MODIFICATION OF THE THERMOPLASTIC POLYHETEROARYLENES WITH ALIPHATIC POLYETHERS AND POLYESTERS: SYNTHESIS AND DYNAMIC MECHANICAL PROPERTIES

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Abstract

Poly(propylene oxide), poly(ethylene adipate) and poly(1,6-hexane diol/neopentile glycol-alt-adipic acid), all terminated with 2,4-toluylene diisocyanate, have been used to synthesize segmented poly(urethane-imide)s. Anhydride-terminated poly(ether/ester) prepolymers were prepared by reacting the above macromonomers with 1,3-bis(3',4-dicarboxyphenoxy)benzene dianhydride. Each prepolymer reacted with 1,4-bis(4'-aminophenoxy)diphenylsulphone to give a poly(urethane-imide). Hydroxy-terminated poly (1,6-hexane diol/neopentile glycol-alt-adipic acid) was also used to prepare poly(ester-alt-ether-imide). In this case, the anhydride-terminated poly(ester-alt-ether) prepolymer prepared by the reaction of poly(1,6-hexane diol/neopentile glycol-alt-adipic acid) with 1,3-bis(3',4-dicarboxyphenoxy)benzene dianhydride reacted with 1,4-bis(4'-aminophenoxy)diphenylsulphone to give poly(ester-alt-ether-imide) .

All the copolymers form high-strength elastic films. Thermal analysis data indicate that the copolymers are stable up to 320^0C. According to the DSC and DMTA data, all the copolymers have a low glass transition temperature (--50 to 0^0C). In all cases, there is the elastic rubbery plateau in the temperature dependences in the range 0--200 ^oC. The copolymers also display a very small loss factor (tan δ), which suggests that their dynamic properties are excellent. An extension of the rubbery plateau to higher temperatures was observed for a poly (urethane-imide) composite with a silicon resin. Above 200^0C, the polymers become flowable. The polymers synthesized behave as thermoplastic elastomers.

Key words: *thermoplastic elastomers; poly(urethane-imide)s; poly(ester-alt-ether-imide)s; dianhydrides; diamines; diisocyanates; polyheteroarylenes; segmented block copolymers; glass transition; stress-strain properties; dynamic mechanical properties; flow properties.*

1. INTRODUCTION

Polyheteroarylenes constitute the class of heat-resistant polymers used to obtain nearly all kinds of polymeric materials capable of prolonged operation in technical devices at temperatures of 300°C and higher [1, 2]. Polyheteroarylenes include polyimides. In the general case, polyimides are synthesized by polyacylation of aromatic diamines with aromatic tetracarboxylic acid dianhydrides. In syntheses of thermoplastic polyimides, up to four benzene rings (nuclei) linked by bridge (frequently named "hinge") atoms or groups of atoms are, as a rule, introduced into the dianhydride and diamine components of the repeating unit of the polymer. This provides macromolecules with the required broad set of conformations in internal rotation of chains [2, 3].

It is a common knowledge that the growing technological demand for polymers in which the target properties are combined with a high thermal stability and improved fabricability is the principal driving force in development of new polymeric materials. Block copolymers have been known for 40 years, but the interest in these materials is undiminishing because macroscopic properties of two different polymers can be combine in a single material in their synthesis or synergic effects can be obtained. The structure of block copolymers is multivariant as regards the architectural type. In particular, a number of studies concerned with the synthesis and properties of multiblock (segmented) copoly(ester-imide)s and copoly(urethane-imide)s of the [A -- (B)k]n architectural type have been reported in the literature. Each repeating unit of these copolymers contains a rigid block of imide or urethane-imide (A) and a flexible polymer block of an aliphatic ester (B)k, thermodynamically incompatible with the former [4]. A characteristic feature of multiblock (segmented) copolymers of the [A -- (B)k]n type is the microphase separation of blocks A and Bk, owing to which introduction of imide rings into repeating units of polyesters and polyurethanes improves the heat resistance and mechanical strength of the corresponding

materials without impairing the properties of such materials as elastomers and membranes for separation of chemical substances [5--8]. Of indubitable interest for modern technology are thermoplastic elastomers (the so-called thermoelastoplastics or elastic highly heat-resistance thermoplastic materials). There is published evidence about modification of linear aromatic polymers and, in particular, polyamides for this purpose [9].

In our opinion, it is appropriate to solve the problem of highly heat-resistant thermoelastoplastics by introduction of flexible blocks of aliphatic polyethers and polyesters of varied chemical structure (ether, ester, or ester-alt-ether) having various molecular masses and terminated with various functional (hydroxy or urethane) groups into the repeating units of the known thermoplastic polyheteroarylenes. It will be recalled that polyurethanes widely known as elastomers belong to the family of multiblock (segmented) copolymers constituted by rigid urethane and flexible polyether and polyester units. An irreplaceable integral part of studies in this area is constituted by those concerned with the dynamic mechanical properties of newly synthesized multiblock (segmented) copolymers.

