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Thermodynamics of dimethylene urethane and poly(dimethylene urethane) in the range from T → 0 to 490 K at standard pressure

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Abstract

By high-precision dynamic calorimetry the temperature dependences of heat capacity of dimethylene urethane (DMU) between 320 and 370 K and partially crystalline poly(dimethylene urethane) (PDMU) in the range 326–490 K at standard pressure have been determined within ±1.5%. The thermodynamic characteristics of fusion of the substances, namely the temperature interval of melting, temperature, enthalpy and entropy of fusion, as well as the characteristics of devitrification and glassy state for poly(dimethylene urethane) have been estimated. The first and the second cryoscopic constants have been calculated for dimethylene urethane. The experimental data obtained in the present work and literature findings on the heat capacity of the substances were used to calculate their thermodynamic functions: the heat capacity $C_p^\circ(T)$, enthalpy $H^\circ(T) - H^\circ(0)$, entropy $S^\circ(T)$ and Gibbs function $G^\circ(T) - H^\circ(0)$ over the range from $T \to 0$ to (370–480) K. Based on the data, the thermodynamic characteristics of polymerization process with five-membered ring opening $\Delta_{\mathrm{pol}}H^\circ$, $\Delta_{\mathrm{pol}}S^\circ$ and $\Delta_{\mathrm{pol}}G^\circ$ of dimethylene urethane with the formation of linear partially crystalline poly(dimethylene urethane) have been evaluated.

Keywords: Dimethylene urethane; Poly(dimethylene urethane); Calorimeter; Heat capacity; Thermodynamic functions

1. Introduction

The present work is a part of complex calorimetric studies of the thermodynamic properties of representatives of cyclic urethane row, their polymerization with ring-opening and linear polyurethanes being formed. In references [1–4] the thermodynamic properties of seven-, six- and five-membered cyclic urethanes and thermodynamic characteristics of the process of their polymerization and the corresponding polyurethanes were examined. The findings about the properties over the range from $T \to 0$ to 350 K were obtained by high-precision adiabatic vacuum calorimetry methods.

Some regularities for the properties of the urethanes and the appropriate polyurethanes depending on their composition, structure and physical state were derived as discussed later [5]. However, it is quite clear that the broadening of the temperature range, where the thermodynamic properties of a promising class of polymeric compounds (polyurethanes) are studied, is of appreciate importance. In the first place, this is accounted for the detection of possible physical transformations, temperatures of the onset of thermal decomposition and in the case of partially crystalline polymers, the estimation of their crystallinity degree from the calorimetric data.

The aim of the present work is to determine the temperature dependence of the heat capacity of dimethylene urethane (DMU) and partly crystalline poly(dimethylene urethane) (PDMU) between 320 and 490 K by the calorimetric method, to study probable physical transitions of the substances and to evaluate their thermodynamic characteristics, to calculate the thermodynamic functions $C_p^\circ(T)$, $H^\circ(T) - H^\circ(0)$, $S^\circ(T)$ and $G^\circ(T) - H^\circ(0)$ of the monomer and the polymer for the range from $T \to 0$ to (370–480) K based on the data obtained by us and given elsewhere [4], to estimate the thermodynamic characteristics of the polymerization process of DMU with ring-opening $\Delta_{\mathrm{pol}}H^\circ$, $\Delta_{\mathrm{pol}}S^\circ$ and $\Delta_{\mathrm{pol}}G^\circ$ with the formation of partly crystalline PDMU.

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2. Experimental

2.1. Sample

Samples of five-membered dimethylene urethane and the corresponding poly(dimethylene urethane) were synthesized at Prof. H. Hocker's laboratory (Lehrstuhl fur Textilchemie und Makromolekulare Chemie der RTWH, Aachen, Germany). The monomer was twice recrystallized from ethyl acetate. Its yield was 75 mass%. According to the data cited in [4], the DMU sample was completely crystalline and its melting temperature was found to be 87–88 °C. PDMU was synthesized by the procedure described in [4]. Hydroxy-phenylurethane was heated to 120 °C and the melt was treated with 1.67 mol% $Bu_2Sn(OCH_3)_2$. The polycondensation was performed at 120 °C and variable pressure (from normal pressure to 10^{-2} mbar) for 3 h. During this time, phenol was removed from the reaction mixture. The polymer was purified by precipitation from DMF solution into diethyl ether, yield 88%. As the elementary analysis data show, the composition of a repeating monomer unit in the polymer conforms to the formula one. By gel-permeation chromatography its number-average molecular weight and the polydispersity were determined to be $\bar{M}_n = 8200$ and $\bar{M}_w/\bar{M}_n = 1.55$. According to our calorimetric data, the PDMU sample was partially crystalline with the degree of crystallinity $\alpha = 33\%$ ($\alpha = 85\%$ was roughly estimated in [4] that was noted by the authors).

