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Thermodynamic properties of linear polyurethanes based on 1,6-hexamethylenediisocyanate with butane-1,4-diol and hexane-1,6-diol in the temperature range from $T \to 0$ to 460 K

N. N. Smirnova,[a]★ K. V. Kandeev,[a] T. A. Bykova,[a] T. G. Kulagina,[a] and A. M. Fainleib[b]

[a]Research Institute of Chemistry, N. I. Lobachevsky Nizhnii Novgorod State University,
Building 5, 23 prosp. Gagarina, 603950 Nizhnii Novgorod, Russian Federation.
Fax: +7 (831 2) 65 6450. E-mail: smirnova@ichem.unn.runnet.ru
[b]Institute of Chemistry of High-Molecular-Weight Compounds, National Academy of Sciences of Ukraine,
48 Khar´kovskoe sh., 02160 Kiev, Ukraine.
Fax: +7 (44) 552 4064. E-mail: fainleib@i.kiev.ua

The temperature dependences of the heat capacity of partially crystalline linear polyurethanes based on 1,6-hexamethylenediisocyanate with butane-1,4-diol and hexane-1,6-diol were studied for the first time in a temperature range of 6—460 K by the methods of adiabatic vacuum and dynamic calorimetry. Physical changes in the state of polyurethanes were revealed and characterized; the standard thermodynamic functions, namely, $C_p°(T)$, $H°(T) - H°(0)$, $S°(T)$, and $G°(T) - H°(0)$, were calculated from the obtained experimental data in the temperature range from $T \to 0$ to 460 K for the polymers in the crystalline, glassy, highly elastic, and liquid states. The energies of combustion of the polymers were measured by the bomb calorimetry method, and the standard thermodynamic characteristics of their formation at 298.15 K were calculated. The thermodynamic characteristics of bulk polycondensation of 1,6-hexamethylenediisocyanate with butane-1,4-diol and hexane-1,6-diol to form linear aliphatic polyurethanes-{4,6} and -{6,6} were determined in the range from $T \to 0$ to 350 K at $p° = 0.1$ MPa. The thermodynamic properties of the polyurethanes under study and polymers of isomeric structure were compared.

Key words: polyurethanes based on 1,6-hexamethylenediisocyanate with butane-1,4-diol and hexane-1,6-diol, heat capacity, enthalpy, entropy, Gibbs function, calorimetry, thermodynamics.

Polyurethanes (PUs) are among the most significant industrial polymers[1,2] and used for designing new promising materials.[3—5]

In the present time, one of the main methods for industrial production of linear PUs is the reaction of diisocyanates with diols[1] that affords *m*,*n*-PUs. Many works on studying the thermodynamic and thermal properties of *m*,*n*-PUs were carried out by calorimetric DTA and DSC methods,[6,7] which are inferior in terms of accuracy and the amount of data obtained to low-temperature adiabatic vacuum calorimetry (AVC). Combined studies by precision AVC methods are necessary to compare the thermodynamic properties of aliphatic polyurethanes, to study dependences of these properties on the composition, structure, and physical state, and to prepare related composite materials. These studies have previously[8—10] been performed for linear aliphatic *n*-PUs synthesized by the polymerization of cyclic urethanes with ring opening and interaction of isocyanato alcohols.

The following tasks were given priority in the present work:

1) calorimetric study of temperature dependences of the heat capacity of partially crystalline linear PUs based on 1,6-hexamethylenediisocyanate with butane-1,4-diol (PU-{4,6}) and hexane-1,6-diol (PU-{6,6}) and determination of the thermodynamic characteristics of possible physical transformations in the 6—460 K temperature range;

2) calculation of the standard thermodynamic functions $C_p°(T)$, $H°(T) - H°(0)$, $S°(T)$, and $G°(T) - H°(0)$ for the temperature range from $T \to 0$ to 460 K using the obtained data;

3) measurement of the energy of combustion of PU-{4,6} and PU-{6,6}, calculation of the standard thermodynamic characteristics of their formation at T = 298.15 K and thermodynamic parameters of polycondensation in the range from $T \to 0$ K to 350 K;

4) comparison of the thermodynamic characteristics of PU-{4,6} with those of PU-{6,6} and with the corre-

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sponding parameters for isomeric PUs to reveal the dependence of the thermodynamic properties of PU-{4,6} and PU-{6,6} on the composition and isomerism.

