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Synthesis and physicochemical properties of polyurethane block copolymers and their compositions with plasticizers

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The synthesis of polyurethane block based on oligoesterdiols 4,4´-methylene-bis(phenylisocyanate), and various chain elongating agents was studied. The properties of these copolymers were compared (using literature data) with selected properties of polyurethanes obtained by the reactions of oligoetherdiols, *viz.*, oligo-3,3´-bis(azidomethyl)oxetanediol and oligo-3-azidomethyl-3´-methyloxetanediol with diisocyanates. The complex of rheological and physicomechanical properties of the initial and plasticized polyurethane block copolymers was studied. Regularities of their deformation behavior were established. The process of mutual solubility was studied by the microinterference method for a wide range of systems block copolymers—plasticizers. On the basis of the data obtained, the phase diagrams were constructed for limitedly compatible systems.

Key words: polyurethane, block copolymer, thermoelastoplastic, plasticizer, phase equilibrium, physicomechanical properties, viscosity.

Polyurethane block copolymers with alternating rigid and flexible chain fragments, whose structure can be controlled depending on the nature and content of these fragment and which manifest the properties of both thermoplastics and thermoelastoplastics, are important objects of experimental research and a promising class of polymer materials of diverse design. In particular, these thermally reversible polymers can be used both the individual state and in a mixture with plasticizers as bindings for polymer composites of various design.[1—3] At present, in spite of sufficiently extensive studies in the area of polyurethane block copolymers[4—10] with the properties of thermoelastoplastics, data on the systems, which can be treated at lower temperatures than those for classical systems, including due to the presence of plasticizers,[11—13] are almost lacking.

The purpose of the present work is the synthesis and study of the physicochemical and physicomechanical properties of individual and plasticized block copolymers of various compositions.

Experimental

Polyurethane block copolymers (PU) of various compositions based on oligoesterdiols, namely, industrial oligoesters OMA-2100 (copolymer of butanediol, diethylene glycol, and sebacic acid) and OMA-1950 (copolymer of ethylene glycol and sebacic acid) produced at the OOO "Firma Zapad" (Kazan, Russia), were used as high-molecular-weight objects. 1,4-Butanediol (BD), 1,4-butenediol, and 1,6-hexanediol (Aldrich), which were used without additional purification, and polyester PDA-800 (oligoester based on adipic acid and diethylene glycol) produced at the Kazan Plant of Synthetic Rubber (Kazan, Russia) served as chain elongating agents.

The initial oligomeric and low-molecular-weight diols were dried *in vacuo* ($P_{res} \leq 10$ Torr, 80±2 °C) for 6—10 h to the residual moisture content ≤0.005% determined by the Fischer method.[14]

4,4´-Methylene-bis(phenylisocyanate) (MDI) (Aldrich) was distilled *in vacuo* at 50—55 °C (12 Pa) and stored in sealed ampules. The content of isocyanate groups was 99.9% of the theoretical value.

Polyurethane block copolymers were synthesized in a high-performance temperature-controlled micromixer (1400 rpm) under an inert gas atmosphere in methylene dichloride at 25 °C and in the bulk at 60—70 °C.

The completeness of urethane formation was monitored by IR spectroscopy from the disappearance of the absorption bands corresponding to the isocyanate groups.

Dimethyl phthalate (DMP), diethyl phthalate (DEP), diallyl phthalate (DAP), dibutyl phthalate (DBP), and adipodinitrile (ADN) (reagent grade) were used as plasticizers.

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Electronic images were obtained on a Philips EM-301 transmission electron microscope with an accelerating voltage of 80 kV. The samples were prepared according to a standard procedure of carbon—platinum responses[15]: thermally evaporated carbon was condensed on the surface pre-etched in an oxygen plasma, and then a platinum layer was sputtered at an angle of 30°.

Phase and relaxation transitions and thermomechanical properties of polyurethanes and related plasticized systems were studied by the DSC method and thermomechanical analysis (TMA). The Mettler—Toledo Star system for thermal analysis consisting of a DSC822^e/500 calorimeter and a TMA/SDTA840 (Mettler) thermomechanical analyzer was used. Calorimetric studies were carried out at a heating rate of 10 deg min^{-1}.