The immediate goal of our study was to synthesize the following materials and examine their dynamic mechanical properties: family of multiblock (segmented) copoly(urethane-imide)s of 1,3-bis(3',4-dicarboxyphenoxy) benzene, produced using poly(propylene oxide) (Mn 2300), poly(ethylene adipate) (Mn 2700), and poly(1,6-hexanediol/neopentylglycol-alt-adipic acid) (Mn 900) terminated with 2,4-toluylenediisocyanate, and also copoly(ester-imide) produced with poly(1,6-hexanediol/neopentylglycol-alt-adipic acid) (Mn 900) terminated with hydroxy groups. The goal of the study also included an analysis of changes in the dynamic mechanical properties of poly(urethane-imide) upon its doping with an organosilicon resin soluble in this compound.

2. MATERIALS AND METHODS OF STUDY

2.1. Materials

The following starting substances were used to synthesize the polymers: 1,3-bis(3',4-dicarboxyphenoxy)benzene (dianhydride R), mp 163--165°C (manufactured by TekhKhimProm Limited Liability Company, Yaroslavl); 1,4-bis(4'-aminophenoxy)diphenylsulfone diamine (diamine BAPS), mp 194--196°C (Wakayama Seika Co., Ltd. (Japan)); poly(propylene oxide) terminated with 2,4-tolylenediisocyanate (TDI 2300), (Mn 2300) (Aldrich); poly(ethylene oxide) terminated with 2,4-tolylenediisocyanate (TDI 2300), (Mn 2300) (Aldrich); poy(ethylene adipate) terminated with 2,4-tolylenediisocyanate (TDI 2700), (Mn 2700) (Aldrich); and poly(1,6-hexanediol/neopentyl glycol-alt-adipic acid) (ALT) with terminal hydroxy groups, Mn = 900 (Aldrich).

Synthesis of copoly(ester-imide) (R-ALT-R)BAPS based on dianhydride R, diamine BAPS, and aliphatic copolyester ALT, terminated with hydroxy groups. A thermostated three-necked vessel equipped with a mechanical stirrer and an inlet tube for argon was charged with 4.0 g (0.00444 mol) of macromonomer ALT and 3.57 g (0.00890 mol) of powdered dianhydride R. The mixture was melted at 160°C in the course of 2 h in a flow of argon, and then the temperature was lowered to 90°C and the contents of the vessel were diluted with 10 mL of N-methylpyrrolidone (MP). The solution was agitated for an additional hour until the system was completely homogenized, and then was cooled to room temperature. Then a solution of 1.92 g (0.00445 mol) of diamine BAPS was added dropwise under agitation and then, in 0.5 h, 10.5 mL of MP was additionally introduced and the contents of the vessel were agitated at room temperature for 2 h, with a prepolymer [copoly(ester-amido-acid)] solution obtained. The vessel with the prepolymer solution was kept in a freezer box overnight and then it was equipped with an inlet tube for argon, mechanical stirrer, and a Dean--Stark apparatus with a reflux. Toluene was introduced into the vessel under agitation in a volume equal to 1/3 of the prepolymer solution, the contents were heated to 165°C and water released in imidization (forpolymer curing) in the form of an azeotropic mixture with toluene was evaporated at this temperature, with control over its volume. The azeotropic evaporation was continued for 3.5 h and then the temperature was raised to 210°C for a short time until the imidization was nearly complete. The solution was cooled to room temperature, filtered through a Schott filter, degassed in a vacuum, and used to cast films on the surface of hydrophobized glass slides. The films were dried at 60°C and stepwise heated at 160, 180, and 210°C for 2 h and finally at 220°C for 0.5 h. The thickness of the films was 40 µm.

Synthesis of copoly(urethane-imide) (R-TDI ALT-R)BAPS from dianhydride R, diamine BAPS, and aliphatic copolyester ALT, secondarily terminated with 2,4-toluylenediisocyanates. A thermostated three-necked vessel equipped with a mechanical stirrer and an inlet tube for argon was charged with 4.0 g (0.00445

mol) of copolyester ALT terminated with hydroxy groups and 1.55 g (0.00890 mol) of 2,4-toluylenediisocyanate (TDI). The mixture was agitated in a flow of argon at room temperature for 1.5 h, and then the temperature was raised to 140°C and the agitation was continued for additional 1.5 h. In this stage of synthesis, a copolyester (TDI ALT) terminated with isocyanate groups was obtained, further used without isolation. With this circumstance taken into account, 3.57 g (0.00890 mol) of powdered dianhydride R was introduced into the vessel in a flow of argon and its contents were continued to be heated until carbon dioxide bubbles ceased to evolve, which is due to the formation of imide structures. Then the temperature of the resulting melt was lowered to 90°C, 14 mL of MP was added to the melt in a flow of argon, and the mixture was agitated for approximately 0.5 h until the solution formed was fully homogenized. After the solution was cooled to room temperature, a solution of 1.92 g (0.00445 mol) of diamine BAPS was added dropwise in the course of 10--15 min and 16 mL of MP was gradually additionally introduced in 0.5 h. The solution of the prepolymer [copoly(urethane-imide-acid)] formed as a result of the reaction was kept at room temperature under agitation for 2 h. The vessel with the prepolymer solution was kept in a freezing box overnight. The thermal imidization of poly(urethane-imide-acid) in a solution with MP was performed by removing water released in the process via azeotropic evaporation with toluene under the conditions specified in the preceding example for the case of copoly(ester-amido-acid). Films of the target copoly(urethane-imide) were obtained under the same conditions.