Experimental

The PU-{4,6} and PU-{6,6} samples synthesized according to a described[11,12] procedure were used. These samples are characterized by the following structure of repeated monomeric units:

PU-{4,6} (M = 258.32 g mol^{-1}) —
$[\text{—O—CO—NH—}(CH_2)_6\text{—NH—CO—O—}(CH_2)_4\text{—}]_n$,

PU-{6,6} (M = 286.37 g mol^{-1}) —
$[\text{—O—CO—NH—}(CH_2)_6\text{—NH—CO—O—}(CH_2)_6\text{—}]_n$.

Before measurements, the samples were evacuated at ~340 K and placed into calorimetric ampules under a dry argon flow. The microstructure and composition were characterized by NMR, IR spectroscopy, and elemental analysis. PU-{4,6}. Found (%): C, 55.57; H, 8.69; N, 10.73. Calculated (%): C, 55.80; H, 8.58; N, 10.84. PU-{6,6}. Found (%): C, 58.78; H, 9.39; N, 9.85. Calculated (%): C, 58.72; H, 9.15; N, 9.78. Gel-permeation chromatography gave for PU-{4,6} and PU-{6,6}, respectively: $M_w = 11.55 \cdot 10^4$ and $6.70 \cdot 10^4$, $M_w/M_n = 1.27$ and 1.09. The crystallinity (α), determined calorimetrically from an increase in the heat capacity upon devitrification of the amorphous part of the samples by a known procedure,[13] was 78 and 75% for PU-{4,6} and PU-{6,6}, respectively.

A completely automated BKT-3 thermophysical setup (adiabatic calorimeter) was used to measure the heat capacity and temperatures and enthalpies of physical changes in the state of the studied PUs in a range of 6—350 K. The setup structure and measurement procedure have been reported earlier.[14] The measurement error of C_p° at helium temperatures, in the range of 10—40 K, and at $T > 40$ K was ±2, ±0.5, and not higher than ±0.2%, respectively.

An automated ADKTTM setup was used for the determination of the heat capacity in an interval of 320—460 K. This setup operates according to the principle of triple thermal bridge.[15] The measurement error of C_p° in the indicated temperature range was not higher than ±1.5%, the error of measurement of the temperatures of physical transitions was ±0.5 K, and that of the enthalpies of physical transformations was 1%.

The energies of combustion of PU-{4,6} and PU-{6,6} were measured in a V-08 calorimeter with an isothermal shell and a static bomb. The calorimeter was modified at the Research Institute of Chemistry of the Nizhnii Novgorod State University. The structure of the calorimeter, measurement procedure, and results of calibrations and verifications have been described earlier.[16] The verification of the calorimeter on the combustion of reference succinic acid gave the enthalpy of combustion corresponding to the nameplate value with an error of 0.017%.

The heat capacities C_p° of PU-{4,6} and PU-{6,6} were measured in a range of 6—460 K. The weights of the samples placed in calorimetric ampules of the BKT-3 setup were $0.2015 \cdot 10^{-3}$ and $0.1586 \cdot 10^{-3}$ kg, and those for ADKTTM were $0.3392 \cdot 10^{-3}$ and $0.2195 \cdot 10^{-3}$ kg, respectively. The heat capacity of PU-{4,6} was 45—65% (35—50% for PU-{6,6}) of the total heat capacity of the ampule filled with the substance in the adiabatic vacuum calorimeter and 30—50% (25—40%) in the dynamic calorimeter. The experimental values of heat capacity were averaged by power and semilogarithmic polynomials in such a way that the root-mean-square deviation of the experimental C_p° values from the smoothed curve $C_p^\circ = f(T)$ would not exceed the measurement error of the heat capacity. Measurements of C_p° in the dynamic calorimeter were carried out in the continuous heating regime with a rate of 0.017 K s^{-1}.

