Available online at www.sciencedirect.com

SCIENCE DIRECT®

ELSEVIER

Thermochimica Acta 445 (2006) 7–18

thermochimica acta

www.elsevier.com/locate/tca

Thermodynamics of linear polyurethanes on basis of 1,4-diisocyanatobutane with 1,4-butanediol and 1,6-hexanediol in the range from $T \rightarrow 0$ to 490 K

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

[a] *Chemistry Institute, Nizhny Novgorod State University, Gagarin Pr. 23/5, 603950 Nizhny Novgorod, Russia*
[b] *Institute of Macromolecular Chemistry of NASU, 02160 Kiev, Kharkivske shose 48, Ukraine*

Received 7 February 2006; received in revised form 2 March 2006; accepted 7 March 2006
Available online 22 March 2006

Abstract

The temperature dependence of heat capacity and characteristics of physical transformations of partially crystalline linear aliphatic polyurethanes based on 1,4-diisocyanatobutane with 1,4-butanediol and 1,6-hexanediol have been studied over the range 6.5–490 K by precision adiabatic vacuum and dynamic calorimetry. The calorimetric data were used to determine the thermodynamic quantities of devitrification and fusion and to calculate the standard thermodynamic functions $C_p^0(T)$, $H^0(T) - H^0(0)$, $S^0(T)$ and $G^0(T) - H^0(0)$ of linear polyurethanes in totally crystalline and amorphous states. The values of the fractal dimension D in the function of multifractal generalization of Debye's theory of the heat capacity of solids were estimated and the character of heterodynamics of their structures was detected. The energies of combustion of the substances were measured in a calorimeter with an isothermal shield and a static bomb. The enthalpies of combustion and the standard thermodynamic characteristics of formation of the polymers at $T = 298.15$ K were calculated too. The standard thermodynamic characteristics of polycondensation processes in bulk of 1,4-diisocyanatobutane with 1,4-butanediol and 1,6-hexanediol followed by the formation of linear polyurethanes were determined in the range from 0 to 350 K. A comparative analysis of the corresponding standard thermodynamic properties of the polymers under consideration and polyurethanes of isomeric structure was made and some dependences of their change on various conditions were found.

Keywords: Polyurethanes; Calorimetry; Heat capacity; Thermodynamics

1. Introduction

For today linear polyurethanes (PU) belong to the most important products of large-tonnage commercial manufacture owing to their versatile physicochemical properties and, as a result, universal operating characteristics and ecological safety [1,2]. Besides, those are of certain interest for designing new promising composition materials with the given combination of predicted characteristics [3–5].

In connection with a high significance of the objects, a wide range of studies of their physicochemical properties has been performed up to now [1,2]. However, the thermodynamic characteristics of PU, synthesized via the interaction of diisocyanates with diols (m,n-PU), were determined only by differential thermal analysis (DTA) and differential scanning calorimetry (DSC) and the data obtained are compared unfavorably by their precision and quantity with those measured by low-temperature adiabatic vacuum calorimetry. Complex thermodynamic studies are necessary for comparing the thermodynamic properties of aliphatic polyurethanes and detecting the most general regularities of their dependences on the composition, structure and physical states as well as for examining based-on-them composition materials with good prospects. Works of such level were carried out earlier [6–8] for n-PU prepared through the ring-opening polymerization of cyclic urethanes and the interaction of isocyanato-alcohols.

The goal of the present work was to calorimetrically measure the temperature dependence of the heat capacity of the partially crystalline linear PU based on 1,4-diisocyanatobutane with 1,4-butanediol (PU-{4,4}) and 1,6-hexanediol (PU-{6,4}) over the range 6.5–490 K, to determine the thermodynamic parameters of their possible physical transformations, to calculate from the data obtained the standard thermodynamic functions $C_p^0(T)$, $H^0(T) - H^0(0)$, $S^0(T)$, $G^0(T) - H^0(0)$ for completely crystalline

---

[*] Corresponding author. Tel.: +7 8312 65 64 50; fax: +7 8312 65 64 50.
E-mail address: smirnova@ichem.unn.runnet.ru (N.N. Smirnova).

0040-6031/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.tca.2006.03.017

and amorphous PU-{4,4} and PU-{6,4} between 0 and 490 K, to measure the energies of combustion of PU-{4,4} and PU-{6,4}, to estimate the standard thermodynamic characteristics of formation of the polymers at $T = 298.15$ K and the standard thermodynamic characteristics of their polycondensation in bulk from 0 to 350 K, to compare the thermodynamic characteristics of PU-{4,4}, PU-{6,4} and the corresponding isomeric PU and to elucidate the influence of the composition and structure on them.

2. Experimental

2.1. Sample

Samples of PU-{4,4} and PU-{6,4} were prepared with scientific workers of A.M. Fainleib's team by the procedure described elsewhere [9,10]. The microstructure and the composition of monomeric units in the polymers PU-{4,4} ($M = 230.26$ (g/mol)) [–O–CO–NH–$(CH_2)_4$–NH–CO–O–$(CH_2)_4$–]$_n$ and PU-{6,4} ($M = 258.32$ (g/mol)) [–O–CO–NH–$(CH_2)_4$–NH–CO–O–$(CH_2)_6$–]$_n$ were characterized by NMR, IR spectroscopy and the elemental analysis: for $(C_{10}H_{18}N_2O_4)_n$ $(230.26)_n$: Calcd. C 52.16, H 7.87, N 12.16; Found C 52.27, H 7.74, N 12.28 and for $(C_{12}H_{22}N_2O_4)_n$ $(258.32)_n$: Calcd. C 55.79, H 8.58, N 10.84; Found C 55.63, H 8.82, N 10.90. By the method of gel-permeation chromatography it was found that for PU-{4,4} $\bar{M}_w = 6.07 \times 10^4$, $\bar{M}_w/\bar{M}_n = 1.09$ and for PU-{6,4} $\bar{M}_w = 5.85 \times 10^4$, $\bar{M}_w/\bar{M}_n = 1.04$. The degree of crystallinity (α) was determined to be 83% and 86% for PU-{4,4} and PU-{6,4}, respectively, by calorimetric method [11]. At once prior to the experiments the samples were evacuated under vacuum at a temperature about 340 K and located in calorimetric ampoules in dry argon flow.

2.2. Apparatus and methods

To measure the heat capacity, temperatures and enthalpies of physical transformations of the tested PU in the range 6.5–350 K, a totally automatic thermophysical device – a BKT-3 adiabatic vacuum calorimeter – was employed. The calorimeter design and the operation procedure were demonstrated previously [12]. From the results of the calorimeter calibration and check it was ascertained that the measurement uncertainty of the heat capacity of the substances at helium temperatures is within to 2%, with increasing temperature up to 40 K it decreases down to 0.5% and becomes equal to 0.2% over the range 40–350 K. The uncertainty of measuring temperatures of physical transformations is ±0.02 K and of the enthalpies of physical transitions ±0.2%.

To study the heat capacity of the substances between 320 and 500 K an ADKTTM automatic device – a dynamic calorimeter operating by the principle of the triple thermal bridge – was used [13,14]. The uncertainty in C_p^0 measurements over the above temperature interval is not more than ±1.5%, the temperatures of physical transformations ±0.5 K and the enthalpies of physical transformations ±1.5%.

The energy of combustion, $\Delta_c U$, of PU was measured in an improved calorimeter (V-08) with a static bomb and an isothermal shield. The calorimeter design, the procedure of measuring the energies of combustion and the results of calibration and testing are given elsewhere [15]. It should be noted that while checking the calorimeter by burning succinic acid, prepared at D.I. Mendeleev Research Institute of Metrology, the value of the standard enthalpy of combustion of the acid coincided with the certificate value within ±0.017% was obtained by us. In runs on burning PU polyethylene ampoules were used. The energy of combustion of polyethylene was measured in 10 previous experiments and its average was $\Delta_c U$ (p.e.) = −46,421 ± 10 (J/g) under conditions of the calorimetric bomb.