Copoly(urethane-imide)s (R-TDI 2300-R)BAPS and (R-TDI 2700-R)BAPS were synthesized from dianhydride R, diamine BAPS, and aliphatic polyesters TDI 2300 and TDI 2700, respectively, by a method closely similar to that in the above example of synthesis of copoly(urethane-imide) **(R-TDI ALT-R)BAPS).** In these cases, the starting polyesters had terminal isocyanate hydroxyl groups and the synthesis was performed without the initial stage in the synthesis of the target products, in which the terminal hydroxy groups are replaced with isocyanate groups (to give urethane bonds), necessary in the case of ALT.

In the case of **(R-TDI 2300-R)BAPS**, the reaction vessel was charged with TDI 2300 and dianhydride R, with the latter taken in a double molar excess. The reaction mixture was heated in a flow of argon to 140°C and kept at this temperature under vigorous agitation until the resulting melt was fully homogenized and bubbles of carbon dioxide formed in the course of the reaction ceased to evolve. Further, the synthesis followed the procedure for (R-ALT-R)BAPS.

In the case of **(R-TDI 2700-R)BAPS,** a mixture of TDI 2700 and dianhydride R taken in a double molar excess was kept at a temperature of 165°C, Further, the synthesis followed the procedure for (R-TDI ALT-R)BAPS.

Organo-inorganic composites based on (R-TDI ALT-R)BAPS were prepared using organosilicon resin **TL176** (provided by the Institute of Synthetic Polymeric Materials, Russian Academy of Sciences). The **TL176** resin dissolved in toluene was added to the solution of copoly(urethane-imide-acid), obtained in the course of synthesis of **(R-TDI ALT-R)BAPS**. The resulting solution was sonicated (treated with ultrasound) and then used to cast films on glass substrates. The films were dried to remove the solvents, gradually heated, with the temperature raised to 220°C, and detached from the substrates. The thickness of the films was 40 µm, and the composite contained 5 wt % **TL176** resin.

2.2. Methods of Study

IR spectra of the films were recorded with a Bruker Vertex Fourier spectrometer with a Pike frustrated-total-internal-reflection (FTIR) microattachment; Zn-Se crystals were used as FTIR elements (reflection angle 45°).

The mechanical characteristics of the films were determined at room temperature in the uniaxial tension mode on samples in the form of 2-mm-wide strips and a working part length of 25 mm. The tests were carried out on a UTS Testsysteme URS 10 versatile mechanical test machine at a tensile speed of 25 mm/min.

The temperature transitions of film samples of a block copolymer and composites based on it were determined by differential scanning calorimetry (DSC) on a NETZSCH DSC 204 F1 instrument (Germany) at a heating rate of 5°C/min in the range from --60 to 100°C.

The temperature dependences of the dynamic elastic modulus (E'), loss modulus (E''), mechanical loss tangent (tanδ) of the film samples were obtained by the method of dynamic mechanical analysis (DMA) on a NETZSCH DMA 242 installation (Germany). The measurements were made at a frequency of 1 Hz, the strain amplitude was 0.1%, the temperature was raised at a rate of 5°C/min. The glass transition temperature (Tg) of the film samples was determined from the temperature at which tanδ has a maximum.

The experiments aimed to determine the activation energy of the α-transition were carried out at six frequencies (1, 5, 10, 20, 50, 100 Hz) at a heating rate of 1 deg/min.

Rheological tests were carried out with an Anton Paar Physica MCR301 rheometer in a CP-25/2 cone-plane measuring unit with a diameter of 20 mm and angle of 2° in Down (strain rate decreasing from 100 to 0.0001 s--1) and Top (increasing strain rate) shear modes, and also in a Down dynamic mode at circular frequencies of 100 to 0.1 s--1 and a strain of 1%.

3. RESULTS AND DISCUSSION

The so-far developed highly heat resistant thermoplastic polymers include polyheteroarylene **R-BAPS** of general formula:
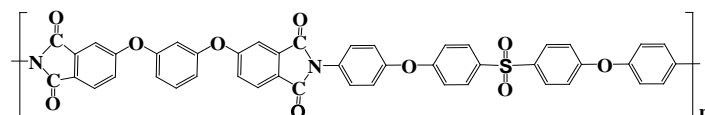
produced from an aromatic compound, 1,3-bis(3',4-dicarbophenoxy(benzene dianhydride (dianhydride R), and aromatic amine 1,4-bis(4'-aminophenoxy)diphenylsulfone (diamine BAPS), which is of interest as a binder for glass-reinforced and carbon-filled plastics [3]. The present study was undertaken to compare the dynamic mechanical properties of this aromatic polyimide with its derivatives, multiblock (segmented) copoly(ester/urethane-imide)s containing aliphatic radicals (residues of aliphatic polyether or polyester) as repeating units, together with aromatic radicals (residues of aromatic imide or urethane-imide).