The procedure based on measuring the deformability of samples upon compression on a standard setup for polymer testing (UIP-70M) was used to estimate the level of viscosity of individual and plasticized polymers.[16]

Thermodynamic compatibility and mutual diffusion in the systems based on polyurethanes and plasticizers were studied in a wide temperature range from –20 to +100 °C.[17,18] Prior to tests the temperature of the samples was maintained constant at 120 °C for 20 min, and then the process of diffusion band formation at a specified temperature was studied.

The strain-strength characteristics in the tension mode of individual and plasticized block copolymers were studied on a rupture machine at a clamp displacement velocity of ~50 mm min^{-1} with automated recording of the tension diagram.[19]

Results and Discussion

Polyurethane block copolymers were prepared by the reaction of oligoesterdiol (OMA-1950 or OMA-2100) with MDI at their ratios of 2.5 and 3 and with low-molecular-weight diol or with an additive of PDA-800.

Polyurethaneoxetane block copolymers (PUO) were synthesized[20] from oligoetherdiols, *viz.*, oligo-3,3´-bis-(azidomethyl)oxetanediol (oligo-BAMO) and oligo-3-azidomethyl-3´-methyloxetanediol (oligo-AMMO), by the cationic polymerization of the corresponding cyclic ethers 3,3´-bis(azidomethyl)oxetane and 3-azidomethyl-3-methyloxetane, respectively, in dichloroethane using boron trifluoride etherate as a catalyst[21] and a mixture of diisocyanates hexamethylenediisocyanate and *p*-toluilenediisocyanate (standard chain elongating agent). Polyurethanes of both types are synthesized by the two-stage method, which can be presented in the general case as follows:

Stage 1. Formation of prepolymers by the interaction of oligodioles with an excess of diisocyanate

$$x\,\mathrm{HO{-}R^1{-}OH} + (x + 1)\,\mathrm{OCN{-}R^2{-}NCO} \longrightarrow$$

$$\longrightarrow \mathrm{OCN{-}[{-}R^2NHOCO{-}R^1O{-}CONH{-}]_{\mathit{x}}{-}R^2{-}NCO}.$$

Stage 2. Formation of the urethane block copolymer by the interaction of the prepolymer with a chain elongating agent

$$x\,\mathrm{OCN{-}[{-}R^2NHOCO{-}R^1O{-}CONH{-}]_{\mathit{x}}{-}R^2{-}NCO} +$$

$$+\, x\,\mathrm{HO{-}R^3{-}OH} \longrightarrow$$

$$\longrightarrow \mathrm{OCN{-}[{-}R^2NHOCO{-}R^1O{-}CONH{-}]_{\mathit{x}}{-}}$$

$$\mathrm{{-}R^2{-}[{-}NHOCO{-}R^3{-}OCONH{-}({-}R^2NHOCO{-}}$$

$$\mathrm{{-}R^1O{-}CONH{-})_{\mathit{x}}{-}R^2{-}]_{\mathit{x}-1}{-}NHOCO{-}R^2{-}OH}.$$

The total ratio of the functional groups [NCO]/[OH] or [NCO]/([OH] +[NH]) for PU and PUO, respectively, is maintained close to 1. The synthesized block copolymers are grouped as copolymers of the type $(\mathrm{AB})_n$ (A designate rigid, and B are flexible blocks), which provides the formation of a three-dimensional network due to the formation of domains of the rigid block, which are distributed in the elastic matrix.

Evidently, the distinction of the initial components used in the synthesis of polyurethanes results in the difference in their structure. So, in PU the regions of the oligoesterdiol chain play the role of flexible blocks, and rigid blocks are mainly formed due to hydrogen molecular bonds >NH...O=C< (self-associates of urethane groups). Self-associates of the azide groups belonging to the oligo-BAMO chain are also observed in PUO. They are formed due to dipole—dipole interactions,[22] owing to which oligo-BAMO having the symmetrical structure can form crystal structures. The crystal structures of oligo-BAMO and related polyurethanes are confirmed by the DSC data (Fig. 1). They form rigid blocks and the network of physical bonds in PUO in cooperation with the self-associates of the urethane groups.