3. Results and discussion

3.1. Heat capacity

The heat capacity of PU-{4,4} was measured in the range 7.5–490 K and between 6.5 and 480 K for PU-{6,4}. The masses of the samples located in the calorimetric ampoules of the BKT-3 and ADKTTM calorimeters were 0.1782 and 0.2945 g for PU-{4,4} and 0.1415 and 0.3586 g for PU-{6,4}, respectively. With PU-{4,4} in five series of measurements and in the case of PU-{6,4} in six series, reflecting the experiment sequence, 205 and 433 experimental C_p^0 values, respectively, were obtained (Tables 1 and 2). The measurements of C_p^0 in the ADKTTM calorimeter were made for PU-{4,4} with continuous heating at a rate of ~0.017 (K/s) and at three different rates of heating of the calorimeter and the substance for PU-{6,4}. The heat capacity of PU-{4,4] was from 30 to 50% of the total heat capacity of the ampoule and the substance in the adiabatic calorimeter and from 20 to 35% in the dynamic one. As to PU-{6,4}, its C_p^0 was from 40 to 60% and from 30 to 40% of the total heat capacity of the ampoule and the substance, respectively. The averaging of the experimental points of C_p^0 was carried out on a computer in the form of degree and semilogarithmic polynomials so that the root-mean-square deviation of the C_p^0 points from the smoothed $C_p^0 = f(T)$ curve did not exceed the uncertainty of the heat capacity measurements.

Figs. 1 and 2 show the experimental C_p^0 values and the smoothed curves $C_p^0 = f(T)$ for PU-{4,4} and PU-{6,4}. It was found that the samples in the temperature interval under study exist in the partially crystalline and liquid states (curves ABDE, A′B′D′E′ and NGH, N′G′H′, respectively, Fig. 1). Each polymer exhibits two physical transformations: the devitrification of an amorphous part of PU-{4,4} between 240 and 300 K and of PU-{6,4} from 265 to 300 K (sections BD and B′D′, Fig. 1) and the fusion of a crystalline part over the range 360–480 K for PU-{4,4} and between 340 and 470 K for PU-{6,4} (sections EFF*G and E′F′F*′G′, Fig. 1).

From the experimental C_p^0 values in the range 20–50 K the value of the fractal dimension D of the polymers was evaluated. According to the fractal theory of the heat capacity [16,17], D is the most important parameter that specifies the character of heterodynamics of the substance structure. For solids of a chain structure the relation C_p^0 versus T at lower temperatures is proportional to T^1, of a layer structure to T^2 and of steric one to T^3 [18]. In the fractal theory of the heat capacity [16], an exponent of a power at T in the heat capacity function is denoted by D and is called the fractal dimension. This follows specifically from Eq. (1):

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

where N is the number of particles in a molecule, k the Boltzmann constant, $\gamma(D+1)$ is γ-function, $\xi(D+1)$ is Riemann ξ-function,

Table 1
Experimental values of heat capacity of polyurethane-{4,4} (M = 230.26 (g/mol))

T (K)	C_p^0 (J/(K mol))	T (K)	C_p^0 (J/(K mol))	T (K)	C_p^0 (J/(K mol))
Series 4		64.39	91.70	147.58	175.3
7.73	2.53	66.95	95.10	151.24	178.5
8.52	2.60	69.50	97.90	154.91	181.1
9.34	3.50	72.05	101.3	158.57	183.7
10.01	3.90	74.63	104.8	162.23	187.5
10.68	4.71	77.19	108.3	165.90	190.4
11.37	5.00	79.75	111.6	169.55	194.2
12.09	5.50	82.31	114.9	173.21	196.7
13.01	6.36	84.85	117.4	176.86	199.1
14.05	7.38	87.39	119.7	180.51	202.6
15.09	8.602	89.94	121.1	184.16	205.9
16.15	9.996	92.48	123.4	187.81	209.1
17.24	11.70	95.04	128.0	191.45	212.6
18.35	13.60	Series 1		195.09	216.0
19.48	15.80	84.92	118.2	Series 2	
22.15	19.59	88.42	120.4	198.74	218.9
24.96	24.73	92.14	124.1	202.44	222.0
27.70	30.19	95.85	127.8	206.07	225.7
30.40	34.71	99.56	131.7	209.71	229.3
33.08	38.74	103.26	136.1	213.34	232.3
35.74	43.28	106.97	139.1	216.96	236.2
38.37	47.82	110.67	142.6	220.58	239.4
40.99	52.66	114.36	146.5	224.20	243.2
43.61	57.31	118.05	149.9	227.81	246.5
46.21	62.18	121.74	153.5	231.42	250.4
48.80	66.56	125.43	156.8	235.03	253.8
51.37	71.57	129.12	160.0	238.64	257.6
55.00	76.70	132.80	163.6	242.25	262.0
56.54	80.38	136.48	166.3	245.84	268.1
59.13	84.40	140.15	169.2	249.44	271.5
61.71	87.90	143.90	171.9	253.02	276.4
256.60	279.8	328.22	392.0	398.9	517
260.20	285.0	331.47	398.0	405.8	537
263.76	289.7	334.73	398.4	413.0	555
267.31	295.3	337.95	402.1	420.4	578
270.84	301.0	341.15	408.8	427.8	602
274.36	305.8	344.36	412.7	435.3	634
277.86	312.4	347.52	418.9	442.7	665
281.36	317.7	350.68	424.4	450.0	721
284.83	322.5	353.83	426.7	457.3	825
288.28	328.3	356.92	434.1	464.4	1079
291.70	334.6	360.00	437.5	466.1	1201
295.11	340.0	363.07	440.6	467.8	1404
298.48	346.2	365.81	445.7	469.4	1652
Series 3		Series 5[a]		471.0	1888
301.84	352.3	340.5	408	472.6	2025
305.18	358.5	348.7	420	474.1	2080
308.51	363.5	355.0	428	475.9	1954
311.84	367.6	363.1	441	477.7	1460
315.03	371.6	370.8	452	479.7	812
318.35	378.1	378.1	465	481.8	586
321.65	382.8	385.2	484	487.8	593
324.94	384.6	392.0	499		

[a] Each fourth value of C_p^0.

Table 2
Experimental values of heat capacity of polyurethane-{6,4} ($M = 258.32$ (g/mol))

T (K)	C_p^0 (J/(K mol))	T (K)	C_p^0 (J/(K mol))	T (K)	C_p^0 (J/(K mol))
Series 3		57.60	105.77	125.32	176.5
6.56	2.45	60.01	109.80	127.80	180.3
7.43	2.88	62.44	113.45	130.28	182.6
8.01	3.96	64.85	116.78	132.75	184.8
9.42	4.99	67.25	119.88	135.22	186.7
10.37	5.94	69.64	122.89	137.73	189.8
11.79	7.46	72.12	126.04	140.21	191.8
12.63	8.82	74.58	129.25	142.68	194.1
13.94	10.1	77.05	132.53	145.14	196.6
14.33	11.2	79.56	135.77	147.60	200.4
15.23	12.40	82.07	138.69	150.06	201.7
16.09	14.12	84.59	141.01	152.51	204.5
16.98	16.01	86.13	142.05	155.00	207.2
17.92	18.27	88.71	143.22	157.49	209.1
18.91	20.65	91.25	144.25	159.98	211.6
19.91	22.96	93.66	146.62	162.47	213.5
22.23	27.81	Series 1		164.96	215.6
24.23	32.42	89.12	143.0	167.45	217.7
26.54	38.80	92.02	146.1	169.93	220.3
28.97	45.01	94.53	148.4	172.42	222.5
31.41	49.50	97.51	148.3	174.91	224.4
33.96	54.91	100.40	152.1	177.47	226.5
36.35	60.22	102.91	154.8	179.96	229.8
38.74	65.60	105.41	157.1	182.45	231.7
41.13	70.94	107.91	159.3	184.94	234.0
43.49	76.22	110.40	161.9	187.43	236.3
45.83	81.46	112.89	164.8	189.92	238.1
48.17	86.65	115.38	166.8	192.40	241.3
50.50	91.74	117.87	168.7	194.90	243.6
52.84	96.67	120.35	172.0	197.39	245.9
55.21	101.38	122.84	175.1	199.87	248.0
202.36	250.0	279.81	358.4	Series 4[a]	
204.85	252.7	282.20	364.2	328.3	456
207.33	254.8	284.60	367.8	336.7	474
209.82	258.7	286.98	374.1	344.8	500
212.31	261.5	289.37	379.8	352.8	528
214.80	263.5	291.75	384.9	359.3	550
217.39	266.2	294.12	389.9	366.1	577
219.87	269.3	296.50	394.6	372.9	604
222.36	273.0	298.87	400.2	381.7	635
224.84	275.2	301.24	403.4	388.5	661
227.33	278.5	303.60	407.5	395.0	687
230.41	281.3	305.94	412.1	402.1	713
233.25	286.7	308.27	414.9	409.6	752
235.73	288.4	310.59	419.3	417.0	799
238.21	290.8	312.89	422.7	424.3	843
240.68	294.4	315.17	428.4	431.6	912
243.16	297.2	317.43	432.4	438.8	1003
245.63	301.4	319.68	436.0	440.6	1036
248.10	304.9	321.91	440.7	442.3	1093
250.57	306.9	324.11	447.0	444.1	1140
253.03	310.3	326.30	450.9	445.9	1227
255.49	312.9	328.45	455.0	447.7	1318
257.94	316.7	330.60	463.7	449.4	1470
Series 2		333.58	469.8	451.1	1561
260.39	319.7	338.53	483.0	452.9	1703
262.83	323.8	342.88	491.2	454.6	1896
265.26	329.8	347.17	508.3	455.5	2005
267.69	332.5	351.38	525.0	458.1	2984
270.17	335.6	355.57	542.9	459.9	2135
272.59	342.9	359.70	554.4	461.6	1981
275.00	347.0	363.76	564.9	463.3	1914
277.41	352.4	367.34	579.3	465.0	1827