We chose the following immediate objects of study:

multiblock copoly(urethane-imide) (R-TDI 2300-R)BAPS based on poly(propylene oxide) (Mn 2300) terminated with 2,4-toluyedenediisocyanate (TDI 2300), of general formula:
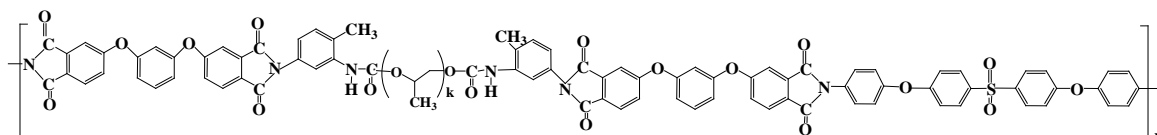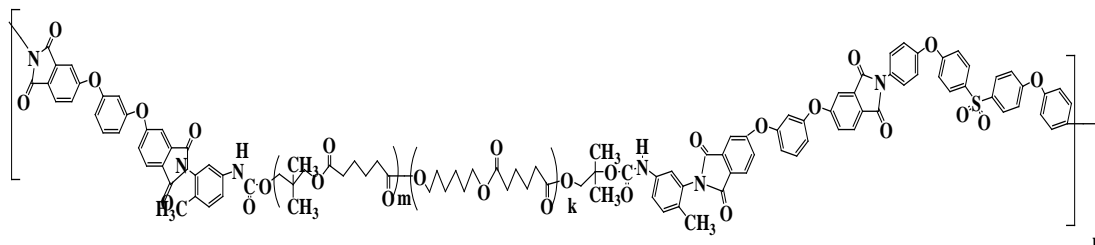

multiblock copoly(urethane-imide) (R-TDI 2700-R)BAPS based on poly(ethylene oxide) (Mn 2700) terminated with 2,4-toluyedenediisocyanate (TDI 2700), of general formula:
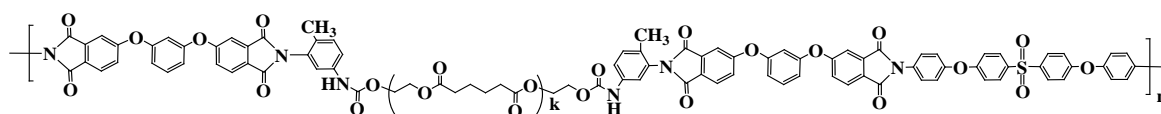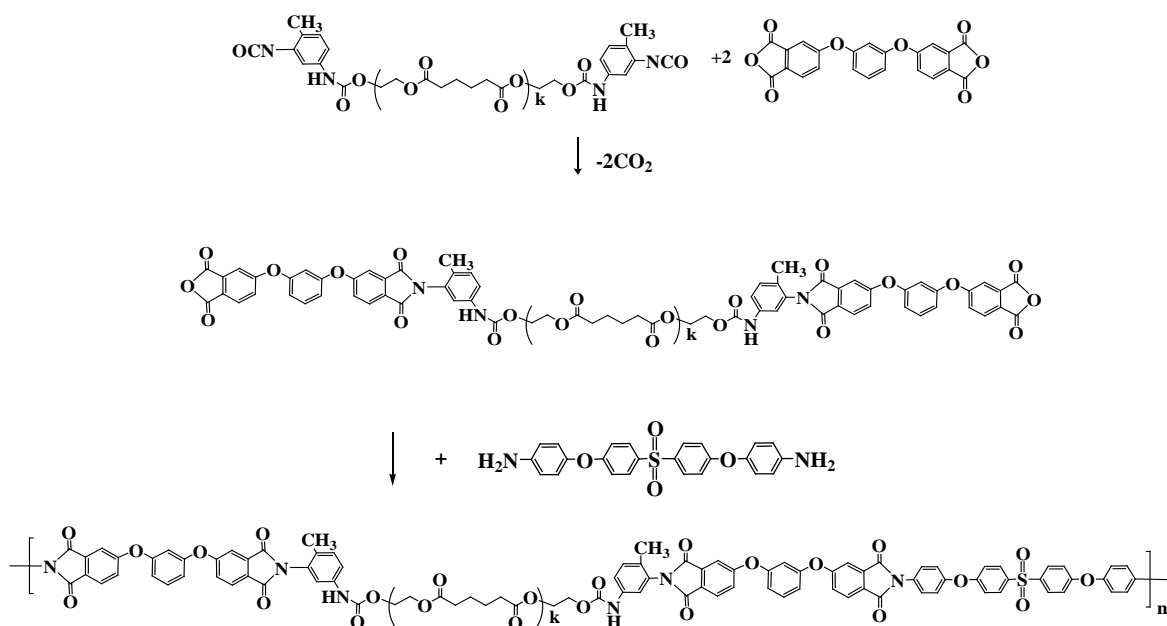

multiblock copoly(ester-imide)BAPS based on a polyester terminated with hydroxy groups: poly(1,6-hexanediol/neopentyl glycol-alt-adipic acid) (Mn = 900) (ALT), of general formula:
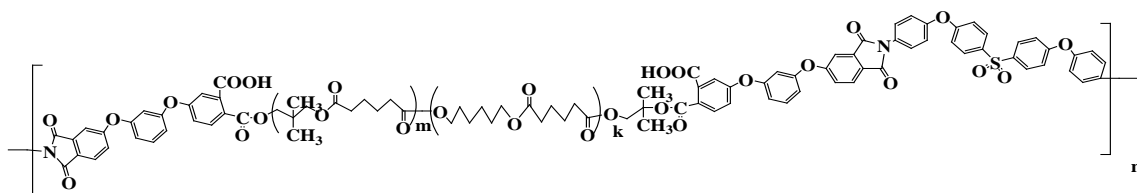
multiblock copoly(uretna-imide) (R-TDI ALT-R)BAPS based on a polyester: poly(1,6-hexanediol/neopentyl glycol-alt-adipic acid) (Mn = 900) (ALT) **secondarily** terminated with 2,4-toluyedenediisocyanate (TDI 2700), of general formula:


