dihedral angles).

— Weight-average molecular weight ($\overline{M}_w$) and number-average molecular weight ($\overline{M}_n$) were determined by means of gel permeation chromatography (GPC) using a Waters GPC apparatus, provided with refraction and photodiode array detectors and Phenomenex-Phenogel MXN column. Measurements were carried out with polymer solutions (0.2 % concentration), using dimethylformamide as eluent. Polystyrene standards of known molecular weight were used for calibration.

— Dynamic mechanical analysis (DMA) experiments were performed on the polymer film specimens (20 mm long, 10 mm wide, and 30—40 μm thick) on a Perkin-Elmer Diamond apparatus at a heating rate of 2 °C/min in nitrogen atmosphere. The variations of the storage modulus E' and tension loss tangent tan δ as a function of temperature were recorded. A supplementary temperature scan was performed within the range of -100 °C to 250 °C, for sample (IIIe), at three frequencies: 0.1 Hz, 1 Hz, 10 Hz. The experiment was performed in order to establish the nature of transitions by calculating the activation energies according to the Arrhenius relationship.

RESULTS AND DISCUSSION

Chemical structure and general characteristic

The structure of the resulting polymers showed characteristic wide absorption bands due to amide NH at 3300—3400 cm^{-1}, amide (I) at 1650 cm^{-1} and amide (II) at 1540 cm^{-1}. The absorption band at 1760 cm^{-1} is characteristic for COO group and it is present in all the spectra. The absorption peak at 2240 cm^{-1} in the spectra of polymers (IIId) and (IIIe) was attributed to CN group. Figure 1 shows the characteristic absorption bands of polymer (IIIe).

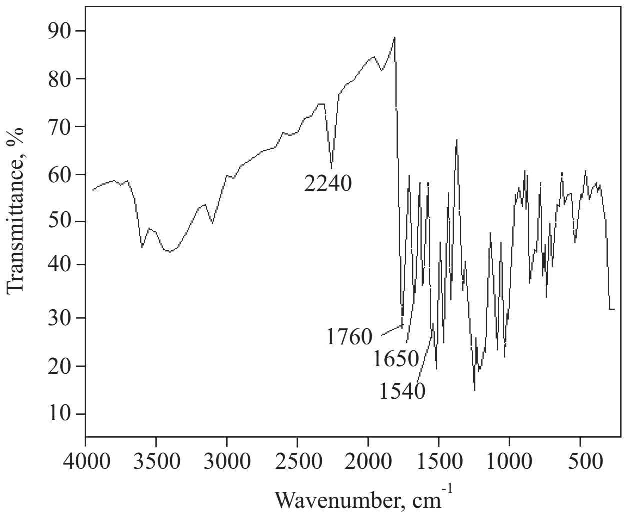


Fig. 1. FT-IR spectrum of polyesteramide (IIIe)

All these polymers are easily soluble in NMP; their improved solubility, compared to the traditional fully aromatic polyamides which are soluble only in sulfuric acid, can be explained by the presence of ester groups which determine the shape of the macromolecules to be far from the linear rigid rod one (Fig. 2).

Due to such a shape, the packing of chains through hydrogen bonds between amide groups is disturbed and thus small molecules of solvent can diffuse easily among the chains, leading to a better solubility. Moreover, it is believed that the presence of one *meta*-catenated benzene ring in each repeating unit of these polymers brings about more flexibility in the chain and makes the polymers soluble in a large variety of solvents.

Inherent viscosities of polymers are in the range of 0.39—0.89 dL/g at a concentration of 0.5 g/dL (Table 1).

Molecular weight values are in the range of $72 \cdot 10^3$—$229 \cdot 10^3$ for $\overline{M}_w$, $36 \cdot 10^3$—$109 \cdot 10^3$ for $\overline{M}_n$ and 2.0—3.7 for $\overline{M}_w/\overline{M}_n$ (Table 1). However, these values have to be taken into consideration with caution since it is known, that calibration with polystyrene may result in questionable data when the polarity and backbone stiffness of the analysed polymers deviate strongly from those of polystyrene.