Table 2 (*Continued*)

T (K)	C_p^0 (J/(K mol))	T (K)	C_p^0 (J/(K mol))	T (K)	C_p^0 (J/(K mol))
466.8	1492	410.3	914	460.1	715
468.8	699	413.9	939	461.4	714
470.9	711	417.6	968	464.7	713
478.6	719	421.2	1000	Series 6[a]	
480.5	721	422.1	1009	338.7	490
Series 5[a]		424.8	1045	349.4	520
329.1	457	427.6	1075	362.0	559
333.7	466	430.3	1109	375.9	614
338.2	479	433.1	1156	389.9	681
341.9	494	435.9	1227	403.3	751
345.5	514	437.7	1275	416.0	820
349.1	532	439.5	1334	427.9	910
352.7	551	441.2	1376	436.6	1044
356.2	565	443.0	1432	439.5	1151
359.7	585	444.7	1477	442.4	1217
363.3	609	446.4	1617	445.2	1336
367.0	626	448.1	1802	448.1	1563
370.7	643	449.8	1951	450.9	1873
374.4	664	451.6	1994	453.1	2118
378.1	683	452.5	2012	458.4	2179
381.7	701	454.2	2234	461.4	1472
385.3	724	455.1	2259	462.5	710
389.0	745	456.0	2440	465.7	715
392.6	770	456.9	2535	468.8	716
396.2	802	457.8	2610	475.1	722
399.7	830	458.2	2510	478.2	724
403.2	857	458.9	2288		
406.7	882	459.4	1579		

[a] Each fourth value of C_p^0.

$\theta_{\max}$ the characteristic temperature and the fractal dimension D is from 1 to 4 according to work [17].

As follows from inferences [16], D can be evaluated from the experimental data on the temperature-dependent heat capacities from a slope of the corresponding rectilinear sections of the plot $\ln C_v$ versus $\ln T$. Without a substantial uncertainty it may be assumed that at $T < 50$ K $C_p^0 = C_v$. From the $\ln C_v$ versus $\ln T$ plot and Eq. (1) it was found that in the range 20–50 K, $D = 2$, $\theta_{\max} = 193.5$ K for PU-{4,4} and $D = 2$, $\theta_{\max} = 187.2$ K in the case of PU-{6,4}. With these values of D and $\theta_{\max}$ Eq. (1) reproduces the experimental C_p^0 values in the temperature range mentioned with an uncertainty of ±1.2%. The D-value points to the layer structure of both polymers [18]. For the polyurethanes this structure is likely to be formed due to hydrogen bonding between urethane groups. It is worth of note that such conclusion conforms fairly well with the proper data of structure examinations of polyurethane based on 1,4-butanediol and 1,6-hexamethylenediisocyanate [19].

3.2. Characteristics of devitrification and glassy state

Characteristics of devitrification and glassy state of PU-{4,4} and PU-{6,4} are listed in Table 3. A devitrification interval of the polymers was determined graphically; temperatures when the character of the relation $C_p^0 = f(T)$ changed were considered as temperatures of the onset ($T_{g,i}^0$) and the end ($T_{g,f}^0$) of devitrification. The devitrification temperature T_g^0 was determined by Alford and Dole method [20] from an inflection of the curve of the temperature dependence of entropy. An increase in the heat capacity $\Delta C_p^0(T_g^0)$, α on devitrifying the samples of PU-{4,4} and PU-{6,4} (sections CK and C′K′) and of the same polymers in a completely amorphous state (CL, C′L′, Fig. 1) was

Table 3
Parameters of devitrification and glassy state of linear polyurethanes

Polymer	$\Delta T_g^0 = T_{g,i}^0 - T_{g,f}^0$ [a] (K)	T_g^0 [b] (K)	$\Delta C_p^0(T_g^0)$, α[c] (J/(K mol))	$\Delta C_p^0(T_g^0)$[c] (J/(K mol))	S_{conf}^0[d] (J/(K mol))	$S^0(0)$[d] (J/(K mol))
Polyurethane-{4,4}	240–300	280 ± 1	28.0	163 ± 5	21 ± 1	20 ± 1
Polyurethane-{6,4}	265–300	283 ± 1	25.6	183 ± 5	26 ± 1	27 ± 1
PPMU [8]	240–290	266 ± 1	–	110	–	8

[a] $T_{g,i}^0$–$T_{g,f}^0$, the temperatures interval of onset and end of devitrification.

[b] T_g^0, the temperature of devitrification.

[c] $\Delta C_p^0(T_g^0)$, α and $\Delta C_p^0(T_g^0)$ the increase of heat capacity on devitrification of sample and amorphous polymers, respectively.

[d] S_{conf}^0, $S^0(0)$ the configuration and zero entropies of amorphous polymers.