The energies of combustion of the PU-{4,6} and PU-{6,6} samples were determined in six entries. The initial oxygen pressure in the calorimetric bomb in each experiment was ~3 MPa, and the initial temperature of the main period was 298.15±0.03 K. The total amount of energy evolved in experiments on burning weighed samples of PU-{4,6} (0.3389—0.3756 g) and PU-{6,6} (0.1849—0.2154 g) in polyethylene ampules ($\Delta U_c = -46421\pm2$ J g^{-1}) was 17035—18213 and 11785—14716 J, respectively. Corrections for the combustion of polyethylene and a cotton filament used for the ignition of substances were 7979—8593 and 33.4—38.5 J, and a correction for the formation of a nitric acid solution was 25.5—33.5 J. The analysis of gaseous combustion products estimated the content of CO_2 and showed that the ratio of the amount of carbonic acid in the combustion products to its amount calculated from the equation of combustion of PU-{4,6} and PU-{6,6} was 99.87—99.90 and 100.1—100.5%, respectively. No carbon monoxide was found in any entry. The average value of the energy of combustion of the polymers was −26381.4±48.4 J g^{-1} (PU-{4,6}) and −28281±28 J g^{-1} (PU-{6,6}). The following values of the energy and enthalpy of combustion of partially crystalline PU-{4,6} and PU-{6,6} were obtained at 298.15 K and standard pressure: $\Delta U_c^\circ = -26534\pm36$ and -28281 ± 28 J g^{-1}, ΔH_c° (α = 78%) = −6817±12 kJ mol^{-1} and ΔH_c° (α = 75%) = −8104±3 kJ mol^{-1}. They correspond to the heat effect of the reactions

$$[\text{—}C_{12}H_{22}N_2O_4\text{—}]\ (\text{p.cr}) + 15.5\ O_2\ (g) \rightarrow$$
$$\rightarrow 12\ CO_2\ (g) + 11\ H_2O\ (\text{liq}) + N_2\ (g),$$

$$[\text{—}C_{14}H_{26}N_2O_4\text{—}]\ (\text{p.cr}) + 18.5\ O_2\ (g) \rightarrow$$
$$\rightarrow 14\ CO_2\ (g) + 13\ H_2O\ (\text{liq}) + N_2\ (g),$$

where physical states of the reactants are given in parentheses: p.cr is partially crystalline, g is gaseous, and liq is liquid.

Results and Discussion

Heat capacity. The experimental C_p° values and averaging curves $C_p^\circ = f(T)$ for PU-{4,6} and PU-{6,6} are presented in Fig. 1. The samples in this temperature interval were found to occur in the partially crystalline and liquid states. For each polymer, two physical transitions were revealed: the devitrification of the amorphous part of PU-{4,6} was observed in the temperature range from 245 to 300 K, and that for PU-{6,6} was at 245—310 K; the breaks in the plots $C_p^\circ = f(T)$ at 350—450 K for PU-{4,6} and 350—445 K for PU-{6,6} were caused by melting of the crystalline fractions of PU. The C_p° values for PU-{4,6} at 230—480 K presented in Ref. 14 differ from the values measured by us in the same range by 20%

