

Block Copolymers with Urethane and Urethane-Urea Rigid Blocks Based on Oligoesterdiisocyanate and a Binary Low-Molecular Hardener

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Abstract—The synthesis of block copolymers with oligoether soft segments, urethane and urethane-urea blocks based on oligoetherdiisocyanate and mixtures of low-molecular diamine and diol has been described. The dependence of the structure and properties of these materials on the hard block composition and regularities of their mechanical behavior in a wide range of stretching rates have been established. The advantages of the new materials compared to the traditional polyurethane ureas have been demonstrated.

Keywords: block copolymers, urethane and urethane-urea blocks, composition, synthesis, structure, properties

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INTRODUCTION

Among block copolymers (BC) with H-bonds, nanoheterogeneous elastomers with alternating soft and hard segments are widely used such as polyurethanes, polyurethane-urea, or materials based on oligodieneurethane epoxides [1–3]. Essential difference in polarity of soft and hard segments (blocks) leads to their microphase separation with the formation of hard domains acting as enhancing nanodispersed filler and cross-linking points of a specific physical network. The H-bonds stabilize the domains of hard blocks. Depending on the chemical structure of the used oligomers, diisocyanates and low-molecular chain extenders, BCs with various combinations of physico-mechanical properties can be synthesized.

One of the promising trends in the efficient regulation of the structure and properties of BC with urethane or urethane-urea hard blocks and technological properties of the reaction mass is the use of combinations of diisocyanates instead of individual ones [4, 5]. Based on the mixtures of two oligodiisocyanates, a series of materials was synthesized that shows improved properties compared to BCs based on individual oligodiisocyanates, including elastomers with heterogeneous hard urethane-urea blocks [5].

Studies of the properties of compositions based on oligoetherdiisocyanates and mixtures of low-molecular diamine and diol are limited to data on elastic and thermal properties of materials synthesized using 4,4'-diaminediphenylmethanediisocyanate, isophoronediamine, and 1,4-butanediol [6]. The nonadditive

change in the elastic modulus of the elastomer at varying the ratio of the hardener components has been shown. It is supposed that the reason is the irregular structure of the hard phase of the material.

Limitations of the BC physico-mechanical properties (the strength and the relative critical deformation ε_{cr}) determine their applicability under various conditions of mechanical action. In this work, the results of studies of rheological, thermal, thermomechanical, and physico-mechanical properties of the compositions based on oligodiisocyanate hardened by mixtures of aromatic diamine and low-molecular diol are presented.

The aim of this work is to improve the properties of the segmented elastomers with specific interactions and the technological properties of the reaction mixtures for their synthesis.

EXPERIMENTAL

The objects of studies were segmented polyurethane (SPU) compositions based on oligotetramethyleneoxidediisocyanate containing urethane and urethane-urea hard blocks. Starting components for their synthesis were oligotetramethyleneoxidediol (OTMD) (BASF) ($M \approx 1000$), 2,4-toluene diisocyanate (BASF), methylene-bis-*o*-chloroaniline (MOCA) (*Mitsubishi International Corp.*) and 1,4-butanediol (BD) (*Acros Organics*) with 0.04% water content.

The SKU-PFL-100 prepolymer was synthesized by the reaction of OTMD with diisocyanate taken in

Table 1. Properties of SPU with urethane or urethane–urea blocks

x_2	N_{dx}	N_x	N_d	σ_{cr} , MPa	ε_{cr} , %	E_{100} , MPa	T_g^s , °C	T_h , °C	C_r , %
	kmol/m ³								
0	1.77	0.06	1.71	44.5	458	14.7	−51	202	36.6
0.2	1.73	0.06	1.67	46.6	487	11.4	−50	202	35.2
0.3	1.59	0.05	1.54	49.9	516	9.5	−48	199	34.5
0.5	1.38	0.05	1.33	56.0	542	7.2	−44	193	33.0
0.6	1.05	0.04	1.01	41.8	564	5.4	−41	185	32.3
0.7	0.62	0.04	0.58	28.7	602	3.4	−40	173	31.6
1.0	0.03	0.03	0	11.3	910	1.9	−37	—	29.1

excess of 2.04. Prepolymer was hardened by a melt of MOCA (melting point 105°C), its mixtures with BD (the MOCA melt was prepared in the presence of BD), and individual BD. The components of the reaction mass were mixed for 3 min at a temperature of 50–52°C and residual pressure in a stirrer of 0.2–0.4 kPa. Before testing, the samples hardened over 3 days at a temperature of 90°C were held at room temperature for no less than 15 days. The completeness of the conversion of NCO groups was controlled by FT-IR spectroscopy. The procedure of sample preparation was the same as in [5]. The molar ratio of NCO groups to the total number of NH₂ and OH groups of the hardener was 1.05.