Non-symmetrical azide-containing oligooxetanediol (oligo-AMMO) acts as flexible block. The absence in the thermogram of oligo-AMMO (see Fig. 1) of the endotherm of melting of the ordered (crystal) structures, which is observed in the thermograms of oligo-BAMO, is explained by the methyl substituent in an oligo-AMMO molecule. The methyl substituent prevents the mutual orien-

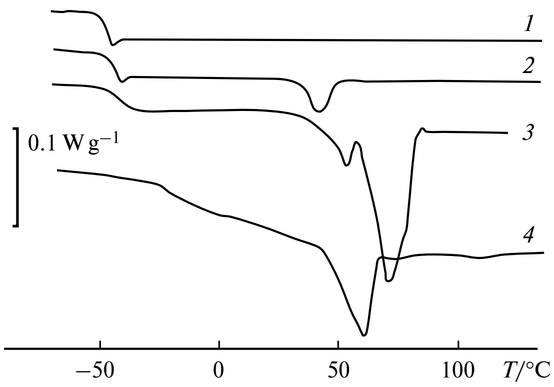

Fig. 1. DSC thermograms[20]: *1*, oligo-AMMO (M_n = 1100); *2*, oligo-BAMO-1 (M_n = 1200); *3*, oligo-BAMO-2 (M_n = 2000); and *4*, PUO containing oligo-BAMO-2. Heating rate 10 °C min^{-1}.

tation of regions of macromolecular chains and the formation of intermolecular physical bonds, confirming validity of consideration of oligo-AMMO as a flexible block.

The shape and size of the melting peak correlating with the degree of crystallinity of oligo-BAMO are determined by its molecular weight (MW) and, depending on MW (in a range of 1000—2500), the size of the melting peak varies from 15 to 30%. It should be mentioned that the melting peak of the crystalline phase characteristic of oligo-BAMO are also observed in PUO obtained[20] involving oligo-BAMO (see Fig. 1, curve *4*), and the shape and value of the peaks change insignificantly.

The studies of morphology of oligo-BAMO showed[10] that it can form crystalline supermolecular structures of two types: radial structures similar to spherulites and elongated crystals (Fig. 2), and the latter are formed in a large amount.

The DSC thermograms for the initial components of PU are shown in Fig. 3: for oligoesters OMA-1950 and OMA-2100, as well as for polyurethane based on one of them. In both cases, a combination of two melting peaks is observed: the peaks are separated for OMA-2100, whereas they are superimposed for OMA-1950. A considerable difference in the heat effects of melting of oligoesters OMA-1950 and OMA-2100 was detected, being 87.5 and 62.8 J g^{-1}, respectively. This difference between oligoesters OMA-1950 and OMA-2100 should also affect the processes of crystallization of polyurethanes synthesized from these esters. Indeed, for the polymer based on OMA-2100 (see Fig. 3), the peak position is shifted but lies in the same temperature range.

A smaller regularity of the structure of PU based on OMA-2100 can result in their degree of crystallinity lower by a factor of 2—3 than that of PU based on OMA-1950.

The presence of ordered areas in the studied polyurethanes was also confirmed by electron microscopy (Fig. 4). The results obtained indicate that the polyurethane samples have a well developed biphase structure with dispersed phase sizes of 50—500 nm.

The heating of the sample during calorimetric measurements changes the shape of the repeatedly recorded thermogram. A comparison of thermograms *1* and *2* (Fig. 5) shows that, after heating during the first calorimetric measurement, the glassy transition temperature increases from −29 to −18 °C accompanied by the appearance of new exotherm at 45—60 °C . These changes can be explained by melting of the domains formed from rigid polyurethane blocks and their subsequent dissolution in the elastic polyester matrix, which results in the increase in the glassy transition temperature of the latter. The exotherm on the repeated thermogram is related to the development of segregation processes leading to the recovery of the domain structure. The newly formed domains then decompose again during heating of the sample to higher temperatures. The decomposition of the domain structure is reversible: after storing of the sample at room temperature, the endotherms are partially recovered within the first day (see Fig. 5, thermogram *3*). The segregation processes associ-