2.2. Apparatus and measurement procedure

To measure the heat capacity, temperatures and enthalpies of physical transitions of the substances in the range 300–650 K, an automated thermophysical device operating by the principle of triple thermal bridge [6,7], a high-precision dynamic calorimeter intended to study the thermodynamic properties of substances at elevated temperatures, was employed. The calorimeter design and the measurement procedure of the heat capacity, temperatures and enthalpies of physical transitions are described in detail elsewhere [6,7]. The reliability of the calorimeter operation was tested by measuring the heat capacity of a standard sample of synthetic corundum as well as the thermodynamic characteristics of fusion of indium, tin and lead. It was found that the calorimeter and the measurement procedure allow one to obtain the data on the heat capacity of substances in solid and liquid states with an uncertainty ±1.5% and the temperatures of physical transitions within about ±0.3 K.

The heat capacities of the same samples were determined earlier between 6 and 340 K [4]. For the measurement of the heat capacity in this interval a BKT-3 automated adiabatic vacuum calorimeter with discrete heating was used. The reliability of the calorimeter operation was tested by measuring the heat capacity of a special purity copper, standard synthetic corundum and K-2 benzoic acid prepared at metrological institutions of the State Standard of the Russian Federation. As the analysis results show, the uncertainty of C_p° measurements at helium temperatures was within ±2%. With rising temperature up to 40 K, it decreased till ±0.5% and at $T > 40$ K it was ±0.2%.

3. Results and discussion

3.1. Heat capacity

The heat capacity C_p° of the monomer was measured between 320 and 373 K and of the polymer in the 326–488 K range. All measurement results are summarized in Tables 1 and 2. The masses of DMU and PDMU samples located in a calorimetric ampoule were 0.3151 and 0.2885 g, respectively. The heat capacity values for the DMU sample were obtained at three different rates of heating of the calorimeter and the substance (Table 3) and for the PDMU sample C_p° was measured at an average rate of heating 0.033 K/s. The heat capacity of DMU and PDMU was between 30 and 40% and from 40 to 50%, respectively, of the total heat capacity (calorimeter ampoule and sample). Averaging of the experimental C_p° values was made on a computer by means of degree and semilogarithmic polynomials so that the root mean square deviation of C_p° from the corresponding smoothed curve $C_p^\circ = f(T)$ did not exceed an uncertainty of measurements.

The temperature dependences of the heat capacity $C_p^\circ = f(T)$ for the DMU sample are illustrated in Figs. 1 and 2 and for the PDMU sample in Fig. 3, the C_p° values in the range from 320 to (370–480) K were measured (circles) in this work, the data between 6 and 340 K were taken from [4]. As Fig. 1 shows, the heat capacity of dimethylene urethane gradually increases with rising temperature. A sharp increase and the following break of the plot $C_p^\circ = f(T)$ between 345 and 370 K (Figs. 1 and 2) are caused with the fusion of crystals. Thus, in the temperature range considered DMU exists in crystalline and liquid states. The experimental values of apparent heat capacity of DMU in the interval of its melting (Fig. 2) depend upon the heating rate of the calorimeter and the substance that is characteristic of first-order phase transitions.

On the relationship C_p° against T of PDMU (Fig. 3), the devitrification of its amorphous part between 335 and 375 K (BE section) and the melting of the crystalline part over the range 410–480 K, accompanied with the polymer decomposition that is shown by a sharp decrease in the heat capacity (MN section), are observed. Besides, the diminution of the sample mass after the experiment by 45% occurs. In the range 400–410 K (Fig. 3) a slight inflection on the curve $C_p^\circ = f(T)$ is observed and the same was noted earlier [8] for vitrifying polymers in a high-elasticity state. The variation of the temperature-dependent heat capacities is reproduced on cooling the sample from $T \sim 400$ K to the temperature of the measurement beginning.