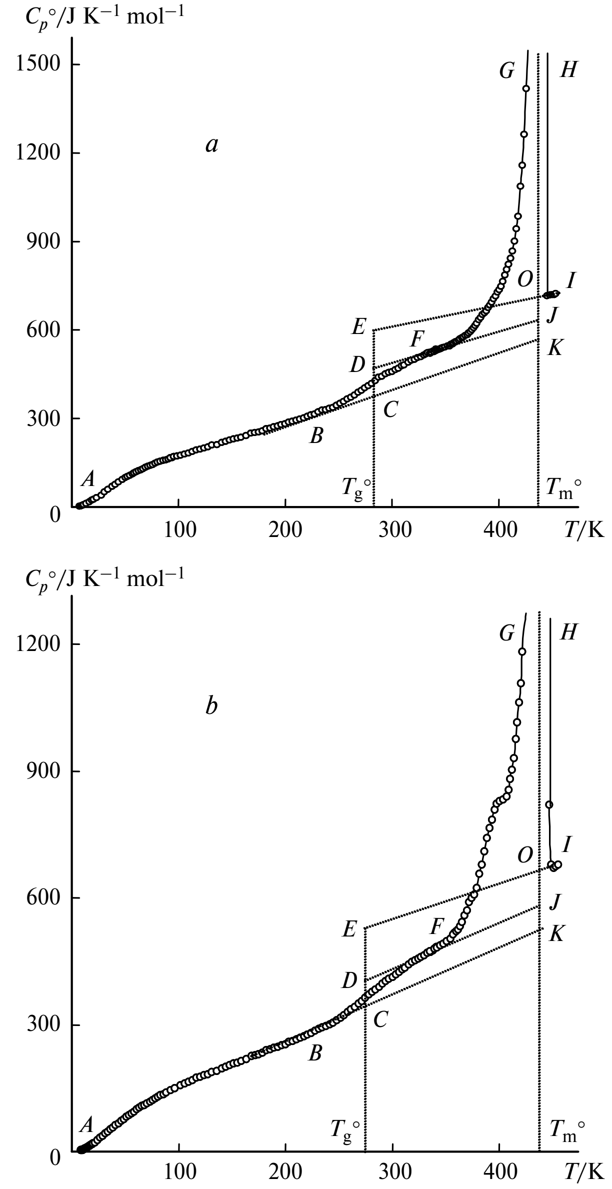


Fig. 1. Temperature plots of the heat capacity of polyurethane-{6,6} (*a*) and polyurethane-{4,6} (*b*) (M = 286.37 and 258.32 g mol^{-1}, respectively): *ABCK* is the crystalline state, *OI* is the liquid state, *ABF* is the partially crystalline state, *ABC* is the amorphous part in the glassy state, *EO* is the amorphous part in the highly elastic state, *FGHI* is the apparent heat capacity in the melting interval, *CD* is an increase in the heat capacity upon devitrification of the sample under study ($\alpha = 75\%$) at the glass transition temperature ($T_g°$), *CE* is an increase in the heat capacity upon devitrification of the completely amorphous PU at $T_g°$, and *KO* is an increase in the heat capacity at the melting temperature ($T_m°$) of the substance with 100% crystallinity.

on the average. However, the authors[14] did not give the characteristics of the PU-{4,6} under study, in particular, crystallinity (α), which does not allow one to analyze the obtained discrepancies, because this is in the region of devitrification of the amorphous fraction of the sample and melting of its crystalline fraction where the heat capacity depends on α of the samples under study.

The multifractal processing of the experimental data for $C_p° = f(T)$ of the substances under study gave the values of the most important parameter of multifractal generalization of the Debye theory of heat capacity of solids[17,18]: fractal dimensionality *D* that characterizes the character of heterodynamics of the solid structure. According to the fractal theory of heat capacity,[17] the power at the *T* parameter in the heat capacity function is designated as *D*. The main equation of the fractal theory of heat capacity can be written as follows:

$$C_v = 3D(D+1)kN\gamma(D+1)\xi(D+1)(T/\theta_{\max})^D, \qquad (1)$$

where *N* is the number of particles in a molecule, *k* is the Boltzmann constant, $\gamma(D+1)$ is the gamma function, $\xi(D+1)$ is the Rieman ξ-function, and $\theta_{\max}$ is the characteristic temperature.

For solids with chain structure[19] at 20—50 K, the $C_p°$ value is proportional to T^1, for layer solids it is proportional to T^2, and for spatial structures $C_p°$ is proportional to T^3. The authors of Ref. 17 believe that *D* can be estimated using experimental data on the temperature dependence of the heat capacity from the slope of the plot of $\ln C_v$ *vs*. $\ln T$. It can be accepted without a substantial error that $C_p° = C_v$ at $T < 50$ K. From the plot of $\ln C_p°$ *vs*. $\ln T$ and Eq. (1) we have in an interval of 25—50 K for PU-{4,6} $D = 2$, $\theta_{\max} = 206.8$ K and for PU-{6,6} $D = 2$, $\theta_{\max} = 194.4$ K. Equation (1) with the values found for the *D* and $\theta_{\max}$ parameters reproduces the experimental $C_p°$ values for PU-{4,6} and PU-{6,6} in the indicated temperature range with the error within 1%. The obtained value indicates a layer structure formed, probably, by hydrogen bonds between the urethane groups. It should be mentioned that this conclusion agrees fairly well with the corresponding data of structural studies for PU-{4,6}.[20]

Characteristics of physical transitions. The parameters of glass transitions and glassy states for PU-{4,6} and PU-{6,6} are presented in Table 1. The glass transition temperature ($T_g°$) was determined by the Alford—Dole method[21] from the break in the temperature plot of the entropy. The $T_g°$ value obtained in Ref. 6 lies in the interval of devitrification temperatures of PU-{4,6} measured

Table 1. Standard thermodynamic characteristics of the devitrification and glassy state of polyurethanes-{4.6} and -{6.6}*

Compound	ΔT_g**	$T_g°$	$\Delta C_p°(T_g°)$	$S°(0)$	$H_g°(0) - H_{cr}°(0)$ /kJ mol^{-1}
	K		J K^{-1} mol^{-1}		
PU-{4,6}	245—300	273±1	191±4	34±1	23±1
PU-{6,6}	245—310	277±1	216±4	35±1	23±1

* Calculated for the completely amorphous substances.

** Interval of devitrification temperatures.

by us; however, the numerical values differ by 20 K. The values presented in Ref. 7 ($T_g° = 332$ K for PU-{4,6} and PU-{6,6}) were determined for the samples prepared as thin films. These differences are related, probably, to different crystallinities of the samples studied by us and in the works[6,7] and to different heating rates when their properties were studied by thermal analysis.