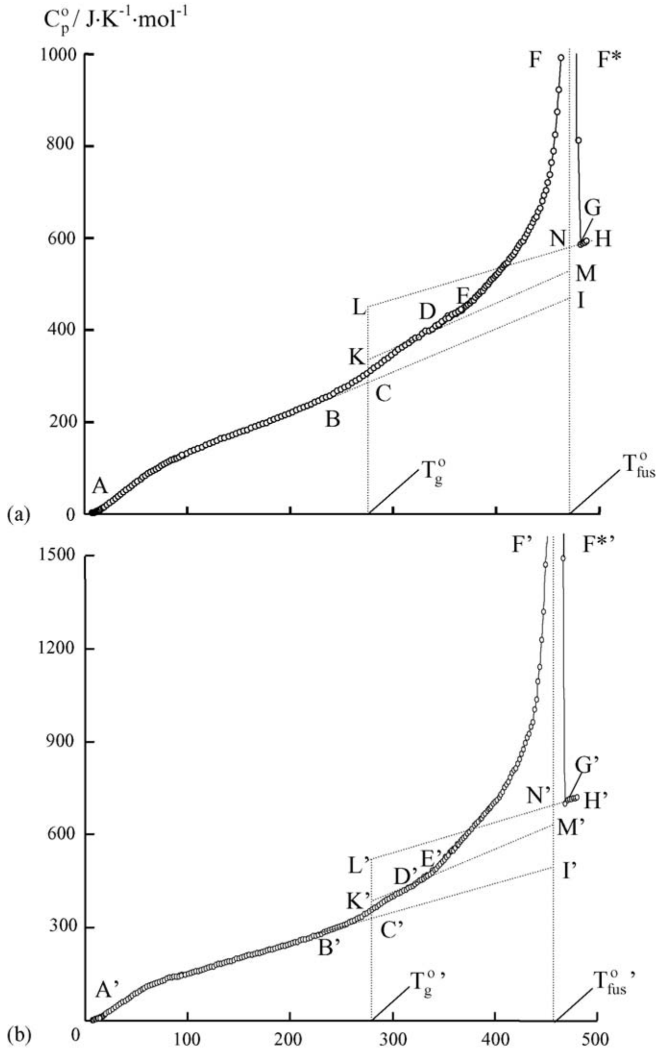


Fig. 1. (a) Temperature dependence of heat capacity C_p^0 of polyurethane-{4,4}; ABCI, crystal; NGH, liquid; ABDE, partially crystalline state; ABC, amorphous part in glassy state; LN, amorphous part in high-elasticity state, EFF*G, the apparent heat capacity in the melting interval; CK, the increase of heat capacity of the sample ($\alpha = 83\%$) at devitrification temperature T_g^0; CL, the increase of heat capacity of the amorphous polymer at devitrification temperature T_g^0; IN, the increase of heat capacity of the crystalline polymer at fusion temperature T_{fus}^0. (b) Temperature dependence heat capacity of polyurethane-{6,4}: A′B′C′I′, crystal; N′G′H′, liquid; A′B′D′E′, partially crystalline state; A′B′C′, amorphous part in glassy state; L′N′, amorphous part in high-elasticity state; E′F′F*′G′, the apparent heat capacity in the melting interval; C′K′, the increase of heat capacity of the sample ($\alpha = 86\%$) at devitrification temperature T_g^0; C′L′, the increase of heat capacity of the amorphous polymer at devitrification temperature T_g^0; I′N′, the increase of heat capacity of the crystalline polymer at fusion temperature T_{fus}^o.

determined graphically by the extrapolation of a normal trend of their heat capacity in high-elasticity (KD and LN, K′D′ and L′N′, Fig. 1) and glassy states (ABC and A′B′C′, Fig. 1) towards the devitrification temperature T_g^0. The data were used to estimate the degree of crystallinity [11] of PU-{4,4} ($\alpha = 83\%$) and PU-{6,4} ($\alpha = 86\%$) as well as the values of the zero and configurational entropies (Table 3) by the following equations:

$$\alpha = \left[\frac{1 - \Delta C_p^0(T_g^0; \alpha)}{\Delta C_p^0(T_g^0)}\right] \times 100\% \tag{2}$$

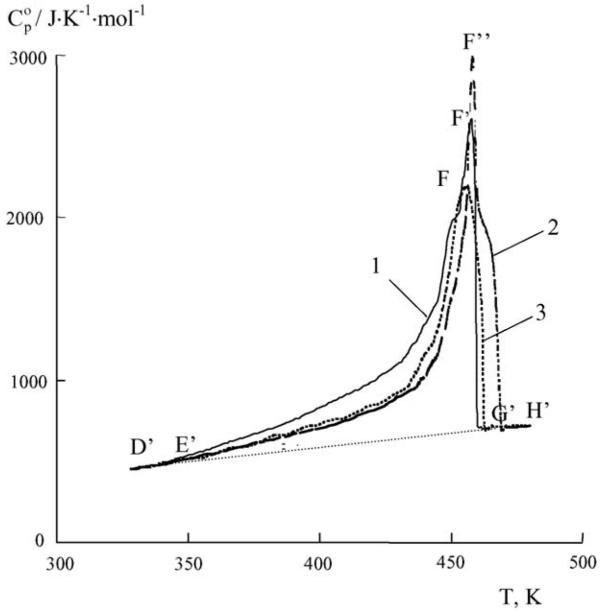


Fig. 2. Temperature dependence of heat capacity of polyurethane-{6,4} in the melting interval at three different rates of heating of calorimeter and substance: (1) 0.0015 (K/s), (2) 0.030 (K/s) and (3) 0.050 (K/s): D′E, crystal; G′H′, liquid; E′FG′, E′F′G′, E′F″G′, apparent heat capacities in the melting interval.

$$S^0(0) = \int_0^{T_{fus}^0} \{C_p^0(\text{cr}) - C_p^0(\text{am})\} \mathrm{d} \ln T + \Delta_{fus} S^0 \tag{3}$$

$$S_{conf}^0 = \Delta C_p^0(T_g^0) \ln \frac{T_g^0}{T_2^0} \tag{4}$$

where C_p^0(cr) and C_p^0(am) are temperature dependences of the heat capacity of the polymers in crystalline and amorphous states (Fig. 1), T_2^0 is Kautzmann temperature [21].

3.3. Thermodynamic quantities of fusion

In Tables 4 and 5 are given the thermodynamic quantities of fusion for PU-{4,4} and PU-{6,4}. The fusion of the PU samples was non-isothermal and occurred at about 120 K that was observed quite frequently for polymers [21].

Temperature corresponding to the maximum value of the apparent heat capacity, $C_{p,max}^0$, in the melting interval was regarded as the melting temperature T_{fus}^0 of PU-{4,4} [21]. The enthalpy of fusion of crystalline PU-{4,4} was calculated by Eq. (5) from the enthalpy of fusion, $\Delta H_{fus}^0(\alpha)$, of the partially crystalline sample, determined graphically as an area between the curves of the apparent heat capacity (EFF*′G and E′F′F*′G′, Fig. 1) and the normal trend of the curve (EMNG and E′M′N′G′, Fig. 1), and the crystallinity degree α:

$$\Delta H_{fus}^0\,(\alpha = 100\%) = \frac{\Delta H_{fus}^0(\alpha)}{\alpha} \tag{5}$$

To determine the thermodynamic quantities of fusion of PU-{6,4} the measurements were made at three rates of heating of the calorimeter and the substance (Table 4, Fig. 2). Temperature corresponding to $C_{p,max}^0$, i.e. temperature at which the major part

Table 4
Thermodynamic quantities of fusion of polyurethane-{6,4}(p = 0.1 MPa)

No.	V[a] (K/s)	$\Delta T^0_{\text{fus}} = T^0_{\text{fus,i}} - T^0_{\text{fus,f}}$ [b] (K)	$T^0_{\text{fus,v}}$ [c] (K)	$C^0_{\text{p,max}}$ [d] (J/(K mol))	ΔH^0_{fus} [e] (kJ/mol)
1	0.015	340–465	457.8	2610	44.3 ± 0.9
2	0.030	345–470	458.1	2984	40.2 ± 0.8
3	0.050	345–465	458.4	2179	39.1 ± 0.8
Mean	–	–	457 ± 1	–	41.2 ± 0.9

[a] V the average rate of heating of calorimeter and substance.
[b] $T^0_{\text{fus,i}}$ and $T^0_{\text{fus,f}}$, the temperatures of onset and end of fusion.
[c] $T^0_{\text{fus,v}}$ the temperatures at which the apparent heat capacity in the melting interval are maximum at the appropriate rate of heating.
[d] $C^0_{\text{p,max}}$ the maximum apparent heat capacity in the melting interval.
[e] ΔH^0_{fus} the molar enthalpy of fusion of partially crystalline polymer at the appropriate rate of heating.

of crystals melts, was considered to be the melting temperature of the sample ($T^0_{\text{fus,v}}$). A true temperature of melting of PU-{6,4} was determined by extrapolating the linear relation $T^0_{\text{fus,v}}$ versus $V^{1/2}$ to the zero rate of heating ($V^{1/2} = 0$). The procedure of T^0_{fus} determination is described in detail [22]. It is worthy that the data on T^0_{fus} of PU-{4,4} and PU-{6,4} are in good agreement with those cited previously [23].

The enthalpy of fusion of PU-{6,4} in each experiment was estimated similarly as demonstrated above for PU-{4,4}. The mean of three ΔH^0_{fus} measurements with regard of the crystallinity degree was taken as the enthalpy of fusion of 100% crystallinity PU-{6,4}.

The entropies of fusion of PU-{4,4} and PU-{6,4} were evaluated from the values of the enthalpy and temperature of fusion. The increase in the heat capacity on melting the polymers was found graphically (IN and I′N′, Fig. 1).