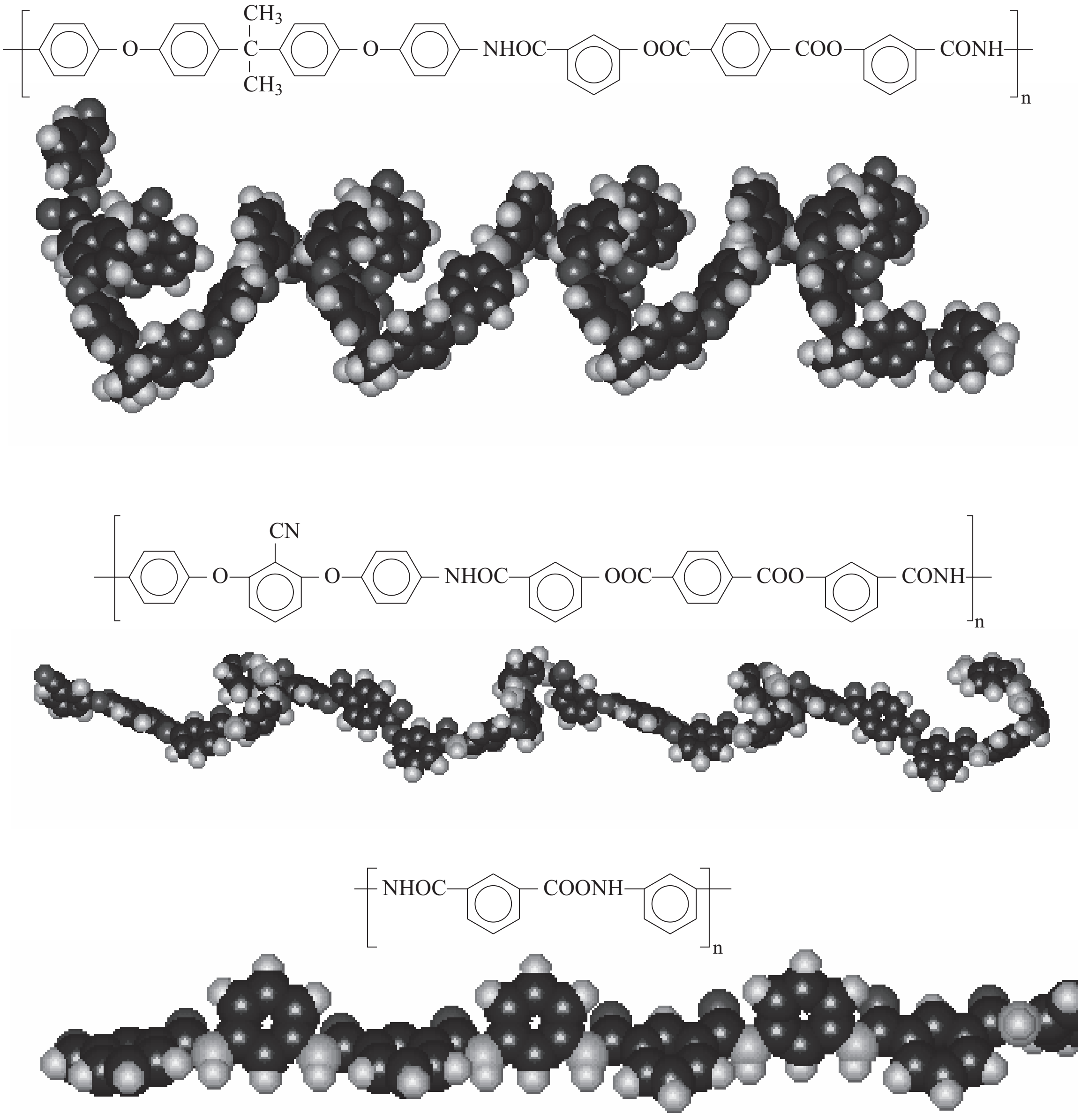


Fig. 2. Model molecules (four repeating units) for polyesteramides (IIIc) and (IIId) and aromatic polyamide