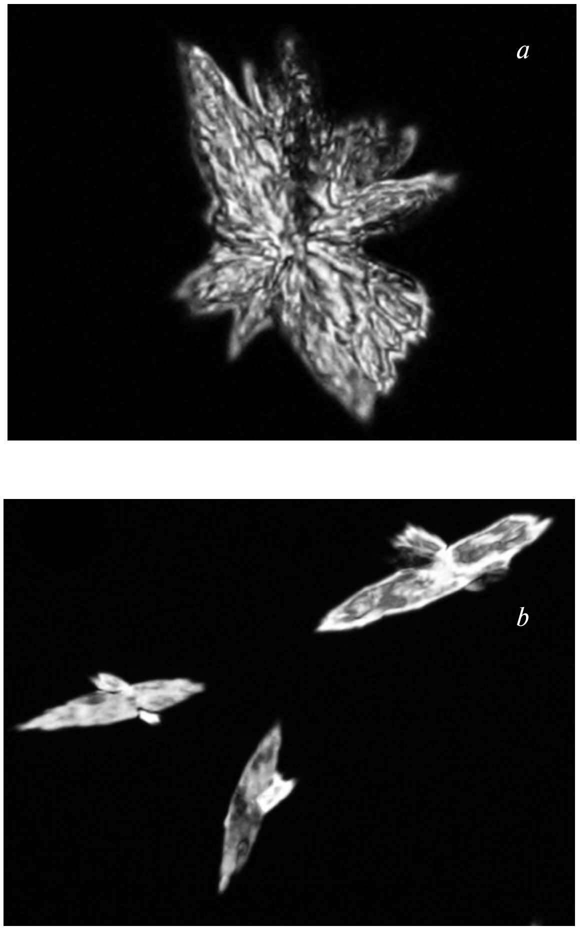

Fig. 2. Types of crystalline structures in oligo-BAMO-1: *a*, spherulites; and *b*, elongated (needle-like) crystals).

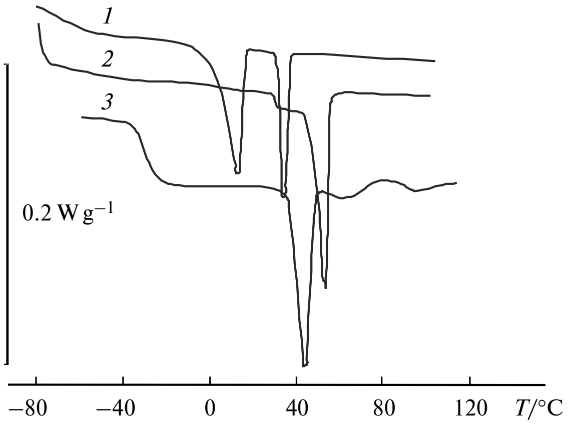

Fig. 3. DSC thermograms of OMA-2100 (*1*), OMA-1950 (*2*), and PU-2 containing OMA-1950 (*3*).