Table 1
Experimental values of heat capacity of dimethylene urethane; $M = 87.08$ g/mol, $p = 101.325$ kPa

T (K)	C_p° (J/(mol K))	T (K)	C_p° (J/(mol K))	T (K)	C_p° (J/(mol K))	T (K)	C_p° (J/(mol K))
Series 1							
319.9	118.3	334.3	122.6	344.7	126.5	357.8	2255
320.7	118.6	334.8	122.6	345.4	126.9	358.1	3097
321.6	118.6	335.3	122.9	346.0	127.1	358.3	3874
322.5	118.9	335.8	122.9	346.7	127.2	358.6	4379
323.3	119.3	336.2	123.2	347.4	127.6	359.1	4920
324.2	119.5	336.7	123.3	348.1	128.1	359.6	4102
325.0	119.8	337.1	123.7	349.5	132.0	359.9	3767
325.9	120.3	337.6	123.7	350.2	135.1	360.2	3460
326.7	120.3	338.1	123.8	350.8	142.8	360.4	3127
327.4	120.5	338.5	123.9	351.5	154.7	360.8	2910
328.2	120.8	339.0	124.0	352.2	169.7	361.5	2792
328.9	120.8	339.5	124.5	352.8	184.0	361.9	2320
329.6	121.0	340.0	124.7	353.5	204.0	362.3	1641
330.3	121.6	340.6	124.9	354.1	230.7	363.1	151.1
330.9	121.6	341.1	125.1	354.7	297.7	364.3	149.6
331.6	121.7	341.6	125.4	355.3	346.0	365.4	150.4
332.2	122.0	342.2	125.6	355.9	437.0	368.1	151.0
332.7	122.1	342.8	126.0	356.5	603.6	370.0	151.0
333.3	122.2	343.4	126.2	357.0	960.5	371.8	152.6
333.8	122.2	344.1	126.3	357.4	1374	372.8	153.5
Series 2							
322.9	119.1	335.9	122.7	351.8	132.0	363.0	1781
323.9	119.3	337.0	122.9	353.0	136.0	363.5	1494
325.0	120.0	338.2	123.2	354.3	149.9	364.3	1131
326.1	120.2	339.5	123.4	355.3	217.3	366.1	407.9
327.2	120.2	340.7	123.4	356.4	419.9	368.1	148.0
328.3	120.7	341.9	123.6	357.5	749.3	370.0	144.0
329.4	120.7	343.1	123.7	358.2	1091	371.8	148.0
330.4	121.5	344.3	124.2	358.8	1460	373.5	149.5
331.5	121.5	345.5	124.8	359.4	2412	373.5	149.5
332.6	121.7	346.8	125.1	360.5	4230		
333.7	122.0	348.1	125.6	361.3	3554		
334.8	122.0	349.3	127.0	361.8	2146		
Series 3							
333.9	122.8	345.2	136.2	356.6	553.6	364.2	1925
335.7	123.3	347.2	145.8	358.1	1127	365.6	1714
337.6	123.8	349.1	156.8	359.4	2033	367.5	758.0
339.4	125.0	351.1	171.9	360.4	2328	370.0	149.5
341.3	125.3	353.0	200.9	361.8	2158		
343.3	129.2	354.9	289.6	362.8	2043		

As follows from the data, poly(dimethylene urethane) was in a partially crystalline state under conditions of our apparatus.

3.2. Thermodynamic characteristics of physical transformations

3.2.1. Fusion

The experimental temperatures and enthalpies of fusion of the DMU sample are listed in Table 3. Temperatures of the beginning and the termination of its fusion were determined graphically (B and D points, Fig. 2). The enthalpies of fusion were calculated as areas between curves 1–3 of the apparent heat capacity in the melting range (Fig. 2) and a normal trend of the heat capacity, i.e. $C_p^\circ = f(T)$, which occurs when no melting takes place. Based on the measurement results, the thermodynamic quantities of fusion of DMU were estimated (Table 3). The thermodynamic equilibrium temperature of melting for DMU was graphically found by extrapolating the relation $T^\circ_{\mathrm{fus,v}}$ versus $V^{1/2}$ to the zero rate of the calorimeter heating $V^{1/2} = 0$, this dependence being the straight line. The procedure of $T^\circ_{\mathrm{fus,v}}$ determination we used is described in detail elsewhere [8]. The enthalpy of fusion $\Delta_{\mathrm{fus}}H^\circ$ of DMU was found as the average of three values of the enthalpy (Table 3). The entropy of fusion $\Delta_{\mathrm{fus}}S^\circ$ was evaluated from the melting temperature T°_{fus} and the $\Delta_{\mathrm{fus}}H^\circ$ values by the expression:

$$\Delta_{\mathrm{fus}}S^\circ = \frac{\Delta_{\mathrm{fus}}H^\circ}{T^\circ_{\mathrm{fus}}} \quad (1)$$

Table 2
Experimental values of heat capacity of partially crystalline poly(dimethylene urethane); $M = 87.08$ g/mol; $p = 101.325$ kPa