3.4. Thermodynamic functions

On calculating the standard thermodynamic functions of PU-{4,4} and PU-{6,4} (Tables 6 and 7), the relations $C^0_{\text{p}} = f(T)$ of the polymers were extrapolated from 7 to 0 K by the equation of Debye's theory of the heat capacity of solids:

$$C^0_{\text{p}} = nD\left(\frac{\Theta_{\text{D}}}{T}\right) \tag{6}$$

where D denotes Debye's heat capacity function, n and Θ_{D} are specially selected parameters.

Eq. (6) with $n = 2$ and $\Theta_{\text{D}} = 64.0$ K for PU-{4,4} and 2 and 51.7 K for PU-{6,4} describes the experimental C^0_{p} values between 6 and 10 K within to ±1.5 and ±1.7%, respectively. While estimating the functions it was assumed that at temperatures between 0 K and the temperature of the measurement onset this equation reproduces the C^0_{p} values of the samples with the same uncertainty.

The enthalpy $H^0(T) - H^0(0)$ and the entropy $S^0(T)$ of PU-{4,4} and PU-{6,4} were evaluated by the numerical integration of the relationships $C^0_{\text{p}} = f(T)$ by temperature and temperature logarithm over the range 0–490 K in the crystalline, glassy, high-elasticity and liquid states. In the calculations of $S^0(T)$ of the polymers in the amorphous state the zero entropy value $S^0(0)$ derived by us was taken into consideration (Table 3). The Gibbs function $G^0(T) - H^0(0)$ of the polyurethanes was estimated from the values of the enthalpy and entropy of heating at the corresponding temperatures. A detailed description of the function calculation was made earlier [11].

3.5. Thermodynamic characteristics of polyurethane formation

The experimental data on burning of PU-{4,4} and PU-{6,4} are presented in Tables 8 and 9. As a result, the energies and enthalpies of combustion of the partially crystalline polymers at T = 298.15 K and standard pressure were determined. The values are keeping with the thermal effect of the reactions:

$$[\text{–C}_{10}\text{H}_{18}\text{N}_2\text{O}_4\text{–}](\text{p.cr.}) + 12.5\text{O}_2(\text{g}) \rightarrow 10\text{CO}_2(\text{g}) + 9\text{H}_2\text{O}(\text{l}) + \text{N}_2(\text{g})$$

$$[\text{–C}_{12}\text{H}_{22}\text{N}_2\text{O}_4\text{–}](\text{p.cr.}) + 15.5\text{O}_2(\text{g}) \rightarrow 12\text{CO}_2(\text{g}) + 11\text{H}_2\text{O}(\text{l}) + \text{N}_2(\text{g})$$

Table 5
Thermodynamic quantities of fusion of crystalline polyurethanes; p = 0.1 MPa

Polymer	$\Delta T^0_{\text{fus}} = T^0_{\text{fus,i}} - T^0_{\text{fus,f}}$ [a] (K)	T^0_{fus} [b] (K)	ΔH^0_{fus} [c] (kJ/mol)	ΔS^0_{fus} [c] (J/(K mol))	$\Delta C^0_{\text{p}}(T^0_{\text{fus}})$[d] (J/(K mol))
Polyurethane-{4,4}	360–480	474 ± 1	41.9 ± 0.6	88.4 ± 1.3	100 ± 3
Polyurethane-{6,4}	340–470	457 ± 1	47.9 ± 1.3	104.8 ± 2.7	135 ± 3
PPMU [8]	370–450	418 ± 1	21 ± 1	50 ± 2	75 ± 4

[a] $T^0_{\text{fus,i}}$ and $T^0_{\text{fus,f}}$ the temperatures of onset and end of fusion.
[b] T^0_{fus} the fusion temperature.
[c] $\Delta H^{\text{o}}_{\text{fus}}$, ΔS^0_{fus}, the enthalpy and entropy of fusion.
[d] $\Delta C^0_{\text{p}}(T^0_{\text{fus}})$ - the increase in heat capacity at the fusion temperature.

Table 6
Thermodynamics functions of polyurethane-{4,4} (M = 230.26 (g/mol), p = 0.1 MPa)

T (K)	$C_p^0(T)$ (J/(K mol)	$H^0(T) - H^0(T)$ (kJ/mol)	H^0 (T) (J/(K mol)	$-[G^0(T) - H^0(0)]$ (kJ/mol)
Crystalline state				
5	0.615	0.000801	0.206	0.000257
10	3.92	0.0111	1.50	0.00394
15	8.61	0.0412	3.88	0.0170
25	24.75	0.2050	11.89	0.09231
50	69.06	1.374	42.58	0.7551
100	131.9	6.565	112.1	4.642
150	177.2	14.35	174.6	11.84
200	220.1	24.26	231.3	22.00
250	268.5	36.46	285.6	34.93
298.15	314.7	50.50	336.8	49.92
350	365.0	68.10	391.1	68.79
400	413	87.5	443	89.7
450	462	109	494	113
474	484	121	519	125
Liquid state				
474	584	163	608	125
490	594	172	627	135
Glassy state				
0	0	0	20	0
10	3.92	0.00620	21	0.201
15	8.61	0.0369	23	0.309
25	24.83	0.2029	31	0.575
50	69.06	1.373	62	1.72
100	131.9	6.574	131	6.55
150	177.2	14.35	194	14.7
200	220.1	24.27	251	25.8
250	268.5	36.47	305	39.7
280	297.0	44.95	337	49.4
High-elasticity state				
280	460.0	44.95	337	49.4
298.15	472.1	53.41	366	55.7
350	504.8	78.39	443	76.8
400	537	104	513	101
450	589	132	578	130
474	584	146	608	142

In brackets are given the physical states of reagents: (p.cr.), partially crystalline; (g), gaseous; (l), liquid.

The data on the enthalpies of combustion of the partially crystalline PU-{4,4} and PU-{6,4} were used to estimate their enthalpies of combustion and formation in the totally crystalline and amorphous (high-elasticity) states at T = 298.15 K and p = 0.1 MPa. From the absolute values of the entropy of the polymers in the crystalline and amorphous states (Tables 6 and 7), carbon in the form of graphite, gaseous hydrogen, oxygen and nitrogen [24,25] the standard entropies of formation ΔS_f^0(cr) and ΔS_f^0 (h.e.) of PU-{4,4} and PU-{6,4} in the crystalline and amorphous states at T = 298.15 K were calculated by methods described earlier [11]. The Gibbs function of formation ΔG_f^0 of the polymers was evaluated from the ΔH_f^0 and ΔS_f^0 values (Table 10) [11]. The values conform to the following processes:

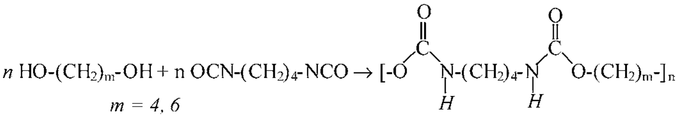
$$10C(gr) + 9H_2(g) + N_2(g) + 2O_2(g) \rightarrow [–C_{10}H_{18}N_2O_4–](\text{cr or h.e.})$$

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

where in the brackets are indicated the physical states of reagents: (gr), graphite; (g), gaseous; (cr), crystalline; (h.e.), high-elasticity.