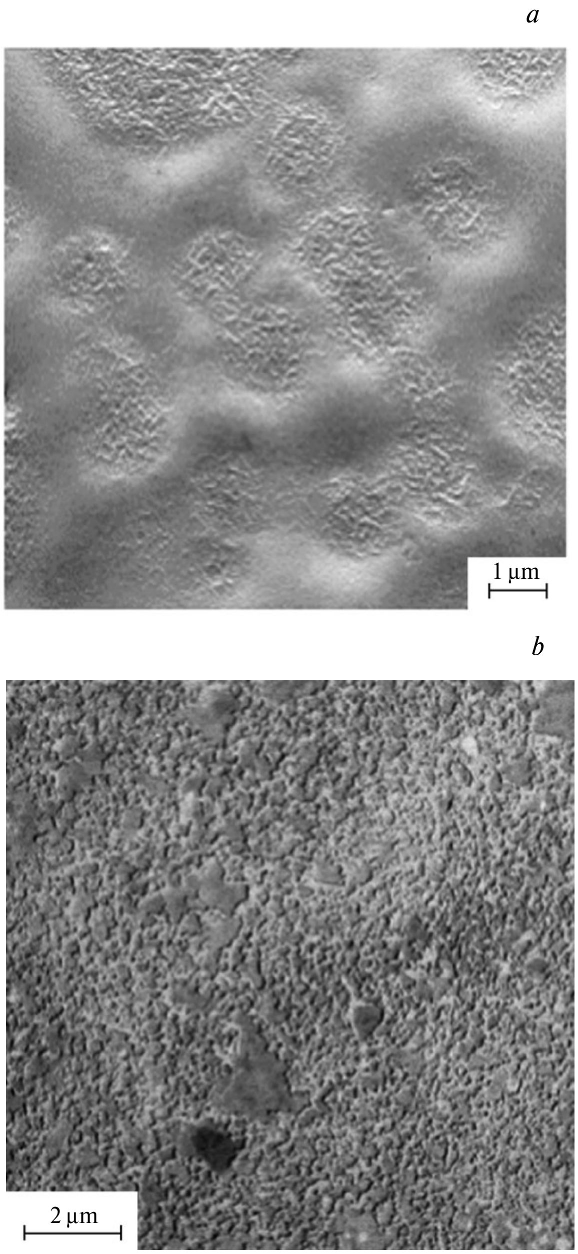

Fig. 4. Images of responses from the PU (*a*) and PUO (see Ref. 8) (*b*) samples.

ated with the recovery of morphology of the studied samples can occur for several months. The shape of the thermograms is affected by the method of preparation of the sample. For example, a sample as a film prepared using a solvent is characterized by the values of heat effects of melting lower by a factor of 1.5 (see Fig. 5, thermogram *4*).

The data on the main characteristics of synthesized polyurethanes, including those on their composition, molecular weight distribution, transition temperatures, and selected physicomechanical characteristics are given in Table 1.

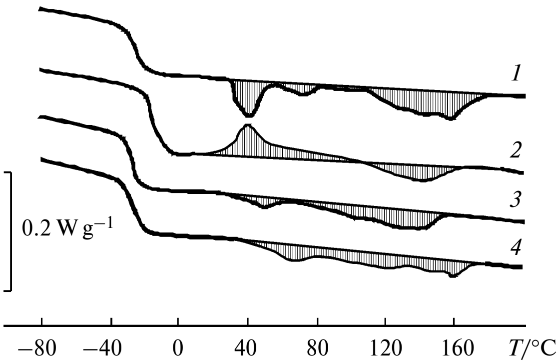

Fig. 5. DSC thermograms of PU-3: *1*, initial sample; *2*, the same sample after short-time heating in the calorimeter to 200 °C; *3*, the same sample after heating to 200 °C and storing at ~20 °C for 1 day; and *4*, the sample as a film obtained from the solution.

The considerably smaller content of the crystalline phase of the polyester segments in PU-3 based on OMA-2100 only is evidently a reason for its significantly lower strength compared to PU-2 based on OMA-1950.

An increase in the strength is observed for PU-4 based on OMA-2100 with a small content of PDA-800 in the solidification system. An analogous effect is observed with an increase in the mole ratios MDI/oligoester from 2.5 (PU-1) to 3 (PU-2) used in the synthesis of the prepolymer (see Table 1). The use of a mixture of BD and hexanediol as a chain elongating agent in the synthesis of PU-6 decreases the strength compared to PU-3 (BD as a chain elongating agent), most likely, due to some elongation of the distance between the nodes of the physical network. The replacement of aliphatic diol BD by a less flexible molecule of *trans*-1,4-butenediol in the synthesis of PU-5 increased its strength compared to PU-3.

Thus, studies performed indicate that the physicochemical characteristics can purposefully be change, according to the classical concepts,[2,23] by the change in the ratio of components in the composition of the studied polyurethanes, namely, the ratio of rigid and flexible blocks.

Since the polymers include plasticizers, their thermodynamic compatibility should be estimated in a wide temperature range. It was shown for the plasticizers studied that DMP is completely compatible with PU-4, while other plasticizers are limitedly compatible (within 30—60%), and the phase diagrams obtained are characterized by the upper critical temperature of dissolution (UCTD) (Fig. 6). The UCTP was attained at 90 °C in the polymer—ADN system.

The DSC thermograms of the plasticized samples of the same polyurethane block copolymer (Fig. 7) shows that plasticization substantially changes the phase structure and boundaries of relaxation transitions. The influence of plasticizers on structure formation can be related to both the facilitation of segregation processes due to an

Table 1. Characteristics of polyurethane block copolymers of various compositions