The increase in the heat capacity upon devitrification of the samples ($\Delta C_p°(T_g°;\alpha)$ — *CD*, see Fig. 1) and for the completely amorphous polymers ($\Delta C_p°(T_g°)$ — *CE*) were determined by the graphical extrapolation of the averaging curves $C_p° = f(T)$ for the highly elastic (*DF* and *OE*) and glassy (*ABC*) states of the polymers to $T_g°$. The data obtained were used for the determination of the crystallinity of PU-{4,6} ($\alpha = 78\%$) and PU-{6,6} ($\alpha = 75\%$) by the equation

$$\alpha = [1 - \Delta C_p°(T_g°;\alpha)/\Delta C_p°(T_g°)] \cdot 100\%. \quad (2)$$

The zero entropies and the difference of zero enthalpies of the polymers in the glassy and crystalline states were calculated by the formulas

$$S°(0) = \int_0^{T_m°} [C_p° \text{ (cr)} - C_p° \text{ (am)}] \mathrm{d}\ln T + \Delta S_m°, \quad (3)$$

$$H_g°(0) - H_{cr}°(0) = \int_0^{T_m°} [C_p° \text{ (cr)} - C_p° \text{ (am)}] \mathrm{d}T + \Delta H_m°, \quad (4)$$

where $C_p°$ (cr) and $C_p°$ (am) are the temperature dependences of the heat capacity of the samples in the crystalline and amorphous states, respectively; $T_m°$, $\Delta H_m°$, and $\Delta S_m°$ are the temperature, enthalpy, and entropy of melting.

The thermodynamic characteristics of melting for the completely crystalline PU-{4,6} and PU-{6,6} are presented in Table 2. Melting of the PU samples under study was non-isothermic and occurred at ~90 K, which is observed rather frequently for polymers.[22] It is considered[6] that PU-{4,6} melts in two stages: in the 350—400 K interval the apparent heat capacity increases rather slowly, which is caused by the destruction of van der Waals bonds between layers of a PU-{4,6} crystal. The second stage covers an interval of 400—450 K and is accompanied by the destruction of hydrogen bonds linking macromolecules in planar networks.

The temperatures corresponding to the maximum values of the apparent heat capacity in the melting interval[22] were taken as the melting points of the samples $T_m°$. The published[6,7] $T_m°$ values are higher than those determined by us by ~10 K, which is related, most likely, to differences in crystallinities of the samples and heating rates of the calorimetric ampule filled with the substance.[22]

The enthalpies of melting of the crystalline PU-{4,6} and PU-{6,6} were calculated from the $\Delta H_m°$ values of the samples, which, in turn, were determined graphically as the areas between the curves of the apparent heat capacity and the normal run with allowance for their crystallinity. The entropies of melting were calculated from the enthalpy and melting point values. The enthalpies of melting of the polymers in the completely crystalline state were determined[7] under the assumption that the enthalpies of melting of the completely crystalline PU-{4,6} and Nylon-{6,6} coincide and the specific entropy of melting (0.4142 J K^{-1} g^{-1}) is independent of the number of methylene groups in the PU. The characteristics obtained for melting of PU-{4,6} and PU-{6,6} are well consistent with published data, and the $\Delta H_m°$ values coincide within the errors of determination of these values.

The calculation procedure for the thermodynamic characteristics of melting of completely crystalline polymer samples and thermodynamic characteristics of devitrification and glassy state of amorphous polymers using the properties of partially crystalline polymers has been described in detail previously.[13]

Thermodynamic functions. When calculating the standard thermodynamic functions of PU-{4,6} and PU-{6,6} (Tables 3 and 4), the $C_p° = f(T)$ plots were extrapolated from 6 to 0 K by the equation of the Debye theory of heat capacity of solids

$$C_p° = n\mathbf{D}(\theta_\mathbf{D}/T), \quad (5)$$

where **D** is the symbol of the Debye function of heat capacity; n and $\theta_\mathbf{D}$ are specially selected parameters.