3.6. *Thermodynamic characteristics of polycondensation processes in bulk*

The polycondensation reaction of 1,4-diisocyanatobutane with 1,4-butanediol and 1,6-hexanediol to form PU-{4,4} and PU-{6,4} proceeds according to the scheme:



$$n\,HO\text{-}(CH_2)_m\text{-}OH + n\,OCN\text{-}(CH_2)_4\text{-}NCO \rightarrow [\text{-}O\text{-}C(=O)\text{-}N(H)\text{-}(CH_2)_4\text{-}N(H)\text{-}C(=O)\text{-}O\text{-}(CH_2)_m\text{-}]_n$$

$m = 4, 6$

In Table 11 are summarized the standard thermodynamic characteristics of polycondensation of PU-{4,4} and PU-{6,4}

Table 7
Thermodynamics functions of polyurethane-{6,4} ($M = 230.26$ (g/mol), $p = 0.1$ MPa)

T (K)	$C_p^0(T)$ (J/(K mol))	$H^0(T) - H^0(0)$ (kJ/mol)	S^0(T) (J/(K mol))	$-[G^0(T) - H^0(0)]$ (kJ/mol)
Crystalline state				
5	1.15	0.00150	0.388	0.000487
10	5.74	0.0180	2.50	0.00695
15	12.2	0.0611	5.91	0.0276
25	34.43	0.2912	17.16	0.1378
50	90.67	1.866	58.65	1.066
100	152.3	8.234	144.5	6.215
150	201.9	17.07	215.5	15.24
200	248.2	28.32	279.9	27.65
250	306.4	42.12	341.2	43.19
298.15	367.8	58.39	400.6	61.04
350	430.0	79.07	464.4	83.47
400	491	102	526	108
450	551	128	587	136
457	559	132	595	140
Liquid state				
457	694	180	700	140
480	719	196	735	157
Glassy state				
0	0	0	27	0
10	5.74	0.0180	29	0.277
15	12.2	0.0611	33	0.433
25	34.43	0.2912	44	0.813
50	90.67	1.866	86	2.42
100	152.3	8.234	171	8.91
150	201.9	17.07	244	19.3
200	248.2	28.32	307	33.1
250	306.4	42.12	368	49.9
283	350.0	52.95	409	62.8
High-elasticity state				
283	533.0	52.95	409	62.8
298.15	548.0	61.14	437	69.2
350	596.0	90.79	529	94.2
400	643	122	611	123
450	687	155	690	155
457	694	160	700	160

calculated from the experimental and literature data [26–28]. The enthalpy of reaction at $T = 298.15$ K was evaluated from the ΔH_f^0 values of the polymers (Table 10) and the corresponding adducts. The reaction enthalpy at other temperatures was calculated by Kirchhoff's equation [21]. In order to estimate the reaction entropy, the absolute values of the entropy of reagents at appropriate temperatures were used. The Gibbs function of polycondensation was evaluated on the base of the ΔH_{pol}^0 and ΔS_{pol}^0 values by Gibbs–Helmholtz equation [21]. The calculation technique is described in detail elsewhere [11].

The Gibbs function of polycondensation ΔG_{pol}^0 has large negative values testifying to a virtually complete shift of the equilibrium towards the polymer formation. A ceiling temperature of polycondensation, as determined by Daiton's procedure [29], was found to be $T_{\text{ceil}}^0 = 635$ K for PU-{4,4} and $T_{\text{ceil}}^0 = 950$ K for PU-{6,4}and in both cases these temperatures substantially exceed the temperatures of the beginning of the PU decomposition.

3.7. *Comparison of thermodynamic characteristics of polyurethanes*

To elucidate some most general regularities of changing the thermodynamic characteristics of PU depending on their composition and structure, it was of interest to compare the properties of the tested PU-{4,4} and PU-{6,4} with those of PU of an isomeric structure, namely, poly(pentamethylene urethane) (PPMU) and poly(tetramethylene urethane) (PTTMU) [8,30].

PPMU, examined previously, [8] is a structural isomer of PU-{6,4}. The isomerism of the above polymers is due, first of all, to the transfer of one methylene group from a diol part to a diisocyanate part of PU-{6,4}and a different arrangement of comonomeric units in a monomer moiety. Isomeric PTTMU, studied over the range 0–300 K in the partially crystalline state ($\alpha = 43\%$), [30] was chosen as an object to be compared with PU-{4,4}. The isomerism of PTTMU and PU-{4,4} is brought about only by the different arrangement of the comonomeric units in the monomeric moiety.

Table 8
Experimental data on combustion energy for polyurethane-{4,4} at $T = 298.15$ K

Value	Experiment				
	1	2	3	4	5
m_{sam} (g)[a]	0.1892	0.1949	0.3107	0.3027	0.3025
$m_{\mathrm{p.e.}}$ (g)[a]	0.1861	0.1773	0.2188	0.2552	0.2555
$m_{\mathrm{thread.}}$ (g)[a]	0.0024	0.0026	0.0023	0.0029	0.0023
W (J/g)[b]	75927	75927	75927	75927	75927
$\Delta R + \Delta(\Delta R)$[c] ($\Omega$)	0.175080	0.171517	0.233317	0.253680	0.253590
$-\Delta_{\mathrm{c}}U_{\Sigma}$[d] (J)	13293.4	13022.8	17715.0	19261.2	19254.3
$-\Delta_{\mathrm{c}}U_{\mathrm{p.e.}}$[e] (J)	8639.1	8230.3	10157.1	11846.6	11859.5
$-\Delta_{\mathrm{c}}U_{\mathrm{thread}}$[e] (J)	40.2	43.5	38.5	48.5	38.5
$-\Delta_{\mathrm{c}}U_{\mathrm{HNO_3}}$[f] (J)	23.0	25.5	18.0	33.5	25.1
$(m^{\mathrm{e}}\mathrm{CO_2}/m^{\mathrm{c}}\mathrm{CO_2})$[g] × 100%	99.83	99.85	–	99.91	–
$-\Delta_{\mathrm{c}}U$[h] (J/g)	24265.9	24234.1	24143.6	24223.7	24235.5

$-\Delta_{\mathrm{c}}\bar{U} = (24220.6 \pm 41.8)$ J/g $= (5577.0 \pm 9.6)$ kJ/mol, the mean energy of combustion of PU-{4,4}; $-\Delta_{\mathrm{c}}U^0 = (5573.9 \pm 9.6)$ kJ/mol, the energy of combustion of PU-{4,4} at standard pressure; $-\Delta_{\mathrm{c}}H^0$ (α) = (5577.7 ± 9.6) kJ/mol, the enthalpy of combustion of PU-{4,4}.

[a] m_{sam}, $m_{\mathrm{p.e.}}$, m_{thread}, masses of the tested sample, polyethylene and a cotton thread, respectively.

[b] W, the energy equivalent of the calorimeter.

[c] $\Delta R + \Delta(\Delta R)$, the change in resistance of platinum-resistance thermometer with correction for heat-exchange.

[d] $\Delta_{\mathrm{c}}U_{\Sigma}$, the total energy released during the experiment.

[e] $\Delta_{\mathrm{c}}U_{\mathrm{p.e.}}$, $\Delta_{\mathrm{c}}U_{\mathrm{thread}}$, amounts of energy released on burning polyethylene and cotton thread, respectively.

[f] $\Delta_{\mathrm{c}}U_{\mathrm{HNO_3}}$, the energy of formation of nitric acid.

[g] $(m^{\mathrm{e}}(\mathrm{CO_2})/m^{\mathrm{c}}(\mathrm{CO_2})) \times 100\%$, the ratio of masses of $\mathrm{CO_2}$ in the combustion products of PU-{4,4} and calculated by its chemical formula.

[h] $\Delta_{\mathrm{c}}U$, the energy released on burning of PU-{4,4}.

The character of the change in the relation $C_{\mathrm{p}}^0 = f(T)$ for PU-{4,4}, PU-{6,4}, PPMU and PTTMU is the same that is, obviously, related to an identical topology of their structure.

True values of the heat capacity for PU-{6,4} in the whole temperature range studied are higher than those of PU-{4,4} that is brought about by the contribution of two additional methylene groups in PU-{6,4}. So, for example, at $T = 298.15$ K this difference per one methylene group is ∼25 (J/(K mol) for the compared PU in the crystalline state that is close to a similar increase in the heat capacity in isomeric PU row [6–8].