Copolymer	Composition	M_n (M_w/M_n)	T_g/T_m	T_f/°C	σ_{max}/MPa	ε_{cr} (%)
PU-1	1 *M* PMA-1950, 2.5 *M* MDI, 1 *M* BD	20000 (3.3)	−33/65	153	47.7	943
PU-2	1 *M* PMA-1950, 3 *M* MDI, 1 *M* BD	23531 (3.3)	−30/48	120	54.6	820
PU-3	1 *M* PMA-2100, 3 *M* MDI, 1 *M* BD	17696 (3.6)	−29/52	120	38.2	1000
PU-4	1 *M* PMA-2100, 3 *M* MDI, 1 *M* (0.9 BD + 0.1 PDA-800)	25615 (2.8)	−27/49	126	60.4	873
PU-5	1 *M* PMA-2100, 3 *M* MDI, 1 *M* butene-1,4-diol	22773 (2.5)	—	118	46.0	891
PU-6	1 *M* PMA-2100, 3 *M* MDI, 1 *M* (0.2 hexane-1,6-diol + 0.8 BD)	36075 (3.4)	—	—	32.6	1100

increase in the molecular mobility of the polymer and a change in the thermodynamic conditions of solubility of rigid segments in the amorphous matrix containing the plasticizer. The thermograms exhibit the step-by-step change in the heat capacity caused by the devitrification of the amorphous matrix, and the presence of the plasticizer results in a regular decrease in the glassy transition temperature and (in some cases) melting point of the microcrystalline phase. The microcrystalline phase (rigid blocks) is almost completely dissolved when using DAP: the melting peaks in the thermograms are degenerated.

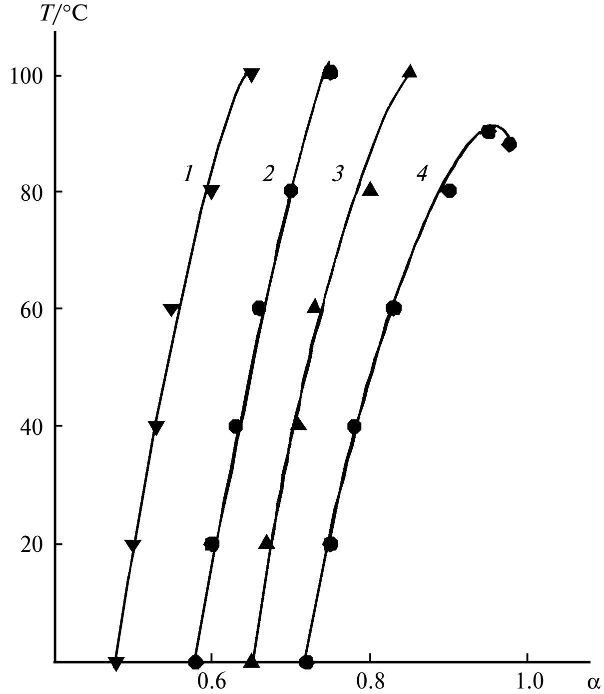

Fig. 6. Phase diagram for the systems based on PU-4 with the plasticizers DBP (*1*), DAP (*2*), DEP (*3*), and ADN (*4*); α is weight fraction.

Several temperature plots of the viscosity for individual and plasticized PU-2 are presented as an example in Fig. 8. Note that the dependences obtained by the procedure applied in this work[16] and the results of viscosity measurements using a capillary viscometer[24] were compared to confirm reliability of the estimated values of viscosity. Since literature data for PU are lacking, applicability of the method was demonstrated for the styrene—isoprenestyrene copolymer. In particular, satisfactory agreement between the results of measurements and published data was shown. All the presented viscosity—temperature plots have a inflection associated with the manifestation of fluidity of the material, which is exhibited as a sharp decrease in viscosity.

The viscosity and flow point decrease regularly with an increase in the plasticizer content in the composition.

Physicomechanical characteristics of materials are very significant for functioning of thermoelastoplastic units. Both the interrelation with the polymer structure and possibilities for controlling them by plasticization are of interest. The tension diagrams are presented in Fig. 9. The tension diagrams of the non-plasticized thermoelastoplastic are S-shaped and qualitatively resemble the tension diagrams of cross-linked elastomers[25]; however, there are substantial distinctions. First, the initial region of the di-

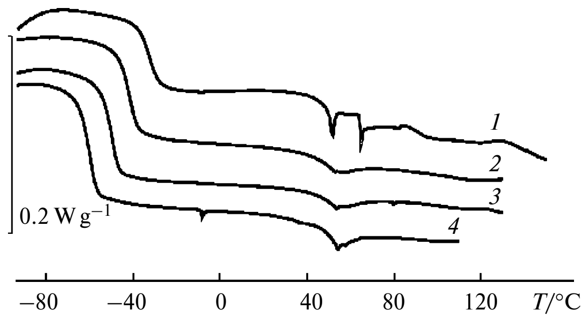

Fig. 7. DSC thermograms of the PU-4 samples with the DAP plasticizer content 0 (*1*), 20 (*2*), 40 (*3*), and 60 wt.% (*4*).