The approaches to syntheses of multiblock (segmented) copoly(ester-imide)s and copoly(uretane-imide)s are known in the literature [10--12]. In our cases, we synthesized copoly(urethane-imide)s with the macromonomers (TDI 2300, TDI 2700, and TDI ALT, respectively) converted by a reaction with a double molar excess of dianhydride R to macromonomers with terminal anhydride groups (to give imide bonds). Owing to the presence of anhydride functional groups, these macromonomers further entered into a polycondensation reaction with aromatic diamine BAPS. This yielded prepolymers, copoly(urethane-amido-acid)s, converted to copoly(urethane-imide)s under heating. We present below, as an example, the scheme for synthesis of copoly(urethane-imide) **(R-TDI 2700-R)BAPS:**

In the case of a multiblock copoly(ester-imide) **(R-ALT-R)BAPS**, the alternant aliphatic copolyester **ALT** having terminal hydroxyl groups yielded, by the reaction with a double molar excess of dianhydride R, a macromonomer with terminal anhydride groups (with ester bonds formed). This macromonomer entered into the polycondensation reaction with diamine BAPS, which yielded the target product in the end. Below is given the synthesis scheme of copoly(ester-imide) **(R-ALT-R)BAPS:**
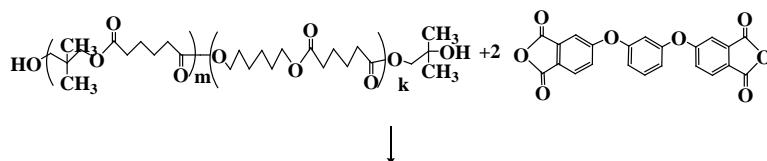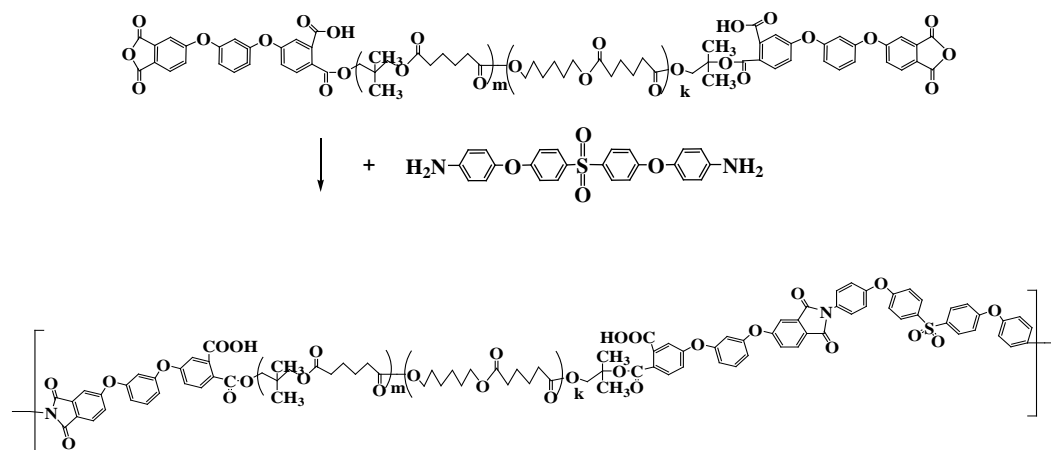
The multistage syntheses considered above were carried out in a single vessel without isolation of the products formed in the intermediate stages. The results of an IR-spectroscopic study of the final products do not contradict the structures suggested for all the polymers synthesized. For example, the IR spectrum of the multiblock copoly(ester-imide) **(R-ALT-R)BAPS** [ν (cm^{-1}): 2700--3200 (stretching vibrations of COOH), 3100 and 3080 (stretching vibrations of the aromatic C--H bond) 2940 and 2860 (stretching vibrations of the aliphatic C--H bond), 1780 (symmetric stretching vibrations of C=O in the imide ring), 1700--1750 (compound band of stretching vibrations of C=O in the ester and carboxylic acid and asymmetric vibrations of C=O in the imide ring), 1380 (stretching vibrations of C--N in the imide ring), 915 (deformation vibrations of the isoimide ring), and 720 (deformation vibrations of the imide ring).