The mechanical properties included the nominal tensile strength σ_{cr} (maximum stress per initial cross-section of the sample), the relative critical strain ε_{cr} , the nominal elastic modulus E_{100} at 100% deformation, and the destructive stress (true strength $f_r = \sigma_{cr} (\varepsilon_{cr} + 100) / 100$), and were determined on an *INSTRON*-3365 universal testing machine at a temperature of 25°C and various stretching rates.

The values of the efficient density of the chemical network N_x and physical network N_d with the nodes (rigid domains) was determined using the technique described in [7] with two solvents, toluene, and tributyl phosphate.

The glassing temperature of the soft phase of the SPU samples was determined on a *DSC 822^e* differential scanning calorimeter (*METLER-TOLEDO*) at a scanning speed of 0.02 degrees/s. The softening temperature of the hard block domains was determined on a *TMA/SDTA 841^e* instrument (*METLER-TOLEDO*) at a scanning speed of 0.05 degrees per second under a stress of 0.015 MPa. The rheological properties of the reaction mass were determined on the *Rheotest-2* instrument with a cone-plate assembly at the temperature of 50 ± 0.2°C and a shift rate of 180 s^{−1}.

The molecular structure of SPU was studied by IR spectroscopy on an *IFS 66/S* FT-spectrometer (*Bruker*) in the absorption region of carbonyl of urethane and urea groups (the range of wavenumbers of 1600–1800 cm^{−1}).

RESULTS AND DISCUSSION

Table 1 presents the values of the density of the chemical network N_x , the efficient density of the physical network with domains of hard blocks playing a role of cross-linking points N_d , and the total efficient network density N_{dx} of the SPU samples synthesized at various BD mole fractions x_2 in a mixture with the MOCA diamine. Furthermore, it presents the physico-mechanical properties of the samples with the individual and heterogeneous hard blocks at the stretching rate of 0.278 s^{−1} (500 mm/min), the values of glassing temperature of their soft phase T_g^s , and the softening temperature of the hard phase T_h .

It can be seen from Table 1 that, despite the slight difference in the concentration of hard blocks of 36.6 ($x_2 = 0$) to 29.1% ($x_2 = 1$), many properties of the materials studied essentially vary. For instance, the relative critical deformation at under stretching ε_{cr} increases from 455 to 910%, while the nominal elastic modulus decreases more than sevenfold. At low concentrations of the urethane–urea blocks in SPU, not only does the glassing temperature of the soft phase T_g^s increase, but the glassing temperature of the hard phase T_h also decreases significantly, which may be due to the formation of more defective (irregular) domain structure of the material.

An analysis of the IR absorption spectra of carbonyl of urethane and urea groups of BC with individual and heterogeneous hard blocks shows that polytetramethyleneoxide–urethane–urea has a typical intensive

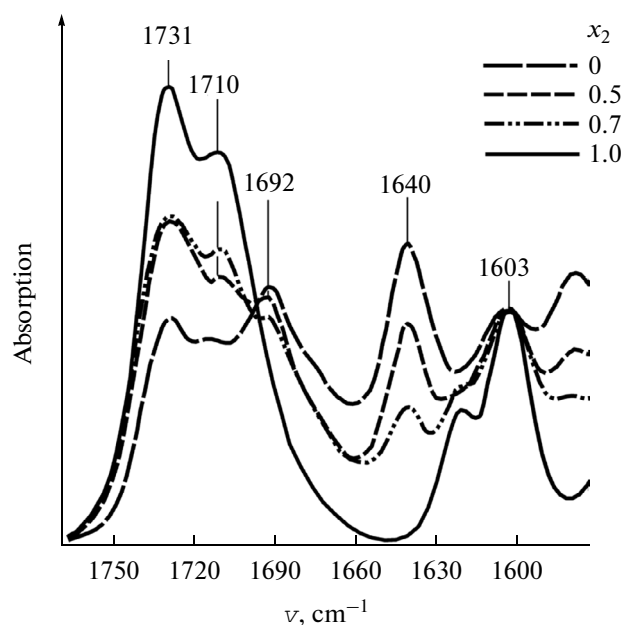


Fig. 1. IR spectra of SPU with various concentrations x_2 of butanediol in the mixture with aromatic diamine.

absorption band at 1640 cm^{-1} of carbonyl of urea groups located in the domains of hard blocks (Fig. 1). The intensity of this band shows the degree of microphase separation of soft segments and urethane–urea blocks in polyurethane–urea [8].