T (K)	C_p° (J/(mol K))	T (K)	C_p° (J/(mol K))	T (K)	C_p° (J/(mol K))	T (K)	C_p° (J/(mol K))
Series 1							
326.1	136.0	367.9	201.4	412.8	200.0	454.7	246.9
327.5	136.8	371.8	206.5	414.6	200.4	456.6	259.0
328.9	137.3	374.8	207.3	416.3	201.3	458.4	274.1
330.2	137.6	376.7	207.4	418.1	202.5	460.3	297.9
331.7	138.2	378.7	207.5	419.8	204.0	462.1	344.4
333.1	138.8	380.6	207.6	421.6	205.5	463.9	451.2
335.0	140.3	382.5	207.5	423.4	207.0	465.6	675.7
336.2	140.4	384.4	207.5	425.2	209.0	467.2	983.7
337.8	141.4	386.3	207.5	426.9	210.2	468.7	1250
339.5	142.6	388.1	207.5	428.7	212.1	470.2	1384
341.2	144.3	390.0	207.5	430.6	213.6	471.7	1453
343.0	146.4	391.8	206.4	432.4	215.1	473.1	2096
344.8	150.4	393.6	205.0	434.2	217.2	474.6	1175
346.7	153.9	395.3	203.5	436.0	219.2	476.5	747.3
348.6	157.4	397.1	202.3	437.9	221.3	478.4	793.5
350.5	161.4	398.9	201.1	439.7	223.0	480.4	724.1
352.5	165.4	400.6	200.6	441.6	225.4	482.4	497.8
354.5	171.1	402.4	200.0	443.4	227.7	484.4	286.7
356.5	174.9	404.1	199.8	445.7	230.0	486.6	173.8
358.5	178.4	406.0	199.6	447.2	232.6	488.7	159.4
360.5	183.5	407.6	199.6	449.0	234.9		
362.6	188.5	409.3	199.6	451.1	237.5		
364.6	193.6	411.1	199.8	452.4	240.0		

Using the values of the thermodynamic quantities of fusion for DMU (Table 3), it is possible to calculate the first A (K^{-1}) and the second B (K^{-1}) cryoscopic constants by equations:

$$A = \frac{\Delta_{\text{fus}}H^\circ}{R(T_{\text{fus}}^\circ)^2} = 0.0161 \pm 0.0002 \qquad (2)$$

$$B = (T_{\text{fus}}^\circ)^{-1} - \frac{1}{2}\frac{\Delta C_p^\circ(T_{\text{fus}}^\circ)}{\Delta H_{\text{fus}}^\circ} = 0.0023 \pm 0.0001 \qquad (3)$$

$\Delta C_p^\circ(T_{\text{fus}}^\circ) = 17.4$ J/(mol K), the increase in the heat capacity on melting DMU (CE section, Fig. 1), was found graphically by the extrapolation of the normal trend of the relation C_p° versus T for the DMU sample in solid and liquid states to the temperature of phase transition T_{fus}° (EC section, Fig. 1).

From the experimental data for PDMU, the beginning of the melting interval (410 K, point F, Fig. 3) and the melting temperature $T_{\text{fus}}^\circ = 473.1$ K were determined, and the temperature corresponding to the maximum value of the apparent heat capacity, $C_{p,\max}^\circ = 2096$ J/(mol K), in the melting range was regarded as T_{fus}°. The normal value of the heat capacity at this temperature was $C_p^\circ = 204.2$ J/(mol K) (point K, Fig. 3). Because of the polymer decomposition being initiated, it is impossible, however, to determine the temperature of the fusion end.

3.2.2. Characteristics of devitrification and glassy state

The devitrification of the amorphous part of PDMU occured in the 335–375 K range. Table 4 shows its thermodynamic characteristics. Temperatures of the onset and end of the devitrification ($T_{\text{g,i}}^\circ$, $T_{\text{g,f}}^\circ$,) were found graphically (Fig. 3). Temperatures, when the character of the relation C_p° versus T changes, were taken as $T_{\text{g,i}}^\circ$ and $T_{\text{g,f}}^\circ$ (points B and E, Fig. 3). The devitrification temperature T_{g}° and an increase in the heat capacity on devitrification $\Delta C_p^\circ(T_{\text{g}}^\circ)$ (CD section, Fig. 3) were determined graphically by the method demonstrated in detail in reference [9]. The configurational entropy S_{conf}° was calculated by the procedure given in [10] using the expression:

$$S_{\text{conf}}^\circ(\alpha) = \Delta C_p^\circ(T_{\text{g}}^\circ, \alpha) \ln 1.29 \qquad (4)$$