All the polymers we synthesized form high-strength elastic films. The stress-strain properties of the films: strength σd, strain-to-fracture εd, and elasticity (Young's) modulus E were determined at room temperature in the uniaxial-sample-tension mode (Table 1). The data in Table 1 suggest that, in contrast to the parent polyimide **R-BAPS**, the synthesized multiblock (segmented) copoly(urethane-imide)s are elastomers as regards the level of their elastic properties (the values of εd are hundreds of percent). Judging from the value of Young's modulus, copoly(urethane-imide) **(R-TDI 2700-R)BAPS** based on poly(ethylene adipate) is a less rigid system than copoly(urethane-imide**) (R-TDI ALT-R)BAPS** based on the alternant polyester having a substantially smaller molecular mass and, consequently, a larger mass fraction of aromatics.

Table 1. Mechanical properties of polymer films and their heat-resistance indices

Polymer	E, MPa	σb, MPa	εb, %	τ_5, ^{0}C	τ_{10}, ^{0}C
(R-TDI ALT-R)BAPS	1210	59	215	323	353
(R-TDI 2700-R)BAPS	13	31	755	304	326
R-BAPS	2550	120	48	515	527

It follows from the results of the thermogravimetric analysis (Table 1) that, as indicated by the thermal stability indices τ_5 and τ_{10}, the copoly(urethane-imide)s have a comparatively high thermal resistance comparable with that of the parent polyimide, which, anyway, exceeds that of aliphatic polyesters. These circumstances suggest that the thermal stability of the films is mostly determined by the aromatic component of the polymers.

Figures 1a--1d show the DSC curves of the polymers synthesized. The curves in Figs. 1a and 1b are not informative in that they cannot be used to determine the temperature limits of devitrification of the aliphatic

blocks, but, at the same time, show that the degree of ordering in domains formed by the flexible aliphatic blocks is insufficient for their crystallization. The curves in Figs. 1c and 1d disturb this pattern. A glass transition temperature associated with the devitrification of the aliphatic block is manifested in Fig. 1c. It is quite probable that the transitions corresponding both to the devitrification of the aliphatic block and to its subsequent melting are manifested in the DSC curve in Fig. 1d) due to the rigidization of the aromatic block in **(R-TDI ALT-R)BAPS**, compared with **(R-ALT-R)BAPS**, upon the introduction of urethane bonds. It is noteworthy that the parent polymer R-BAPS belongs to noncrystallizing polyimides and has Tg = 217°C.
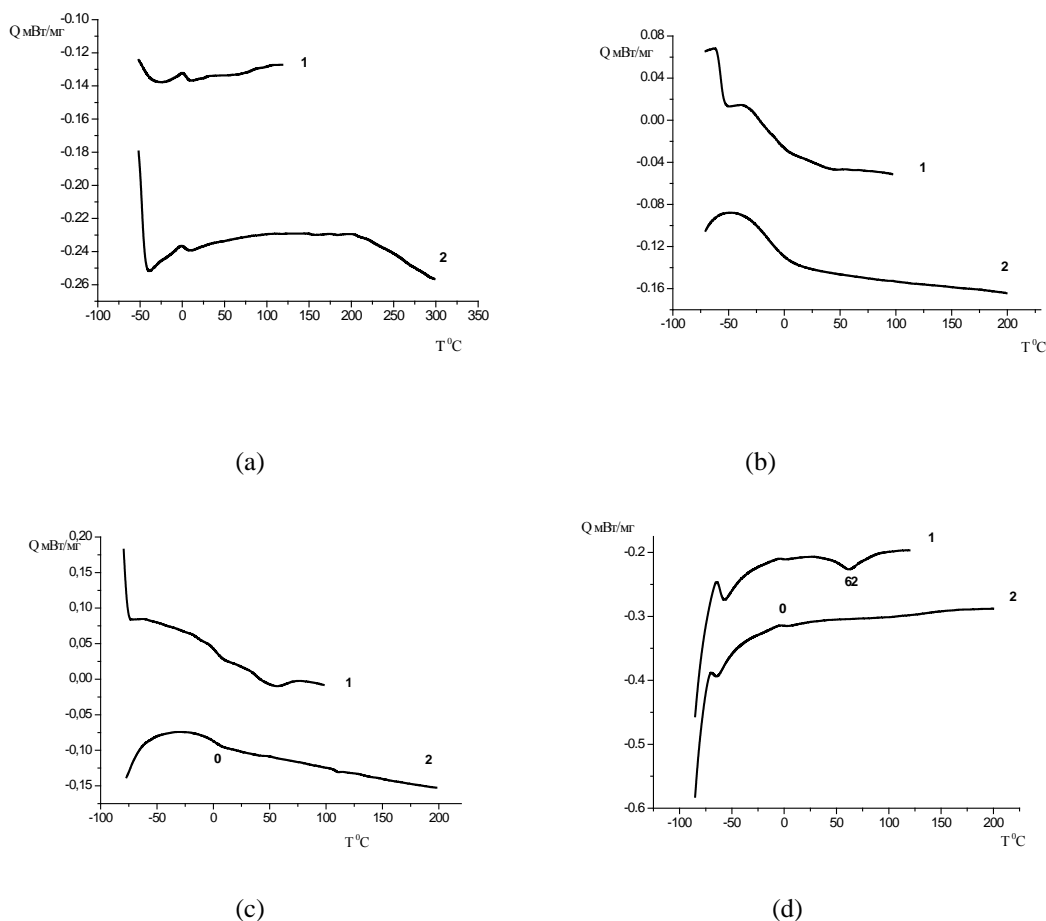

(a)

(b)

(c)

(d)

Fig. 1. DSC curves of the polymers: (a) **(R-TDI 2300-R)BAPS**, (b) **(R-TDI 2700-R)BAPS**, (c) **(R-ALT-R)BAPS**, and (d) **(R-TDI ALT-R)BAPS**. The digits 1 and 2 designate the curves obtained in the first and second scans, respectively.