While comparing the numerical C_{p}^0 values of PU-{6,4} and PPMU, several peculiarities should be highlighted. At extremely low temperatures ($T < 80$ K) C_{p}^0(PPMU) < C_{p}^0 PU-{6,4}) by 5–7% and Debye's characteristic temperature, determined in the range 6–10 K, is higher for PPMU ($\Theta_{\mathrm{D}} = 78.9$, $n = 2$) than that of PU-{6,4} ($\Theta_{\mathrm{D}} = 51.7$, $n = 2$). Atomic groups in PPMU

Table 9
Experimental data on combustion energy for polyurethane-{6,4}at $T = 298.15$ K

Value	Experiment					
	1	2	3	4	5	6
m_{sam} (g)[a]	0.1022	0.1635	0.1617	0.1551	0.2320	0.1320
$m_{\mathrm{p.e.}}$ (g)[a]	0.1924	0.2242	0.2172	0.2330	0.1710	0.2279
m_{thread} (g)[a]	0.0017	0.0026	0.0031	0.0024	0.0033	0.0024
W (J/g)[b]	75998	75998	75998	75998	75998	75998
$\Delta R + \Delta(\Delta R)$[c] ($\Omega$)	0.153677	0.194163	0.189430	0.190707	0.185423	0.185559
$-\Delta_{\mathrm{c}}U_{\Sigma}$[d] (J)	11679.2	14756.1	14396.3	14493.4	14087.5	14102.2
$-\Delta_{\mathrm{c}}U_{\mathrm{p.e.}}$[e] (J)	8931.6	10407.7	10082.6	10365.9	7937.9	10579.2
$-\Delta_{\mathrm{c}}U_{\mathrm{thread}}$[e] (J)	28.5	43.5	51.9	40.2	55.2	40.2
$-\Delta_{\mathrm{c}}U_{\mathrm{HNO_3}}$[f] (J)	35.1	22.5	15.5	13.3	16.7	15.5
$(m^{\mathrm{e}}\mathrm{CO_2}/m^{\mathrm{c}}\mathrm{CO_2})$[g] × 100%	99.70	99.85	99.78	99.81	99.60	99.94
$-\Delta_{\mathrm{c}}U$[h] (J/g)	26260.9	26192.3	26260.5	26266.7	26214.9	26266.3

$-\Delta_{\mathrm{c}}\bar{U} = (26243.7 \pm 25.9)$ J/g $= (6779.3 \pm 6.7)$ kJ/mol, the mean energy of combustion of PU-{6,4}. $-\Delta_{\mathrm{c}}U^0 = (6776.0 \pm 6.7)$ kJ/mol, the energy of combustion of PU-{6,4} at standard pressure. $-\Delta H_{\mathrm{c}}^0(\alpha) = (6782.2 \pm 6.7)$ kJ/mol, the enthalpy of combustion of sample.

[a] m_{sam}, $m_{\mathrm{p.e.}}$, m_{thread}, masses of the tested sample, polyethylene and a cotton thread, respectively.

[b] W, the energy equivalent of the calorimeter.

[c] $\Delta R + \Delta(\Delta R)$, the change in resistance of platinum-resistance thermometer with correction for heat-exchange.

[d] $\Delta_{\mathrm{c}}U_{\Sigma}$, the total energy released during the experiment.

[e] $\Delta_{\mathrm{c}}U_{\mathrm{p.e}}$, $\Delta_{\mathrm{c}}U_{\mathrm{thread}}$, amounts of energy released on burning polyethylene and cotton thread, respectively.

[f] $\Delta_{\mathrm{c}}U_{\mathrm{HNO_3}}$, the energy of formation of nitric acid.

[g] $(m^{\mathrm{e}}(\mathrm{CO_2})/m^{\mathrm{c}}(\mathrm{CO_2})) \times 100\%$, the ratio of masses of $\mathrm{CO_2}$ in the combustion products of PU-{6,4} and calculated by its chemical formula.

[h] $\Delta_{\mathrm{c}}U$, the energy released on burning of PU-{6,4}.

Table 10
Enthalpy of combustion and thermodynamic characteristics of formation of linear polyurethanes ($T = 298.15$ K, $p = 0.1$ MPa)

Polymer	Physical state[a]	$-\Delta H_c^{0}$[b] (kJ/mol)	$-\Delta H_f^{0}$[c] (kJ/mol)	$-\Delta S_f^{0}$ (J/(K mol))	$-\Delta G_f^{0}$[c] (kJ/mol)
Polyurethane-{4,4}	cr	5574 ± 11	933 ± 11	1497 ± 3	487 ± 12
	h.e	5594 ± 11	914 ± 11	1468 ± 4	476 ± 13
Polyurethane-{6,4}	cr	6779 ± 8	1087 ± 8	1706 ± 4	579 ± 9
	h.e	6802 ± 8	1065 ± 8	1669 ± 5	567 ± 10
PPMU [8]	cr	3386.2	546.9	860.1	290.5
	h.e	3396.7	536.4	840.2	285.9

[a] cr: crystalline; h.e: high-elasticity.
[b] ΔH_c^0, the enthalpy of combustion.
[c] ΔH_f^0, ΔS_f^0 and ΔG_f^0, the enthalpy, entropy and Gibbs function of formation of the polymers.

structure seem to be more compactly packed and, consequently, the unfreezing of their oscillation degrees of freedom and the contribution to C_p^0 occur at higher temperatures. The values of the fractal dimension D for PU-{6,4} and PPMU also confirm the same character of heterodynamics of the compared object structure. The heat capacities of PU-{6,4} and PPMU in the crystalline and glassy states over the range from 80 K to T_g^0 coincide within an error of determination. With rising temperature above T_g^0, the heat capacities of the isomers somewhat differ (∼3%) and deviations of the C_p^0 values are higher than the uncertainty of measurements in the above interval. However, judging by their values, the deviations can be explained with graphic extrapolations that are made on estimating the crystallinity degree of the polymers.

The C_p^0 values of the partially crystalline PU-{4,4} and PTTMU between 7 and 80 K differ on an average by 3%, from 80 to 250 K by ∼1.5% and at $T > 250$ K the devitrification of PTTMU seems to start that does not enable the heat capacity values of the isomers to be compared. Thus, the differences in C_p^0 of the polymers exceeding the determination uncertainty are, obviously, connected with their isomerism since at temperatures below T_g^0 the C_p^0 values do not practically depend upon the crystallinity degree α: the heat capacity of amorphous, partially crystalline and crystalline polymers usually coincides within their measurement uncertainty [21].

Wide devitrification intervals of PU-{4,4}, PU-{6,4} and PPMU are caused by a high degree of the sample crystallinity and associated with the effect of reinforcing amorphous fragments of the polymers with crystalline ones. The devitrification temperatures T_g^0 of PU-{4,4}and PU-{6,4} are close, while T_g^0 of PU-{6,4} is higher by 17 K than of PPMU. Hence, the insertion of two additional methylene groups into a repeating monomer unit does not lead to a noticeable change in temperatures of the excitation of their segmental mobility. A tendency to the absence

Table 11
Thermodynamic characteristics of polycondensation in bulk of 1,4-diisocyanatobutane with 1,4-butanediol and 1,6-hexandiol with formation of linear polyurethanes-{4,4} and -{6,4} ($p = 0.1$ MPa)

T (K)	Physical state of monomer and polymer[a]	$-\Delta H_{pol}^{0}$ [b] (kJ/mol)	$-\Delta S_{pol}^{0}$ [b] (J/(K mol))	$-\Delta G_{pol}^{0}$ [b] (kJ/mol)
1,4-Butanediol + 1,4-diisocyanatobutane → polyurethane-{4,4}				
0	cr, cr, cr	96.7	0	96.7
	cr, cr, g	79.6	−20	79.6
100	cr, cr, cr	98.2	24.7	95.7
	cr, cr, g	81.1	6	80.6
200	cr, cr, cr	101	43.6	92.2
	cr, cr, g	83.9	24	79.0
298.15	l, l, cr	145	219	79.3
	l, l, h.e	125	190	68.3
350	l, l, cr	152	239	66.5
	l, l, h.e	124	183	57.9
1,6-Hexandiol + 1,4-diisocyanatobutane → polyurethane-{6,4}				
0	cr, cr, cr	186	0	186
	cr, cr, g	165	−27	165
100	cr, cr, cr	187	13.5	186
	cr, cr, g	167	−13	168
200	cr, cr, cr	192	43.3	183
	cr, cr, g	171	16	168
298.15	cr, l, cr	220	164	171
	cr, l, h.e	197	127	159
350	l, l, cr	252	265	159
	l, l, h.e	220	201	150

[a] cr: crystalline; l: liquid; g: glassy; h.e: high-elasticity.
[b] ΔH_{pol}^0, ΔS_{pol}^0 and ΔG_{pol}^0, the enthalpy, entropy and Gibbs function of polycondensation process.

of an appreciable influence of CH_2-groups in the aliphatic PU on the devitrification temperatures remains, probably, till a certain number of methylene groups. On the contrary, a dissimilarity of spatially located groups in monomeric units of PU macromolecules significantly affects their devitrification temperatures that is, in principle, natural because a mutual kinetic mobility of polymer chain segments has to depend not only on their qualitative composition but also on stereometric factors. A difference in the increment of the heat capacity on devitrifying, $\Delta C_p^0(T_g^0)$, of totally amorphous PU-{4,4} and PU-{6,4} is equal to ca. 20 (J/(K mol) that conforms to Wunderlich's rule about 11.7 ± 2.5 (J/(K mol) contribution to the $\Delta C_p^0(T_g^0)$ value on introducing 1 mol "beads" – the least particles capable of doing independent motions – into a polymer [31].