Table 3
Experimental and mean values of thermodynamic characteristics[a] of fusion of dimethylene urethane; $M = 87.08$ g/mol; $p = 101.325$ kPa

Experiment	V (K/s)	$T_{\text{fus,i}}^\circ - T_{\text{fus,f}}^\circ$ (K)	$T_{\text{fus,v}}^\circ$ (±0.5) (K)	$C_{p,\max}^\circ$ (J/(mol K))	$\Delta_{\text{fus}}H^\circ$ (kJ/mol)	$\Delta_{\text{fus}}S^\text{o}$ (±2) (J/(mol K))
1	0.033	340−370	360.4	2320	18.3 ± 0.9	50
2	0.017	348−370	360.5	4230	16.2 ± 0.8	45
3	0.008	348−364	359.1	4920	17.4 ± 0.7	48
Mean	–	–	360.0	–	17.3 ± 0.8	48

[a] V is the average rate of heating of calorimeter and substance; $T_{\text{fus,i}}^\circ$ and $T_{\text{fus,f}}^\circ$ the temperatures of the onset and end of fusion; $T_{\text{fus,v}}^\circ$ the temperatures at which the apparent heat capacity in the melting interval are maximum at the appropriate rate of heating; $\Delta_{\text{fus}}H^\circ$ the molar enthalpy of fusion.

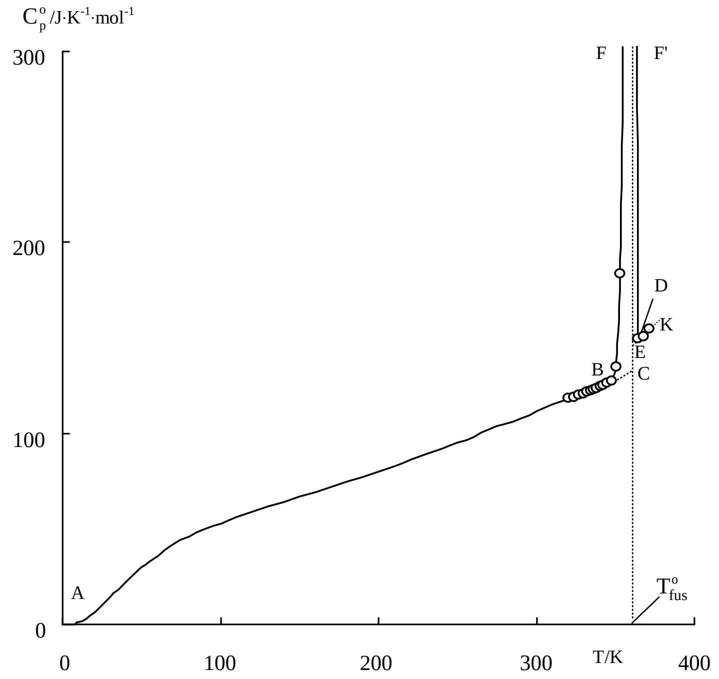


Fig. 1. Temperature dependence of heat capacity of dimethylene urethane; ABC: crystal; BFF′D: the apparent heat capacity in the melting interval; EDK: liquid.

It should be noted that the configurational entropy was evaluated only for the poly(dimethylene urethane) sample with the crystallinity degree $\alpha = 33\%$.

The evaluation of the crystallinity degree $\alpha = 33\%$ was made by the procedure described in detail elsewhere [11] by the equation:

$$\alpha(\%) = \left[1 - \frac{\Delta C^\circ_p(\alpha)}{\Delta C^\circ_p(\alpha = 0)}\right] \times 100 \qquad (5)$$

Table 4

Characteristics of devitrification and glassy state[a] of poly(dimethylene urethane); $M = 87.08$ g/mol; $p = 101.325$ kPa

$T^\circ_{g,i} - T^\circ_{g,f}$ (K)	T°_g (K)	$\Delta C^\circ_p(T^\circ_g), \alpha$ (J/(mol K))	$S^\circ_{conf}(\alpha)$ (J/(mol K))
335–375	356 ± 1	56	14

[a] $T^\circ_{g,i} - T^\circ_{g,f}$ is the temperatures of onset and end of devitrification; T°_g the temperature of devitrification; $S^\circ_{conf}(\alpha)$ the configuration entropy; $\Delta C^\circ_p(T^\circ_g), \alpha$ the increase of heat capacity on devitrification.