We present here the results obtained in measurements of the accumulation modulus (E'), loss modulus (E''), and tanδ as functions of temperature on film samples of multiblock (segmented) block-copolymers synthesized in the study.

Figure 2 shows DMA curves for the parent polyimide **R-BAPS**. The temperature dependence of tanδ exhibits two maxima. The maximum observed at a temperature of 217°C should be attributed to an α-relaxation process reflecting the devitrification of polyimide macrochains. In our opinion, the second relaxation transition at a temperature of 86°C is a β-relaxation transition reflecting the defreezing of rotations about the ether bond Car--O--Car in the structure of the polyimide under consideration.
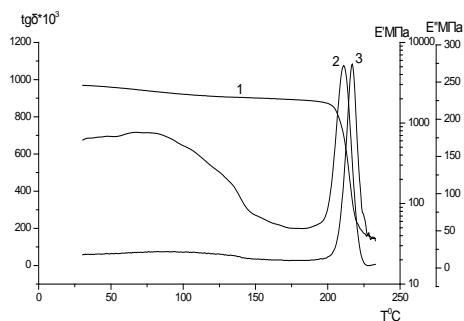
Fig. 2. DMA curves for the polyimide **R-BAPS**.

The results obtained in dynamic mechanical tests of the polymers synthesized are presented in Figs. 3a--3d. In the case of multiblock copoly(urethane-imide)s **(R-TDI 2300-R)BAPS** (Fig. 3a) and **(R-TDI 2700-R)BAPS** (Fig. 3b), the temperature dependences of the loss modulus E" clearly demonstrate maxima at negative Celsius temperatures (at --51 and --20°C, respectively), with portions of nearly temperature-independent E' modulus observed above 50°C, the so-called plateaus of rubber-like high elasticity.
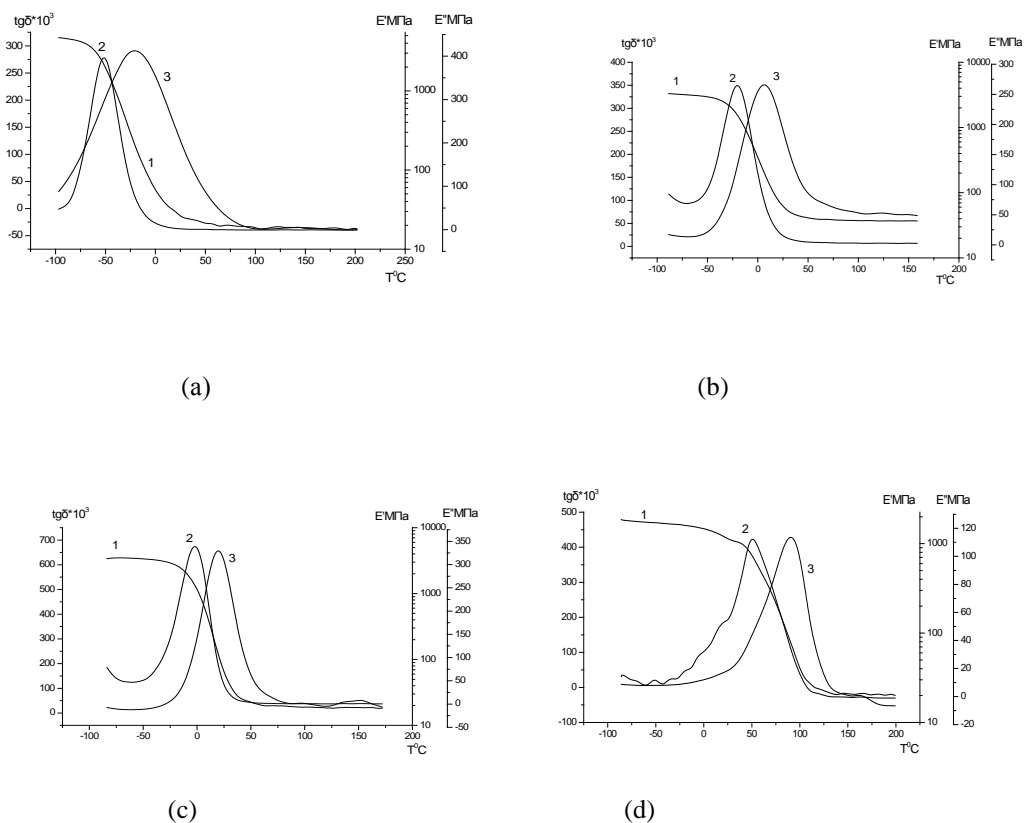

(a)

(b)

(c)

(d)

Fig. 3. DMA curves for the polymers synthesized in the study: (a) **(R-TDI 2300-R)BAPS**, (b) **(R-TDI 2700-R)BAPS**, (c) **(R-ALT-R)BAPS**, and (d) **(R-TDI ALT-R)BAPS**.