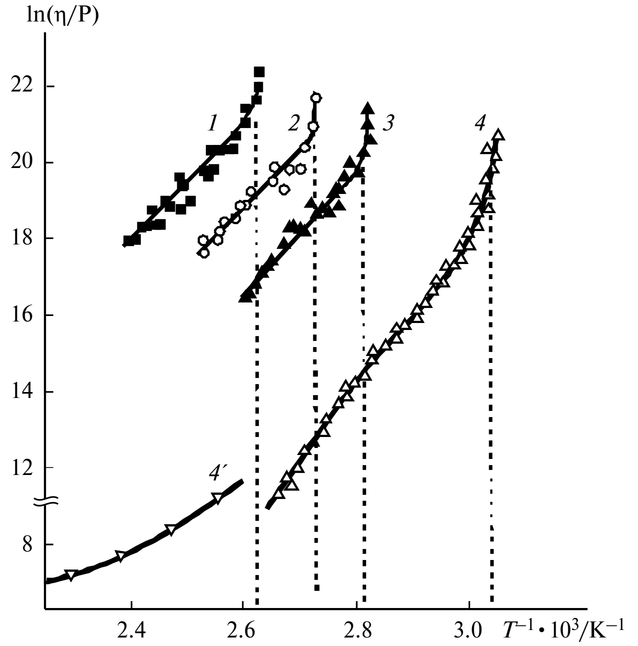

Fig. 8. Temperature dependences of the viscosity (η) for PU-2 with the DAP content 0 (*1*), 30 (*2*), and 50 wt.% (*3*). The temperature dependences of the viscosity for the styrene—isoprenestyrene copolymer obtained by the method used (*4*) and the literature data**24** (*4′*) are presented to confirm reliability of the procedure.

agram, where the elasticity modulus decreases, is more pronounced and distinct for thermoelastoplastics (for the first deformation), while for cross-linked elastomers it is smoother if any. Second, the cross-linked elastomers are characterized by an increase in the slope of the curve (modulus) up to destruction in the last pre-rupture region because of an increase in crystallization strengthening and erection of the chain, and the thermoelastoplastic is characterized by some decrease in the slope of the curve before rupture, which is related, most likely, to the decomposition of bonds between the rigid and elastic blocks of the thermoelastoplastic.

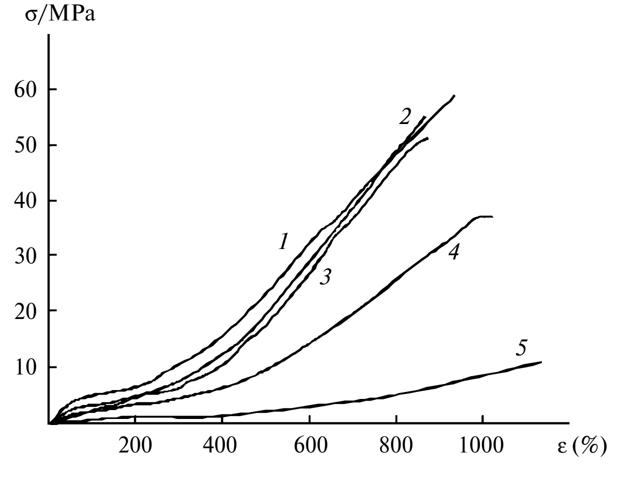

Fig. 9. Tension diagrams for PU-4 (*1*), PU-1 (*2*), PU-2 (*3*), PU-3 (*4*), and PU-2 plasticized with 50% DAP (*5*).

The tension diagrams of the plasticized thermoelastoplastics qualitatively differ from those of cross-linked elastomers only by the length of the last region, which is almost absent from the plasticized thermoelastoplastics.