T a b l e 1. General characteristics of the polymers (IIIa)—(IIIe)

Polymer	Inherent viscosity dL/g	$\overline{M}_w \cdot 10^{-3}$	$\overline{M}_n \cdot 10^{-3}$	$\overline{M}_w/\overline{M}_n$	T_5*) °C	T_{10}**) °C
(IIIa)	0.89	229	109	2.1	352	390
(IIIb)	0.39	72	36	2.0	337	370
(IIIc)	0.442	215	58	3.7	385	405
(IIId)	0.66	165	75	2.2	385	410
(IIIe)	0.68	178	83	2.14	364	370

*) Temperature of 5 % weight loss.

**) Temperature of 10 % weight loss.

All polymers produced transparent, flexible films by casting their NMP-solutions onto glass plates, followed by gradually heating up to 220 °C to remove the solvent.

Thermal properties

The TGA curves are presented in Fig. 3 and the appropriate results are listed in Table 1. So, all the polymers exhibit good thermal stabilities without significant weight loss up to approximately 340 °C. The 5 % weight loss temperatures (T_5) are in the range of 337—385 °C, while the T_{10} were recorded in the temperature range of 370—410 °C. These results indicate that the thermostabilities of these polymers are similar (the thermal degradation occurred approximately in the same range of temperatures) but it should be noted that the introduction of methyl groups in the polymer (IIIb) led to slightly lower decomposition temperature.

Based on the DSC measurements glass transition temperature values of the polymers (IIIa)—(IIIe) are in the range of 190—220 °C as shown in Table 2. The T_g values of the polymers (IIIb) and (IIIc) are slightly lower than in the

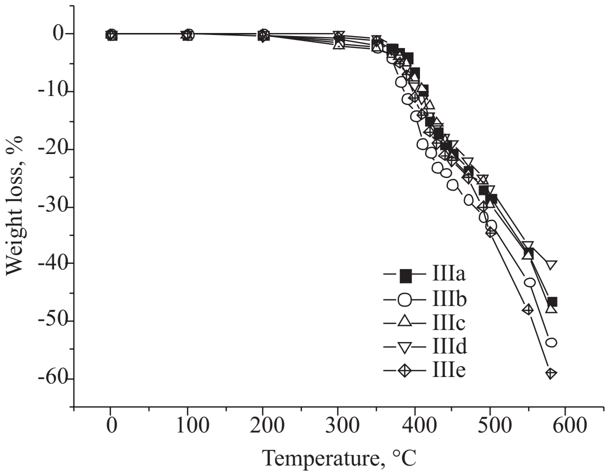


Fig. 3. TGA curves of polyesteramides (IIIa)—(IIIe)

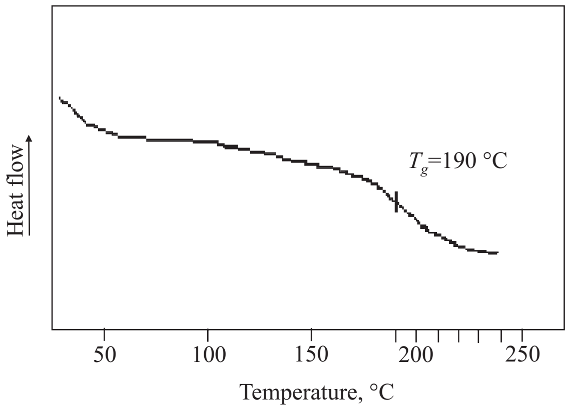


Fig. 4. DSC curve of polyesteramide (IIIb)

case of the other polymers (III), probably due to the presence of methyl groups which have a strong influence on the chain flexibility. A typical DSC curve is shown in Fig. 4.