Copoly(ester-imide) **(R-ALT-R)BAPS** and copoly(urethane-imide) **(R-TDI 2300-R)BAPS** contain in their structure an aliphatic block with a smaller molecular mass than that in the two cases considered above (Mn 900 against Mn 2300 and Mn 2700), i.e., the fraction of aromatics in these copolymers is larger and, according to this

circumstance, the interpretation of the DMA results is more complicated. The occurrence of the peak in the curve E'' (Fig. 3c) at negative Celsius temperatures is indicative of the devitrification of aliphatic blocks in **(R-ALT-R)BAPS**. In the case of **(R-TDI ALT-R)BAPS** (Fig. 3d), the DMA curves show inflections only at a temperature close to 0°C , i.e., the devitrification process is masked by the melting of the crystalline phase (see Fig. 1d). The peaks observed in the temperature dependences of E'' and tanδ for **(R-TDI ALT-R)BAPS** (Fig. 3d) should be attributed to the melting of aliphatic blocks.

On the assumption that the devitrification of aliphatic blocks is not a cooperative process, it is possible to calculate the activation energies of the devitrification of the aliphatic blocks in **(R-TDI 2300-R)**, **(R-TDI 2700-R)BAPS**, and **(R-ALT-R)BAPS**: 99, 139, and 160 kJ/mol, respectively. It is reasonable to believe that the elasticity of the films grows as the activation energy of the devitrivication of flexible blocks becomes lower.

Figure 4 show DMA curves for the composite **(R-ALT-R)BAPS** containing 5 wt % TL176 resin. Comparison of the curves in Fig. 3d and Fig. 4 shows, in the case of the composite, that the E'' and tanδ peaks are shifted to higher temperatures and, what is important, the plateau of the rubber-like elasticity extends into the high-temperature region. It is reasonable to believe that the latter means an increase in the working temperature limit of the material. The effects demonstrate that the dynamic mechanical properties of the polymers synthesized can be controlled. It should also be noted that introduction of TL176 resin into poly(urethane-imide) in an amount of 5 to 90% markedly improves the thermal resistance of the composite. The thermal stability indices $\tau 5$ and $\tau 10$ grow, compared with those for the starting polymer, by 93 and 145°C, respectively.

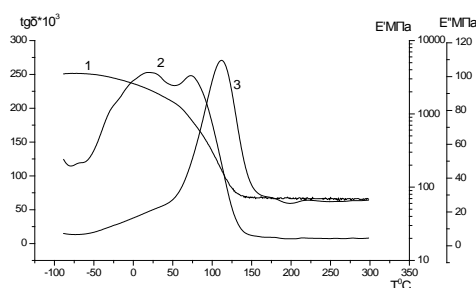Fig. 4. DMA curves for a film of the **(R-ALT-R)BAPS** composite containing 5 wt % TL176 resin.

Key: (1) tanδ (2) MPa

At temperatures higher than 200°C, the polymers pass to the flowing state, which is indicated by the rheological tests of the polymers synthesized. For example, it was shown that, in the case of the copoly(uretane-imide) **(R-TDI 2700-R)BAPS**, the polymer melts are a non-Newtonian fluid without supramolecular structures in the temperature range from 210 to 260°C. The viscosities (Pa·c) at different shear rates and temperatures are listed in Table 2.

Table 2. Viscosity of molten **(R-TDI 2700-R)BAPS** (Pa·c)

Temperature, °C	Shear rate, s^{-1} (circular frequency, rad/s)					
	0.001	0.01	0.1	1	10	100
210	3400	2320 ÷ 3340	798 ÷ 6500	411 ÷ 6290	260 ÷ 3560	72.2 ÷ 1250
220	-	1900	-	1470 ÷ 1800	-	-
230	-	1100	-	780	-	-
240	-	780	-	310	-	-
250	-	540	-	122	-	-
260	-	470	-	54.5	-	-

Note. The table summarizes the results of dynamic and shear tests in Down and Top modes.

The viscous flow is characterized by a high activation energy that is strongly dependent on the shear rate (circular frequency): 197.5 kJ/mol at 0.01 s--1 and 441 kJ/mol at 1 s--1. Despite the comparatively narrow temperature range in which the polymer flows, being not destructed and cross-linked, it is possible to find processing conditions of the **(R-TDI 2700-R)BAPS** thermoplastic elastomer.

4. CONCLUSIONS

The properties of the multiblock polymers synthesized in the study: copoly(ester-imide) and copoly(urethane-imide)s sharply differ from those of the parent polyheteroarylene. The results of stress-strain tests demonstrate that the polymers exhibit elongations at break that are longer by an order of magnitude, compared with the known aromatic polyimides. In contrast to these latter, the polymers synthesized in the study have glass-transition points at negative Celsius temperatures. The DMA of the polymers revealed temperature ranges in which the storage modulus E' is nearly temperature independent, being comparatively small. At temperatures above 200°C, the polymers form processable melts: they flow without being destructed or cross-linked. With consideration for the aforesaid, the polymers can be regarded as thermoplastic elastomers (thermoelastoplastics).

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