The fusion of the polymers takes place in a wide temperature range that is basically characteristic of linear aliphatic PU [32]. The T_{fus}^0 values of PU, examined in the given work, are different by 17 K. The result is in good agreement with the law of parity for the relation between T_{fus}^0 of polymers and the number of CH_2-groups in their composition [24]. It should be noted that the empirical value $T_g^0/T_{fus}^0 \approx 0.61 \pm 0.02$ typical for the majority of polymers [21] does not vary and true for PU-{4,4} and PU-{6,4}. Meanwhile, it should be emphasized that the melting temperature T_{fus}^0 of PU-{6,4} is higher by 40 K as compared to that of PPMU. Apparently, this is related to the effect of macromolecule isomerism on the parameters of a crystalline lattice of lamellar crystals. The fusion enthalpies ΔH_{fus}^0 of PU-{6,4} and PPMU differ by about 10%. It is appreciably larger than the determination uncertainty and, perhaps, not only the gross-composition of monomeric units and the crystallinity degree of polymers but a steric arrangement of groups in macromolecules exert influence upon ΔH_{fus}^0 as well.

The comparison of the numerical values of the standard thermodynamic characteristics of formation of the isomeric polyurethanes showed that those coincide within the uncertainty of their determination. It is worth of note that it is impossible to completely exclude the effect of the spatial arrangement of groups in the macromolecules on the standard thermodynamic characteristics since such influence can lie within the uncertainty with regard of the extrapolation method of estimating the crystallinity degree of the polymers.

Unfortunately, because of the absence of literature data on C_p^0 of PTTMU at $T > 300$ K, it turned out that it is impossible to compare the standard thermodynamic characteristics of physical transformations of PU-{4,4} and PTTMU as well as the standard thermodynamic characteristics of their formation in the crystalline and amorphous states and, consequently, to estimate a relative thermodynamic stability of isomers. It should be noted only that, according to the data [30], the T_{fus}^0 value of PTTMU, determined by DTA equal to 480 K, agrees quite well with the value for PU-{6,4} obtained by us.

Acknowledgements

The work was performed with the financial support of the *Russian Foundation of Basic Research* (Project Number 05-03-32363) and the *Ministry of Education and Science* of the Russian Federation.

References

[1] R. Versteegen, Well-Defined Thermoplastic Elastomers: Reversible Networks Based on Hydrogen Bonding, Eindhoven University of Technology, Eindhoven, 2003.
[2] Z. Wirpsza, Polyurethanes, Chemistry, Technology and Applications, Ellis Horwood, London, 1993.
[3] S.G. Dmitrenko, Yu.A. Zolotov, Russ. Chem. Rev. 71 (2002) 159.
[4] L.F. Kosyanchuk, Yu.S. Lipatov, V.F. Babich, L.N. Perepelitsyna, Polym. Sci. Ser. A 45 (2003) 644.
[5] S.I. Grishchuk, T.T. Alekseeva, Yu.S. Lipatov, Polym. Sci. Ser. A 45 (2003) 366.
[6] B.V. Lebedev, V.V. Veridusova, H. Hocker, H. Keul, Macromol. Chem. Phys. 203 (2002) 1114.
[7] V.V. Veridusova, B.V. Lebedev, Polym. Sci. Ser. A 43 (2001) 193.
[8] B.V. Lebedev, T.G. Kulagina, N.N. Smirnova, A.V. Markin, B. Meijer, R. Versteegen, Macromol. Chem. Phys. 205 (2004) 230.
[9] G.M. Yenwo, J.A. Manson, J. Pulido, L.H. Sperling, A. Conde, N. Demia, J. Appl. Polym. Sci. 12 (1977) 1531.
[10] G.M. Yenwo, L.H. Sperling, J.A. Manson, Polym. Eng. Sci. 17 (1977) 251.
[11] B.V. Lebedev, Thermochim. Acta 297 (1997) 143.
[12] R.M. Varushchenko, A.I. Druzhinina, E.L. Sorkin, J. Chem. Thermodyn. 29 (1997) 623.
[13] M.Sh. Yagfarov, Z. Fiz. Khim. 43 (1969) 1620;
M.Sh. Yagfarov, Chem. Abstr. 71 (1969) 64942g.
[14] A.G. Kabo, V.V. Diky, Thermochim. Acta 347 (2000) 79.
[15] B.V. Lebedev, E.G. Kiparisova, Russ. J. Phys. Chem. 70 (1996) 1253.
[16] T.S. Yakubov, Dokl. Chem. 310 (1990) 145.
[17] A.D. Izotov, O.V. Shebershneva, K.S. Gavrichev, Abstracts of the Third Russian Conference by on Thermal Analyses and Calorimetry, Kazan, 1996.
[18] V.V. Tarasov, Zh. Fiz. Khim. 24 (1950) 111;
V.V. Tarasov, Chem. Abstr. 44 (1950) 4742f.
[19] W. Borchet, Angew. Chem. 63 (1957) 40.
[20] S. Alford, M. Dole, J. Am. Chem. Soc. 77 (1955) 4774.
[21] B.V. Lebedev, N.N. Smirnova, Chemical Thermodynamics of Polyalkanes and Polyalkenes, Nizhny Novgorod University Press, Nizhny Novgorod, 1999, p. 27.
[22] V.A. Bershteiin, B.M. Egorov, Differential Scanning Calorimetry in Physical Chemistry of Polymers, Khimiya, Leningrad, 1990, p. 139.
[23] O. Bayer, Angew. Chem. A 59 (1947) 257.
[24] J.D. Cox, D.D. Wagman, V.A. Medvedev, CODATA Key Values for Thermodynamics, Hemisphere Publishing Corp., New York, 1984.
[25] M.W. Chase, NIST-JANAF thermochemical tables, J. Phys. Chem. Ref. Data, fourth ed. (1998) (Monograph 9).
[26] N.N. Smirnova, K.V. Kandeev, T.A. Bykova, T.G. Kulagina, J. Chem. Thermodyn. 38 (2006) 376.
[27] V.P. Nistrtatov, A.G. Babinkov, K.G. Shvetsova, S.A. Lapteva, Thermodyn. Org. Soedin. 8 (1979) 33;
M. Zabransky, V. Ruzicka, V. Majer, E.S. Domalski, J. Phys. Chem. Ref. Data (1996) (Monograph 6).
[28] N.N. Smirnova, K.V. Kandeev, T.A. Bykova, Russ. J. Phys. Chem. 79 (2005) 857.
[29] F.S. Daiton, K.J. Ivin, Quart. Rev. 12 (1958) 61.
[30] B.V. Lebedev, T.A. Bykova, E.G. Kiparisova, A.M. Kochetkov, H. Hocker, J. Kusan, H. Keul, Macromol. Chem. Phys. 200 (1999) 1863.
[31] B. Wunderlich, U. Gaur, Pure Appl. Chem. 52 (1980) 445.
[32] Yu.S. Lipatov, Yu.Yu. Kercha, L.M. Sergeeva, Structure and Properties of Polyurethanes, Naykova Dumka, Kiev, 1970, p. 64.