With the increase in the concentration of urethane segments in the composition of the heterogeneous hard blocks, the intensity of the absorption band at 1710 cm^{-1} of carbonyl of urethane groups linked by H-bonds with oxygen of polyethers increases, which proves the increase in the concentration of urethane hard blocks in the soft phase of the polymer. In the extreme case, at the use of prepolymer of individual BD as a hardener, the spectral curve consists of two bands, i.e., an absorption band of free carbonyl (1731 cm^{-1}) and an absorption band of carbonyl of urethane groups (1710 cm^{-1}) linked by disordered H-bonds. The absorption band at $1700\text{--}1703\text{ cm}^{-1}$ of carbonyl of self-associates of urethane groups [9] of urethane blocks is absent. Thus, despite the high concentration of hard urethane blocks, this is a single-phase material. The same conclusion is drawn based on the fact that the total efficient network density of SPU synthesized using individual butanediol is equal to the efficient density of the chemical network N_x . The network density caused by hard domains is $N_d = 0$.

Thus, as compared to polyurethane–urea with high degree of microphase separation of urethane–urea hard blocks, the material with heterogeneous hard blocks has higher solubility of hard blocks (proton donors) in soft phase of SPU. As a result, the efficient density of physical network N_d caused by hard

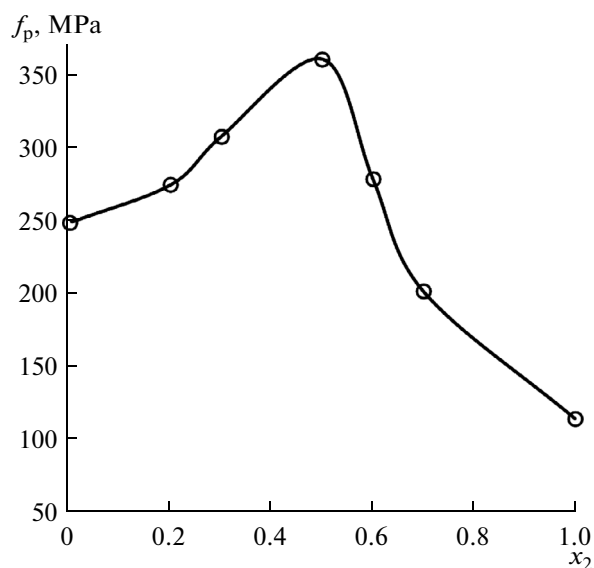


Fig. 2. Dependence of true strength of SPU on the concentrations x_2 of butanediol in the mixture with MOCA ($\nu = 0.278\text{ s}^{-1}$).

domains must decrease and the glassing temperature of soft phase must increase, which is actually observed in the experiment. The decrease in the content of the hard phase in SPU with an increase in the urethane blocks concentration leads to a significant decrease in nominal modulus value. According to the experimental results, the classic polytetramethylene–oxide–urethane–urea is not the optimal material from the point of view of high strength properties of BC.

The highest nominal σ_{cr} and true f_r strength of SPU are reached at the optimal combination of interchain interaction in the soft phase and the microphase separation between soft and hard blocks. For the material studied, the maximum value of nominal (Table 1) and true strength (Fig. 2) is observed at equal content of urethane and urethane–urea ($x_2 = 0.5$) blocks. The true strength of SPU is 1.5 times higher than the strength of the starting polyester–urethane–urea (Fig. 2). It is noteworthy that the high strength of SPU is observed upon an increase in the relative critical strain of the elastomer.

Studies of the physicochemical properties of materials with the same and different hard blocks at various stretching rates ν showed that with a decrease in the stretching rate relative critical strain ε_{cr} of the elastomers changes insignificantly while the nominal modulus regularly decreases (Table 2). The dependence of the true strength f_r of heterogeneous SPU on the stretching rate is not direct, as for the usual single-phase crosslinked elastomers, but inverse. The lower the stretching rate, the higher the strength of the material (Fig. 3).