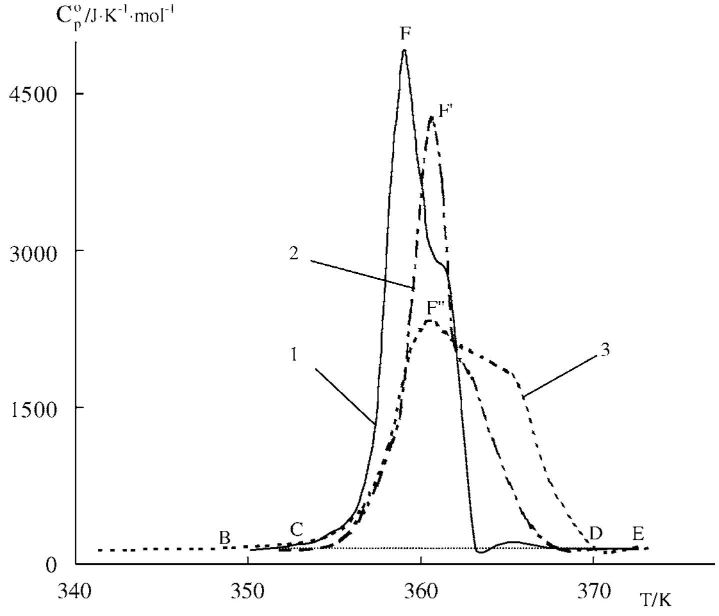


Fig. 2. Temperature dependence of heat capacity of dimethylene urethane in the melting interval at three different rates of heating of calorimeter and substance: (1) 0.008 K/s; (2) 0.017 K/s and (3) 0.033 K/s; BC: crystal; DE: liquid; CFD, CF′D, CF″D: apparent heat capacities in the melting interval.

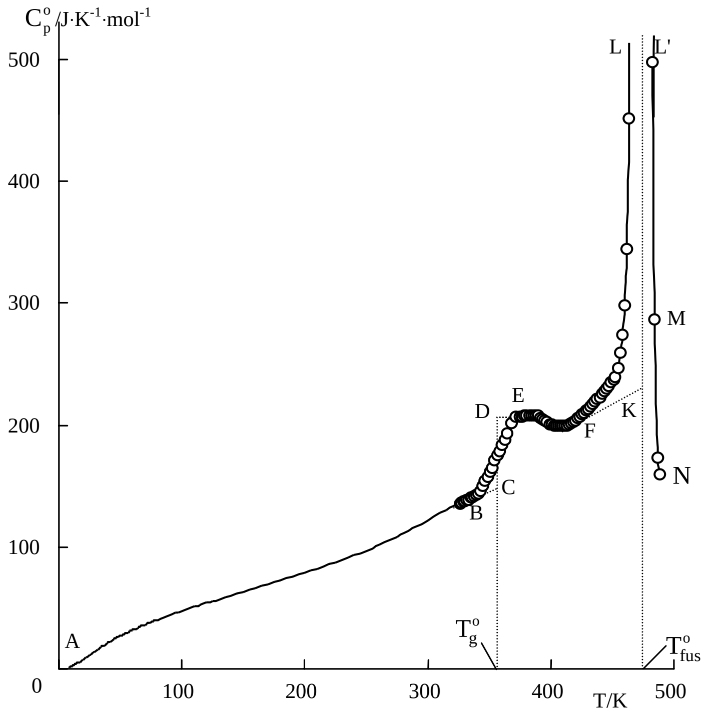


Fig. 3. Temperature dependence of heat capacity of partially crystalline ($\alpha = 33\%$) poly(dimethylene urethane); ABC: amorphous part in glassy state; DEFK: amorphous part in high-elasticity state; BE: heat capacity in the interval of devitrification; CD: increase in heat capacity on devitrification of amorphous part; FLL'M: apparent heat capacity in the melting interval of crystalline part; MN: onset of thermal decomposition of the polymer.

where $\Delta C_p^\circ(\alpha)$ is the increase in the heat capacity on devitrification of an amorphous part of PDMU (CD section, Fig. 3) and $\Delta C_p^\circ(\alpha = 0)$ is the increase in the heat capacity on devitrification of completely amorphous PDMU. The value $\Delta C_p^\circ(\alpha = 0) = 83$ J/(mol K) was calculated by the expression describing the relation between the increase in the heat capacity ΔC_p° on devitrification of completely amorphous poly(urethanes) and the number of methylene groups *m*. The proper data needed in calculations were taken from [12].