T a b l e 2. The storage modulus E' (at -98 °C) and glass transition temperatures of the polyesteramides

Polymer	$E' \cdot 10^{-9}$, Pa	T_g*), °C	T_g**), °C	tan δ
(IIIa)	1.1	218	232	1.154
(IIIb)	1.52	190	199	0.915
(IIIc)	0.657	190	213	1.348
(IIId)	1.98	221	228	1.042
(IIIe)	1.78	205	205.5	0.6565

*) Determined from DSC curves.

**) Determined from DMA curves (tan δ peak).

The T_g values were also measured by DMA and the results are also shown in Table 2. The T_g was in this case determined as a peak temperature in tan δ curves and the obtained values are higher than those obtained by DSC measurements.

Dynamic mechanical analysis

Figure 5 depicts the dependence of the storage modulus E' *versus* temperature for the polyesteramides in the range of -100 °C to 260 °C at 1 Hz. As it is seen in this figure, the values of E' are over 10^9 Pa in the glassy region, except the polymer (IIIc) which shows the lowest storage modulus value also in Table 2. This fact can be attributed to the high flexibility of the isopropylidene units, which are present in the macromolecular chain of the polyesteramide (IIIc). These units increase the free volume of the macromolecular chains, which results in more flexible structures, in comparison with the other polyesteramides. The polymer (IIIa), without methyl groups in its structure, is obviously more rigid than the polymer (IIIb), which contains methyl substituents and evidently exhibits a higher value of E'. With the exception of polymer (IIIe), the E' values of the samples studied herein decreased slowly with temperature up to 140—200 °C, depending on their structure.

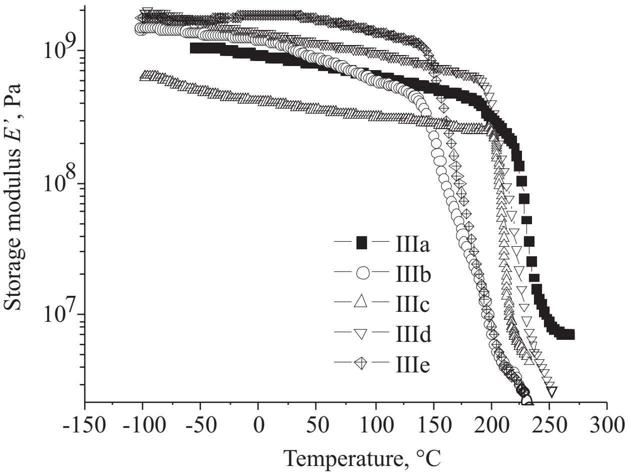


Fig. 5. Dynamic storage modulus vs temperature of the polyesteramides (III) at 1 Hz

Regarding the sample (IIIe), this polymer exhibits an increase of the storage modulus value in the temperature range of -50 °C—50 °C; this may be ascribed to some crystallization phenomenon of the macromolecular chains. At low temperature (-100 °C), the storage modulus value of polymer (IIId) is higher than that of the polymer (IIIe), obviously, because the *para* linked aromatic rings are more rigid than the *meta* ones (Table 2). However, the different orientation of *meta*-rings chain segments exhibits an increased mobility and, therefore, it cannot be excluded that a cold crystallization may explain the increased value of the storage modulus of the polyesteramide (IIIe).

It is well known that the temperature at which E' starts to decrease rapidly corresponds to the glass transitions. Similarly, the peaks tan δ reports on the physical transitions in the polymer film. The T_g values determined by DMA measurements were slightly higher than those determined by DSC measurements (Table 2). This finding was also reported by other authors for similar compounds [22]. The magnitude of the tan δ at T_g represents a measure of the energy-damping characteristic of the polymer film and is related with the impact strength of the material. The results presented in Table 2 reveal that the energy-damping characteristic of these polymers are different. The polymer (IIIb) — the sample with substituted methyl group on the benzene rings — and polymer (IIIe) — the one which contains much more *meta*-catenation — have shown the smallest values of the tan δ magnitude. In the same time the polymer (IIIc), which contains isopropylidene linkage, has exhibited the highest magnitude of tan δ at T_g, suggesting a superior impact strength of the material [23].