Equation (5) with the parameters n and $\theta_\mathbf{D}$ equal to 2 and 59.5 K for PU-{4,6} and 2 and 50.6 K for PU-{6,6} describes the experimental $C_p°$ values in an interval of 6—10 K with errors of ±1.2 and ±1.4%, respectively. It was accepted in the calculation of the functions that at

Table 2. Standard thermodynamic characteristics of melting of polyurethanes-{4.6} and -{6.6}*

Compound	ΔT_m**	$T_m°$	$\Delta C_p°(T_m°)$	$S_m°(0)$	$\Delta H_m°$ /kJ mol^{-1}
	K		J K^{-1} mol^{-1}		
PU-{4.6}	350—450	442±1	121±3	111.1±2.2	49.1±0.8
PU-{6.6}	350—445	441±1	146±3	120.2±2.5	53.0±1.1

* Calculated for the completely crystalline substances.

** Interval of melting points.

Table 3. Thermodynamic functions of polyurethane-{4,6} (M = 258.32 g mol^{-1})

T/K	$C_p°(T)$	$S°(T)$	$H°(T) - H°(0)$	$-[G°(T) - H°(0)]$
	J K^{-1} mol^{-1}		kJ mol^{-1}	
		Crystalline state		
5	0.762	0.255	0.00103	0.000320
50	80.21	50.46	1.622	0.9013
100	156.2	131.0	7.649	5.450
200	255.9	270.1	28.29	25.74
298.15	366.3	392.6	58.75	58.30
400	482	516	101	105
442	529	566	123	127
		Liquid state		
442	650	677	172	127
460	663	704	184	140
		Glassy state		
0	0	34	0	0
50	80.17	84	1.622	2.60
100	156.2	165	7.649	8.85
200	255.9	304	28.29	32.5
273	337.8	396	49.89	58.1
		Highly elastic state		
273	528.8	396	49.89	58.1
298.15	546.7	443	63.41	68.7
400	619	614	123	123
442	650	677	149	150

Table 4. Thermodynamic functions of polyurethane-{6,6} (M = 286.37 g mol^{-1})

T/K	$C_p°(T)$	$S°(T)$	$H°(T) - H°(0)$	$-[G°(T) - H°(0)]$
	J K^{-1} mol^{-1}		kJ mol^{-1}	
		Crystalline state		
5	0.992	0.331	0.00120	0.000414
50	99.72	66.18	2.096	1.213
100	174.5	161.5	9.191	6.962
200	283.5	315.8	32.07	31.09
298.15	403.8	451.3	65.79	68.78
400	521	586	113	122
441	568	640	135	147
		Liquid state		
441	714	760	188	147
450	721	774	195	154
		Glassy state		
0	0	35	0	0
50	99.72	101	2.096	2.96
100	174.5	197	9.191	10.5
200	283.5	351	32.07	38.1
277	379.0	458	57.51	69.2
		Highly elastic state		
277	595.0	458	57.51	69.2
298.15	609.6	502	70.26	79.4
400	684	691	136	140
441	714	760	165	170

temperatures between 0 K and the temperature of the beginning of measurements this equation reproduces the $C_p°$ values of the samples with the same error.

The enthalpy $H°(T) - H°(0)$ and entropy $S°(T)$ for PU-{4,6} and PU-{6,6} were obtained by the numerical integration of $C_p° = f(T)$ over the temperature and logarithm of temperature in the region from $T \to 0$ to 480 K in the crystalline, glassy, highly elastic, and liquid states. The zero entropy $S°(0)$ (see Table 1) was taken into account in the calculation of $S°(T)$ of the polymers in the amorphous state. The Gibbs function $G°(T) - H°(0)$ of the polymers was calculated from the values of enthalpy and entropy of heating at the corresponding temperatures. For details of the calculation of the functions, see Ref. 13.

Thermodynamic characteristics of formation and bulk polycondensation. Using the obtained data on the enthalpies of combustion of partially crystallized PU-{4,6} and PU-{6,6}, we calculated their enthalpies of combustion and formation in the completely crystalline and amorphous (highly elastic) states at T = 298.15 K and p = 0.1 MPa. The standard entropies of formation $\Delta S_f°$ (cr) and $\Delta S_f°$ (am) for PU-{4,6} and PU-{6,6} in the crystalline and amorphous states at T = 298.15 K were calculated from the absolute values of entropy of the polymers in the crystalline and amorphous states (see Tables 3 and 4), carbon in the form of graphite, and gaseous hydrogen H_2 (g), oxygen O_2 (g), and nitrogen N_2 (g).[23] The Gibbs functions of formation $\Delta G_f°$ of the polymers were calculated from the $\Delta H_f°$ and $\Delta S_f°$ values (Table 5). The resulting values correspond to the following processes:

$$12\,C\,(gr) + 11\,H_2\,(g) + N_2\,(g) + 2\,O_2\,(g) \to$$
$$\to [\text{—}C_{12}H_{22}N_2O_4\text{—}]\ (cr\ or\ h.e),$$

$$14\,C\,(gr) + 13\,H_2\,(g) + N_2\,(g) + 2\,O_2\,(g) \to$$
$$\to [\text{—}C_{14}H_{26}N_2O_4\text{—}]\ (cr\ or\ h.e),$$

where the physical states of the reactants are given in parentheses: gr is graphite, g is gaseous, cr is crystalline, and h.e is highly elastic.