Table 5
Thermodynamic functions of dimethylene urethane; $M = 87.08$ g/mol; $p = 101.325$ kPa

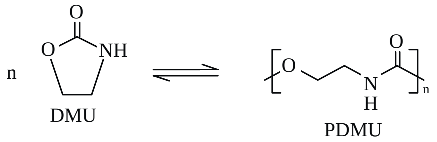
T (K)	C_p° (T) (J/(mol K))	$H^\circ(T) - H^\circ(0)$ (kJ/mol)	$S^\circ(T)$ (J/(mol K))	$-[G^\circ(T) - H^\circ(0)]$ (kJ/mol)
Crystalline state				
0	0	0	0	0
5	0.0993	0.0001	0.0331	0.00004
10	0.7920	0.00200	0.2666	0.00065
15	2.642	0.01000	0.8925	0.00340
20	5.683	0.0304	2.040	0.0104
25	9.521	0.0680	3.706	0.0246
30	13.61	0.1258	5.801	0.0482
50	29.93	0.5671	16.72	0.2688
100	53.21	2.725	45.70	1.845
150	66.76	5.736	69.94	4.755
200	80.20	9.402	90.94	8.785
250	95.02	13.78	110.4	13.82
298.15	110.9	18.73	128.5	19.58
300	111.5	18.94	129.2	19.81
320	118.1	21.23	136.6	22.47
330	121.3	22.43	140.3	23.86
340	124.6	23.66	143.9	25.28
350	128.5	24.92	147.6	26.73
360	130.8	26.22	151.3	28.23
Liquid state				
360	148.2	43.52	199.3	28.23
370	151.4	45.02	203.4	30.24
372	152.7	45.33	204.2	30.65

3.3. Thermodynamic functions

From the experimental data on the temperature dependence of the heat capacity, measured by us and cited in reference [4], the thermodynamic functions of the monomer between $T \rightarrow 0$ and 372 K and the polymer in the range from $T \rightarrow 0$ to 484.4 K were calculated (Tables 5 and 6). For DMU, the appropriate thermodynamic characteristics of fusion were taken into account in the calculation. On calculating the absolute values of entropies for PDMU, as demonstrated in [13], it was assumed that its $S^\circ(0) = S^\circ_{\mathrm{conf}}(0)$. In the case of PDMU, all calculations were made per mole of a repeating monomer unit for the sample of the crystallinity degree $\alpha = 33\%$. The enthalpy $H^\circ(T) - H^\circ(0)$ and entropy $S^\circ(T)$ were estimated by the numerical integration and the Gibbs function $G^\circ(T) - H^\circ(0)$ was calculated from the values of $H^\circ(T) - H^\circ(0)$ and $S^\circ(T)$ at the corresponding temperatures, as shown, for example, in [12].

3.4. Thermodynamic characteristics of DMU polymerization

The reaction of DMU polymerization with five-membered cycle opening with the formation of linear partially crystalline ($\alpha = 33\%$) PDMU proceeds according to the scheme:



The enthalpy $\Delta_{\mathrm{pol}}H^\circ$ and entropy $\Delta_{\mathrm{pol}}S^\circ$ of DMU polymerization over the range from $T \rightarrow 0$ to 330 K were estimated earlier [4]. Because of the experimental data deficiency, while calculating $\Delta_{\mathrm{pol}}S^\circ$ in [4] an approximate value of $S^\circ(0)$ was taken. In the present work, the enthalpy of polymerization $\Delta_{\mathrm{pol}}H^\circ$ at other temperatures was evaluated by Kirchhoff's formula, the entropy of polymerization $\Delta_{\mathrm{pol}}S^\circ$ was calculated from the absolute values of entropies of reagents (Tables 5 and 6) and the Gibbs function $\Delta_{\mathrm{pol}}G^\circ$, from the values of $\Delta_{\mathrm{pol}}H^\circ$ and $\Delta_{\mathrm{pol}}S^\circ$ at the corresponding temperatures. To calculate $\Delta_{\mathrm{pol}}S^\circ$, the value $S^\circ(0) = 14$ J/(mol K) derived in this work was used. The thermodynamic characteristics of polymerization, estimated by the procedure described in detail earlier [14], are listed in Table 7.