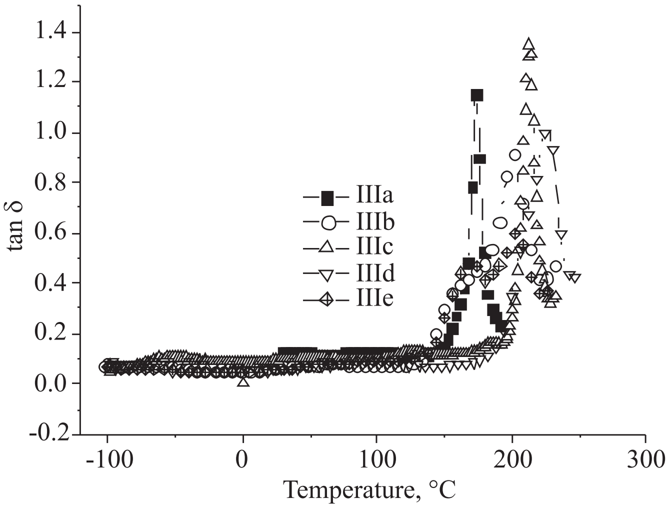


Fig. 6. Loss tangent (tan δ) vs temperature of the polyesteramides at 1 Hz

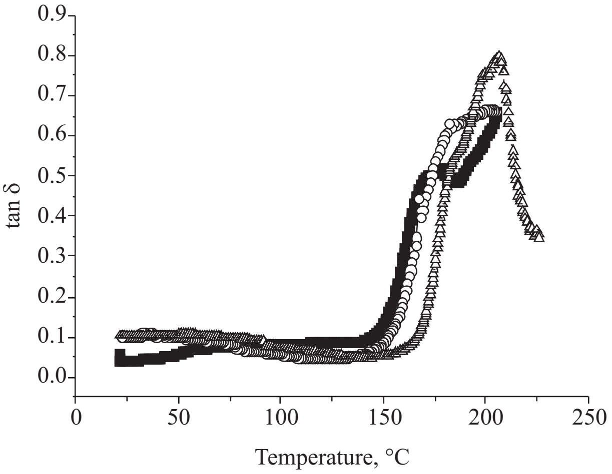


Fig. 7. Heating (■ — 21 → 205 °C) — cooling (○ — 205 → 21 °C) — heating (Δ — 21 → 226 °C) cycle for the polyesteramide (IIIe)

In Figure 6 two peaks appeared in tan δ for polymer (IIIe) — 0.568 and 0.6565, respectively — which may be attributed to some constrains in the macromolecular chains. Moreover, two domains with different relaxation times, may possibly exist because at the second heating the first peak, which is present at lower temperature (168 °C), diminishes. This means that in this domain the macromolecular segments are more rigid. On the other hand, at higher frequencies this peak becomes a shoulder because the chain segments have not enough time to respond to the external stimulus; at further frequency increase, the shoulder in loss tangent was less pronounced. The same behavior appears in the case of polymers (IIIb) and (IIId), with the observation that in the case of polymer (IIId), the shoulder disappears almost completely with an increase in the frequency. In this case, probably, the chain segment, has a relaxation time higher than in polymer (IIIb) because it is more flexible than the polymer IIId and, consequently, has not enough time to respond to the external stimulus.

The experiment performed for sample (IIIe) is shown in Fig. 7. It consists of a first heating until 205 °C, followed by a cooling down to room temperature and then a re-heating up to 226 °C. In the second heating phase the broad peak which appears in the first heating phase became shoulder and moved to a slightly higher temperature.

The activation energy, E_a, for the glass transition can be calculated from the Arrhenius equation:

$$f = A \exp(-E_a / RT) \quad (1)$$

where: *f — the experimental frequency of transition, A — a constant, E — the activation energy, R — the universal gas constant, T — the temperature corresponding to the maximum of the tan δ curve in Kelvin scale.*

It is worthy of note that the temperature peak shifts to higher temperatures as the frequency increases (Fig. 8).