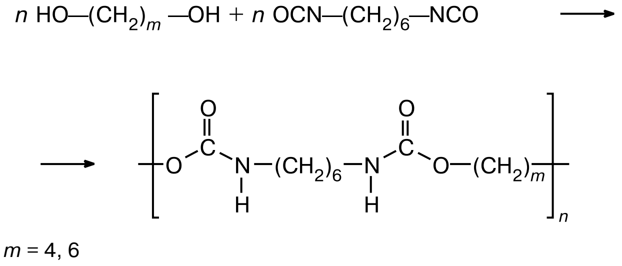
The reactions of polycondensation of 1,6-hexamethylenediisocyanate with butane-1,4-diol and hexane-1,6-diol to form PU-{4,6} and PU-{6,6} proceed *via* Scheme 1.

Table 5. Standard thermodynamic parameters of formation of polyurethanes-{4.6} and -{6.6} at T = 298.15 K

Compound	Physical state*	$-\Delta S_f°$	$-\Delta H_f°$	$-\Delta G_f°$
		/J K^{-1} mol^{-1}	kJ mol^{-1}	
PU-{4.6}	cr	1713.6±2.1	1054±14	544±15
	h.e	1663±4	1027±14	530±16
PU-{6.6}	cr	1927.4±2.3	1127±4	552±5
	h.e	1877±4	1099±4	539±6

* The data for the crystalline (cr) and highly elastic (h.e) states are presented.

Scheme 1



The standard thermodynamic characteristics of the polycondensation of PU-{4,6} and PU-{6,6} calculated from the obtained experimental and published data[24—26] are presented in Table 6. The procedure of calculation of the values is described in detail.[13] The Gibbs function of polycondensation ($\Delta G_{\text{pol}}°$) has high negative values, indicating the virtually complete shift of equilibrium toward polymer formation. The limiting temperature of polycondensation determined by the Daiton method[27] is higher than 600 K, which considerably exceeds the temperature of the onset of PU destruction.

Comparison of thermodynamic properties of PUs. To reveal some most general regularities of changing the thermodynamic characteristics of polyurethanes with a change in their composition and structure, let us try to compare PU-{4,6} and PU-{6,6} studied in this work between each other and with polyurethanes of isomeric structure.

The character of changing $C_p°$ with the temperature rise is the same for PU-{4,6} and PU-{6,6} due to their identical structures. The heat capacity values of PU-{6,6} everywhere lie higher than the corresponding values for PU-{4,6}, which is caused by the presence of two additional methylene groups in the composition of PU-{6,6}. For example, at $T = 298.15$ K in the crystalline state this difference per methylene group is ~20 J K^{-1} mol^{-1}, which is close to similar increases in the heat capacity in the series of isomeric PUs (see Refs 8—10).

The wide intervals of devitrification (about ~60 K) for PU-{4,6} and PU-{6,6} are caused by the high crystallinity of the samples and related to the effect of screening of the amorphous areas by the crystalline regions. The devitrification temperatures $T_g°$ of the compared homologues are close, indicating an insignificant dependence of the temperatures of excitation of segmentary mobility of linear aliphatic PUs on their composition. The difference in increases in the heat capacities upon devitrification $\Delta C_p°(T_g°)$ of the completely amorphous PU-{4,6} and PU-{6,6} is ~25 J K^{-1} mol^{-1}, which corresponds to Wunderlich′s rule, according to which the introduction of 1 mole of "beads" into polymer makes the contribution to $\Delta C_p°(T_g°)$ equal to 11.5±2.3 J K^{-1} mol^{-1}.[28]

Table 6. Standard thermodynamic characteristics* of the bulk synthesis of linear polyurethanes based on 1,6-hexamethylenediisocyanate (**A**) with butane-1,4-diol or hexane-1,6-diol (**B**) with formation of polyurethanes-{4,6} and -{6,6}