The limiting temperature of polymerization, calculated by Dainton's method, is $T^\circ_{\mathrm{ceil}} > 500$ K and it is higher than that

Table 6
Thermodynamics functions of partially crystalline ($\alpha = 33\%$) of poly(dimethylene urethane); $M = 87.08$ g/mol; $p = 101.325$ kPa

T (K)	C°_p (T) (J/(mol K))	$H^\circ(T) - H^\circ(0)$ (kJ/mol)	S° (T) (J/(mol K))	$-[G^\circ(T) - H^\circ(0)]$ (kJ/mol)
Glass state				
5	0.232	0.00030	14.1	0.0701
10	1.720	0.00460	14.6	0.142
15	4.340	0.0194	15.8	0.217
20	7.660	0.0493	17.5	0.300
30	14.72	0.1610	21.9	0.496
40	21.18	0.3412	27.1	0.741
50	26.83	0.5827	32.4	1.04
100	47.50	2.480	57.9	3.31
150	63.38	5.260	80.2	6.78
200	79.07	8.820	101	11.3
250	97.03	13.20	120	16.8
298.15	120.8	18.43	139	23.1
300	121.8	18.65	140	23.3
350	147.0	25.41	161	30.8
356	149.8	26.30	163	31.8
High elasticity state				
356	205.8	26.30	163	31.8
360	206.0	27.12	166	32.5
370	206.2	29.19	171	34.1
380	206.5	31.25	177	35.9
390	206.5	33.32	182	37.7
400	201.2	35.35	187	39.5
410	200.3	37.38	192	41.4
420	201.0	39.39	197	43.4
430	201.6	41.40	202	45.4
440	202.1	43.42	206	47.4
450	202.9	45.44	211	49.5
460	203.5	47.48	215	51.6
470	204.1	49.51	220	53.8
480	204.8	51.56	224	56.0
484.4	205.0	52.46	226	57.0

Table 7
Thermodynamic characteristics of bulk polymerization of dimethylene urethane to partially crystalline ($\alpha = 33\%$) poly(dimethylene urethane) at $p = 101.325$ kPa

T (K)	Physical state of monomer and polymer[a]	$-\Delta_{\mathrm{pol}}H^\circ$ (kJ/mol)	$-\Delta_{\mathrm{pol}}S^\circ$ (J/(mol K))	$-\Delta_{\mathrm{pol}}G^\circ$ (kJ/mol)
298.15	cr; p.cr	1.7[b]	−11	4.9
330	cr; p.cr	1.3[b]	−12	5.3
350	cr; p.cr	0.9	−13	5.5
370	l; p.cr	17.2	32	5.4

[a] cr: crystalline; l: liquid; p.cr: partially crystalline.
[b] Data of reference [4].

of the beginning of the thermal decomposition of PDMU [15].

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References

[1] B.V. Lebedev, N.N. Smirnova, E.G. Kiparisova, Macromol. Chem. Phys. 198 (1997) 41.

[2] B.V. Lebedev, N.N. Smirnova, V.L. Telnoy, Macromol. Chem. Phys. 197 (1996) 3807.

[3] B.V. Lebedev, T.A. Bykova, E.G. Kiparisova, A.M. Kochetkov, H. Hocker, J. Kusan, H. Keul, Macromol. Chem. Phys. 200 (1999) 1863.

[4] B.V. Lebedev, T.G. Kulagina, N.N. Smirnova, V.V. Veridusova, J. Kusan, H. Keul, H. Hocker, Macromol. Chem. Phys. 201 (2000) 2469.

[5] B.V. Lebedev, V.V. Veridusova, H. Hocker, H. Keul, Macromol. Chem. Phys. 203 (2002) 1114.

[6] M.Sh. Yagfarov, Zh. Fiz. Khimii 43 (1969) 1620.

[7] A.G. Kabo, V.V. Diky, Thermochim. Acta 347 (2000) 79.

[8] V.A. Bershetein, V.M. Egorov, Differential Scanning Calorimetry in Physicochemistry of Polymers, Khimiya, Leningrad, 1990.

[9] S. Alford, M. Dole, J. Am. Chem. Soc. 77 (1955) 4774.

[10] A.B. Bestul, S.S. Chang, J. Chem. Phys. 40 (1964) 3731.

[11] B.V. Lebedev, Thermochim. Acta 297 (1997) 143.

[12] B.V. Lebedev, N.N. Smirnova, T.G. Kulagina, A.V. Markin, T.A. Bykova, L.Y. Tsvetkova, Polymer Processing Society, Asia/Australia Meeting, Taipei, Taiwan, 2002, p. 201 (Abstract).

[13] B.V. Lebedev, I.B. Rabinovich, Dokl. Acad. Nauk SSSR 237 (1997) 641.

[14] B.V. Lebedev, N.N. Smirnova, Macromol. Chem. Phys. 195 (1994) 35.

[15] F.S. Dainton, K.J. Ivin, Q. Rev. (London) 12 (1958) 61.