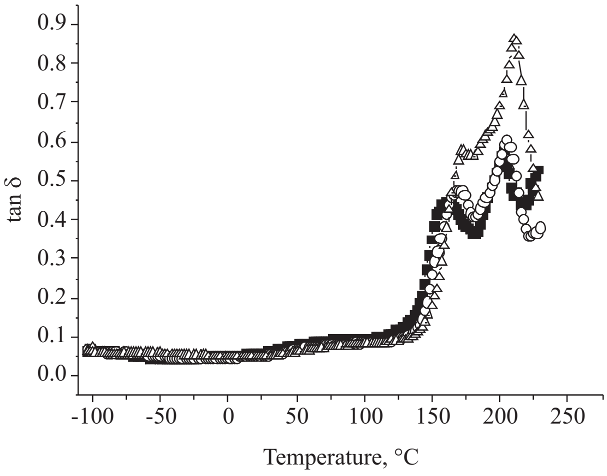


Fig. 8. Loss tangent (tan δ) vs temperature of polyesteramide (IIIe) at three frequencies: 0.1 Hz (■), 1 Hz (○) and 10 Hz (Δ)

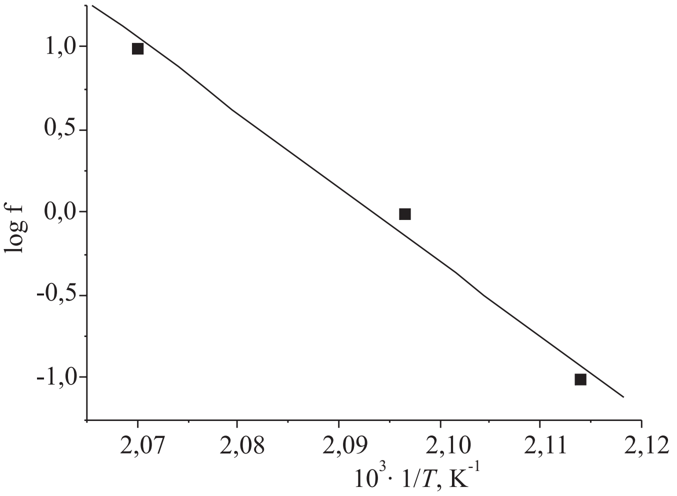


Fig. 9. Arrhenius plot corresponding to glass transition of polymer (IIIe) (y = 93.89—44845.68x)

When the applied stress is faster, the macromolecules have less time to react and a higher temperature is claimed to stimulate the long-range coordinated molecular movement characteristic for glass transition [24, 25].

The value of the tan δ peak for polymers rises with increasing frequency, *i.e.* liquid-like viscoelastic behavior prevails at high frequency values. Figure 9 contains the Arrhenius plot relative to the transition occurring above 190 °C. The activation energy E_a calculated from the Arrhenius plot is 373 kJ/mol with a linear relative coefficient of 99.33 — this means the value activation energy value corresponds to a α-transition.

Wide-angle X-ray diffraction measurements performed on the films obtained from polyamides (IIIa)—(IIIe) have shown an amorphous structure that may be attributed to the presence of ester, isopropylidene or benzonitrile groups, which significantly increases the disorder in chains and, hence, less chain packing density.

CONCLUSIONS

By introducing into the chain of aromatic polyamides the flexible isopropylidene, ether or CN groups as the substituents in the benzene rings, together with ester groups, products with substantially improved solubility (particularly in NMP), and processability into thin flexible films were obtained. Some of them are also soluble in other amidic solvents, such as DMAc and DMF, which is very convenient for practical applications. The polymers have a fairly high molecular weight and a narrow polydispersity. They demonstrate high thermal stability, with a decomposition temperature above 340 °C and glass transition in the range of 190—220 °C. The viscoelastic properties analysis revealed that the incorporation of the methyl substituents on the benzene ring or *m*-catenation led to lower values of tan δ magnitude, while the presence of the isopropylidene linkages increased the impact strength of the material. DMA experiments performed at different frequencies allowed to determine the activation energy of the relaxation process which corresponds to a α-transition.

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