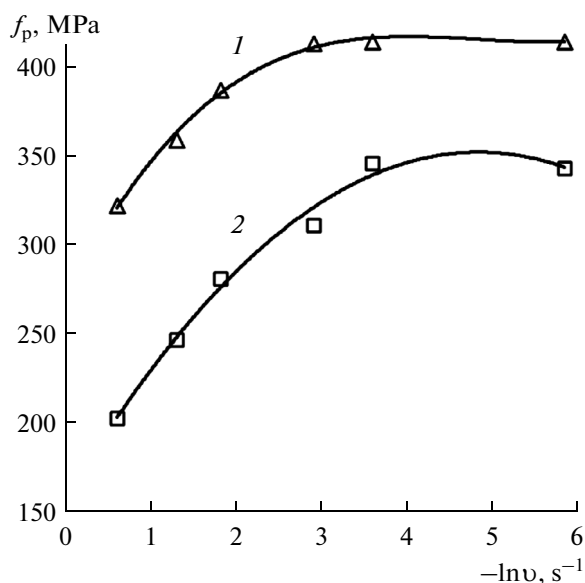


Fig. 3. Dependence of true strength on stretching rate of SPU (1) with various hard blocks ($x_2 = 0.5$); (2) without urethane blocks ($x_2 = 0$).

This is because the orientation of hard blocks in the domains in the direction of the force action at large strains of the heterogeneous elastomer. With a decrease in the rate of mechanical action, the degree of orientation of the hard blocks increases [9], which contributes to the strengthening of the polymer. On the contrary, relaxation of the labile physical network contributes to the decrease in the material strength at low values of v . The mechanism of BC strengthening with specific interaction under various conditions of strain is detailed in [9].

For SPU with only urethane–urea hard blocks, the factor of orientation of hard blocks is predominant, which leads to a strong difference between the highest and the lowest values of the true strength f_r (1.7 times). At higher stretching rates, hard blocks do not have enough time to orientate, which leads to a decrease in the strength of the material [9]. As a result of the substitution of half of the urethane–urea blocks by urethane blocks, which are soluble in the soft phase of the polymer ($x_2 = 0.5$), the interchain interaction in it increases. The influence of the orientation of hard blocks on the strength of elastomers is mainly compensated by the relaxation of the labile physical network at slow stretching. Thus, the SPU strength in a wide range of stretching rate values (0.56–0.003 s⁻¹) changes by no more than 1.3 times (Fig. 3, curve 1).

Thus, the new material with urethane and urethane–urea blocks shows improved strength properties as compared to polyurethane–urea and a higher stability of these properties at change of the mechanical action rate.

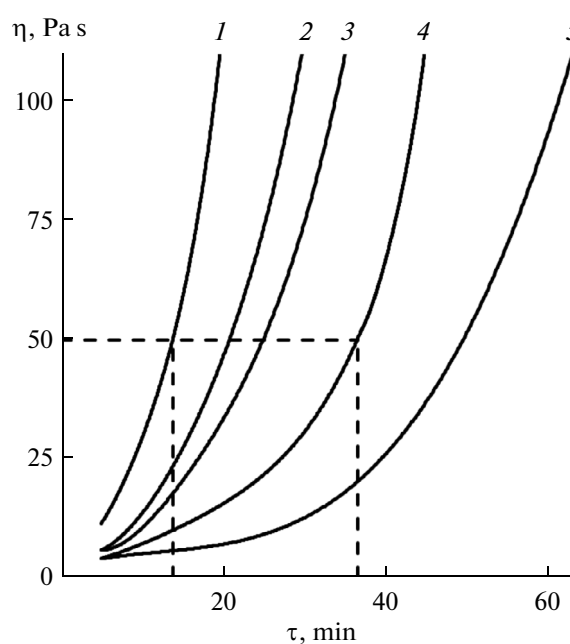


Fig. 4. Curves of increase in dynamic viscosity η at temperature of 50°C of compositions at mole fraction x_2 of butanediol in the hardener mixture: (1) 0; (2) 0.2; (3) 0.3; (4) 0.5; (5) 0.7.

The rheological kinetics of the reaction mixtures with various mole fractions of 1,4-butanediol in the hardener (BD + MOCA) composition was studied. It has been shown that upon an increase in the BD mole fraction in the hardener mixture, the time of keeping the low dynamic viscosity η of the reaction mixture essentially increases (Fig. 4). At $x_2 = 0.5$, the stability of the reaction mixture (viscosity point $\eta = 50$ Pa s is acceptable for processing the reaction mass by the casting technique) is more than 30 min, which is acceptable for fabricating products of various configurations, including oversized products.