The common distinctive feature is high values of rupture strains and the presence of residual strains, if the material is unloaded not long before rupture. The sample of PU-3 based in OMA-2100 without a PDA-800 additive has the lowest strength. As a whole, all the PU samples studied demonstrated high physicomechanical characteristics typical of these materials (see Table 1).

The generalized results of studying the influence of the composition on the glass transition temperature, flow point, phase state, and structure are presented in Fig. 10 for the PU-2—DAP system as an example. The phase diagram consists of uniphase regions I, II, and III in which the plasticized thermoelastoplastic differs by the physical state and of region IV corresponding to the biphase system. These regions are separated by the lines that characterize the influence of plasticizers on the flow point T_f (curve *1*) and glassy transition temperature (curve *2*). A characteristic feature of the dependences of the flow point on the composition is a weak influence of the plasticizer concentration on T_f in the range of plasticizer concentrations from 0 to 30%. The flow point of these com-

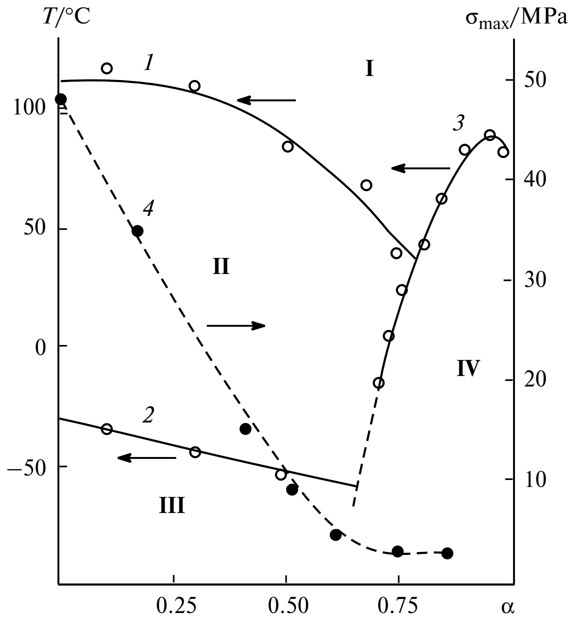

Fig. 10. Generalized diagram of the physical and mechanical properties of the PU-2—DAP system. The dependences of the fluidity (*1*) and glassy transition (*2*) temperatures, the phase diagram binodal of amorphous stratification (*3*), and the dependence of the rupture strength at 20 °C on the plasticizer concentration (*4*); I, II, and III are the regions of uniphase compositions in the visco-fluidity, high-elasticity, and glassy states, respectively; and IV is the region of biphase compositions.

positions is equal to 120—130 °C, which is close to the flow point of non-plasticized polymer. This type of the plots of the flow point *vs* plasticizer content agrees with the results of calorimetric measurements, according to which the destruction of the domain structure of bindings occurs in the same temperature range, where flow processes begin to develop. The further increase in the concentration of plasticizers decreases T_f.

The phase diagram shows that the transition of the plasticized polymer from the high-elasticity to visco-fluidity state occurs at the temperature corresponding to the temperature of the end of melting of the domain microphase.

An increase in the degree of plasticization considerably decreases the strength of the bindings. For instance, the rupture strength of the initial copolymer decreases more than a factor of 15 at the content of DAP plasticizer in the binding higher than 60—70 wt.%, further remaining almost unchanged. A similar change in the mechanical characteristics with the variation of the composition of the plasticized system can possibly be due to the phase decomposition of the system. Note that analogous effects of the dependence of the mechanical properties for the polymer—plasticizer systems have been mentioned earlier.[26]

Thus, the temperature—concentration conditions for the synthesis were established, including the ratio of oligoesterdiols, isocyanates, and chain elongating agents, which provide the preparation of PU with a decreased temperature range of transition to the visco-fluidity state. Structural peculiarities of the formation of the physical and mechanical properties of PU with classical oligoesterdiols and with oligoazidooxetanediols, which form the network of physical bonds due to crystallized blocks, were analyzed in comparison. The rheological and physicomechanical properties of individual and plasticized PU were studied. The generalized diagram of the physical and mechanical properties was presented for one of the studied systems polyurethane block copolymer—plasticizer. An analysis of similar diagrams, including those containing changes of these or other service characteristics depending on the composition, makes it possible to evaluate prospects of using the systems as bindings for composite materials.

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