T/K	Physical state**			$-\Delta S_{\text{pol}}°$	$-\Delta H_{\text{pol}}°$	$-\Delta G_{\text{pol}}°$
	A	**B**	Polymer			
1,6-Hexamethylenediisocyanate + butane-1,4-diol → PU-{4,6}						
0	cr	cr	cr	0	170	170
	cr	cr	gl	−34	148	148
100	cr	cr	cr	36.2	172	168
	cr	cr	gl	2	150	150
200	cr	cr	cr	60.1	176	164
	cr	cr	gl	26	153	148
298.15	liq	liq	cr	251	222	147
	liq	liq	h.e	200	195	135
350	liq	liq	cr	270	228	134
	liq	liq	h.e	192	192	125
1,6-Hexamethylenediisocyanate + hexane-1,6-diol → PU-{6,6}						
0	cr	cr	cr	0	178	178
	cr	cr	gl	−35	155	155
100	cr	cr	cr	26.9	180	178
	cr	cr	gl	−8	157	158
200	cr	cr	cr	62.6	186	173
	cr	cr	gl	28	162	157
298.15	liq	cr	cr	201	216	156
	liq	cr	h.e	150	188	143
350	liq	liq	cr	307	250	142
	liq	liq	h.e	225	212	133

* The values of the thermodynamic functions for polycondensation are given ($\Delta S_{\text{pol}}°$/J K^{-1} mol^{-1}, $\Delta H_{\text{pol}}°$/kJ mol^{-1}, $\Delta G_{\text{pol}}°$/kJ mol^{-1}).

** The following designations were used: cr is crystalline, liq is liquid, gl is glassy, and h.e is highly elastic.

The both polymers melt in a broad interval (about ~100 K), which is characteristic of linear aliphatic PUs. The values of $T_m°$ and specific $\Delta H_m°$ coincide within the error of determination, indicating that their structures are identical. Note that the empirical value $T_g°/T_m° \approx 0.63 \pm 0.02$, which is typical of the most part of polymers,[22] is retained and valid for the PU-{4,6} and PU-{6,6} under study.

The thermodynamic properties of polyhexamethyleneurethane, which is a structural analog of PU-{6,6}, have been studied earlier.[10] Comparing the numerical $C_p°$ values and characteristics of physical transitions, one can distinguish several specific features. The $C_p°$ values for PU-{6,6} and polyhexamethyleneurethane in the crystalline and glassy states in the temperature interval from 80 K to $T_g°$, as should be expected, do not differ within the error of determination of $C_p°$. The heat capacity of polyhexamethyleneurethane is lower (~3—5%) than the $C_p°$ values of PU-{6,6} at temperatures below 80 K. It is most likely that the atomic groups in the composition of polyhexamethyleneurethane are more rigidly retained and, therefore, their vibrational degrees of freedom are liberated (which contributes to $C_p°$) at higher temperatures. When the temperature increases higher than $T_g°$, the heat capacities of the compared isomers somewhat differ (~2—3%) and the deviations of C_p° are higher than the error of its determination in the indicated region. These deviations can be explained by the fact that the method of graphical extrapolation was used for the estimation of the crystallinity of polymers.

A similar situation is observed for PU-{4,6} and "hypothetical" PU based on polytetramethyleneurethane[29] and polyhexamethyleneurethane.

A comparison of the thermodynamic characteristics of physical transitions of polyhexamethyleneurethane and PU-{6,6} showed that structural isomerism exerts no noticeable effect on the parameters of devitrification of the isomers. In particular, the T_g° values coincide within the error of determination. In turn, the parameters of melting of PU-{6,6} and polyhexamethyleneurethane differ ($T_m^\circ = 441.0\pm0.5$ and 445.0 ± 0.5 K, $\Delta H_m^\circ = 53\pm1$ and 32 ± 4 kJ mol^{-1}, respectively), which indicates the influence of isomerism on the parameters of the crystalline lattice of their lamellar crystals.

It is impossible to perform an analogous comparison of PU-{4,6} and "hypothetical" PU based on polyhexamethyleneurethane and polytetramethyleneurethane, because reliable literature data on the thermodynamic characteristics of melting of polytetramethyleneurethane are lacking.

The results of estimation of the relative thermodynamic stability of the isomeric PUs obtained by comparison of their Gibbs functions of formation in the crystalline state indicates a high thermodynamic stability of PU-{6,6} compared to polyhexamethyleneurethane ($-\Delta G_f^\circ = 552\pm8$ and 516 ± 10 kJ mol^{-1}). These results show that the spontaneous isomerization of PU-{6,6} to polyhexamethyleneurethane is impossible.

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