Table 2. Physicomechanical properties of SPU ($x_2 = 0$ and $x_2 = 0.5$) at various stretching rates v

v, s^{-1}	$-\ln v, s^{-1}$	$x_2 = 0$		$x_2 = 0.5$	
		E_{100}, MPa	$\epsilon_{cr}, \%$	E_{100}, MPa	$\epsilon_{cr}, \%$
0.556	0.587	15.8	454	7.6	549
0.278	1.28	14.7	458	7.2	542
0.167	1.79	14.2	451	7.0	537
0.056	2.88	12.9	448	6.7	525
0.028	3.57	12.0	455	6.5	546
0.003	5.81	10.8	457	5.6	590

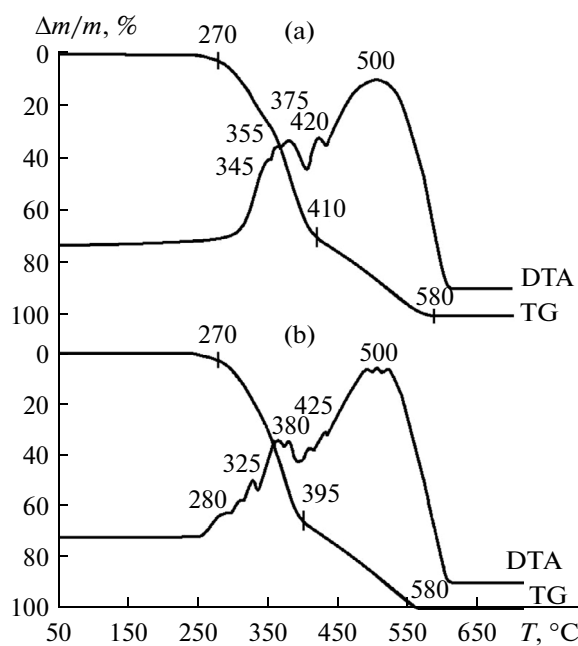


Fig. 5. Derivatograms of SPU (a) with various hard blocks at $x_2 = 0.5$ and (b) without urethane blocks.

In our opinion, the reason for the improved rheological properties of the reaction mass is not only lower rate of the reaction of oligoetherdiisocyanate with butanediol than with diamine. The solubility of hard urethane blocks in the reaction mixture leads to an increased time of the formation of branching cross-linking points caused by the microphase separation of hard urethane–urea blocks and polyester soft segments mixed with urethane blocks.

Thus, the presence of soluble and slightly-soluble hard blocks in the SPU polymeric chains leads to unusual change in structure and properties of such polymers with the change in composition of hard blocks. The nonadditive influence of heterogeneous hard blocks on the properties of BC is pronounced. The possibilities of regulating the physicochemical properties of such type of SPU are much wider. The same refers to regulating the rheological properties of the reaction mass. The combination of diol and diamine leads to essential improvement of manufacturability of the compositions as compared to the technological properties with individual aromatic diamine (at the synthesis of polyether–urethane–urea).

The thermal stability of SPU with individual urethane–urea blocks ($x_2 = 0$) and heterogeneous hard blocks on the *Q-1500D* thermogravimetric analyzer in corundum crucibles was studied at the heating rate of 0.03 degrees/s. It was shown that at temperatures of up to 270°C the both of samples are thermally stable. In the range of 270–395(410)°C the decomposition of SPU is accompanied by the loss of 65% of the initial

weight with the specific rate of 0.02 mg/s. The thermal destruction of the samples is almost finished at 580°C (Fig. 5).

The decomposition of polyurethane–urea hardened with the MOCA chlorine-containing aromatic diamine is accompanied by numerous peaks on the DTA curve corresponding to exothermic effects of oxidation of the decomposition products (see Fig. 5b). The substitution of MOCA for butanediol only leads to a decreased number of peaks on the DTA curve (Fig. 5a). The new material shows the thermal stability compared to one of polyester–urethane–urea.

CONCLUSIONS

BC with urethane and urethane–urea hard blocks were synthesized based on oligotetramethyleneoxide-diisocyanate and the mixtures of the MOCA aromatic diamine and 1,4-butanediol. It has been shown that the physicochemical properties of a new type of materials and the rheological properties of the reaction mass are regulated in a wide range.

A pronounced nonadditive influence of the composition of hard blocks upon elastic, deformation and strength properties of BC was shown. It was established that an equimolar ratio of diol and diamine produces a material of significantly improved strength compared to polyurethane–urea. The strain properties of the elastomer are also better.

The change in the physicochemical properties of the material with heterogeneous hard blocks was first studied in a wide range of stretching rates. The high stability of the strength properties of the new material to the change in the mechanical action rate has been shown (the strength changes no more than 30% at the change of stretching rate of ~ 200 times).

The main reason for the unusual behavior of the elastomers with heterogeneous hard blocks is a stronger interchain interaction in the soft phase of the polymer as a result of the solution of polar urethane hard blocks able to form H-bonds in it.

The new materials can be manufactured and are promising at both high and low rates of mechanical action.

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