# Thermodynamics of semi-interpenetrating polymeric networks based on crosslinked poly(cyanurate) and linear poly(urethane) in the temperature region from $T \to 0$ to 350 K

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The temperature dependences of the heat capacity of linear poly(urethane) (PU) ($M_n = 4 \cdot 10^4$), which was synthesized from 4,4′-diphenylmethane diisocyanate, oligo(butylene glycol adipinate) ($M_n = 1000$), and chain-elongating agent butane-1,4-diol, and three samples of related semi-interpenetrating polymeric networks containing 25, 50, and 75 wt.% of crosslinked poly(bisphenol A) cyanurate were studied in a region of 6—350 K by adiabatic vacuum calorimetry. Their combustion energies were determined in a calorimeter with a static bomb and an isothermic shell. The thermodynamic functions of the compounds under study for the temperature region from $T \to 0$ to 350 K, enthalpies of combustion, and thermodynamic characteristics of formation from simple substances at $T = 298.15$ K and $p = 0.1$ mPa were calculated. The thermodynamic parameters of formation of the semi-interpenetrating networks were calculated. The dependences of the isotherms of the thermodynamic properties and thermodynamic compatibility of the semi-interpenetrating networks on their composition were determined.

**Key words:** semi-interpenetrating polymeric networks, calorimetry, heat capacity, thermodynamic functions, enthalpies of formation.

Semi-interpenetrating polymeric networks (semi-IPNs) of poly(cyanurate)—poly(urethane) are characterized by high thermal and strength parameters due to the presence in their composition of poly(cyanurate) (PC) and poly(urethane) (PU) providing enhanced resistance to impact.[1] These networks were widely studied by IR spectroscopy,[1—3] X-ray diffraction,[4—8] calorimetry,[3,5—8] electron microscopy,[4] dielectric relaxation,[9—11] and other methods.[12—14] The thermodynamic properties of poly(cyanurate)—poly(urethane) completely interpenetrating networks consisting of two networks have been studied earlier,[15] and no methods of precision calorimetry have been applied to semi-IPNs so far. Meanwhile, thermodynamic data would reveal thermodynamic compatibility of the components of the semi-IPNs and dependences of the thermodynamic properties on the composition of the networks, their physical states, and temperature under standard pressure.

The purpose of the present work is to determine the concentration regions of thermodynamic compatibility of the components in the poly(cyanurate)—poly(urethane) semi-IPNs from the precision calorimetric data. Therefore, we carried out precision calorimetric studies of the thermodynamic properties of linear PU (LPU) (**1**) and the related three samples of semi-IPNs containing 25, 50, and 75 wt.% of crosslinked PC (samples **2**, **3**, and **4**, respectively) in an interval of 6—350 K. In other words, the temperature dependence of the heat capacity was studied, the temperatures of physical transformations and the combustion energy were determined, the thermodynamic functions for the temperature region from $T \to 0$ to 350 K and standard thermodynamic characteristics of formation of compounds **1—4** from simple substances at 298.15 K were calculated from the data obtained, and the thermodynamic characteristics of processes of preparation of samples **2—4** by polycyclotrimerization of bisphenol A dicyanate ester (BADCE) in the presence of LPU were calculated for the temperature region from $T \to 0$ to 350 K.

## Experimental

Samples of LPU and semi-IPNs were prepared at the Institute of Chemistry of High-Molecular-Weight Compounds (National Academy of Sciences of Ukraine, Kiev, Ukraine); LPU (Vitur-T261) was synthesized from oligo(butylene glycol

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**Table 1.** Characteristics of LPU and semi-IPN samples

| Sample | Content of crosslinked PC in semi-IPN (wt.%) | Molecular weight of repeating unit | C, $\frac{\text{Found*}}{\text{Calculated}}$ (%) | Molecular formula |
|---|---|---|---|---|
| **1** | 0 | 2526.75 | $\frac{58.50}{58.44}$ | $C_{123}H_{176}N_4O_{51}$ |
| **2** | 25 | 1676.97 | $\frac{62.90}{62.20}$ | $C_{86.84}H_{108.7}N_5O_{28.40}$ |
| **3** | 50 | 1255.05 | $\frac{66.01}{65.92}$ | $C_{68.88}H_{75.28}N_{5.50}O_{17.18}$ |
| **4** | 75 | 1002.60 | $\frac{70.01}{69.65}$ | $C_{58.14}H_{55.29}N_8O_{10.46}$ |

* Found in experiments on combustion.

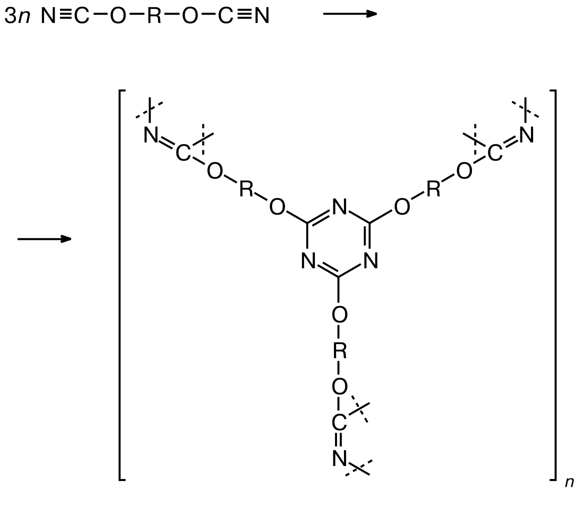
adipinate), 4,4′-diphenylmethane diisocyanate, and butane-1,4-diol.

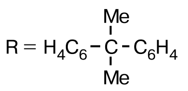
$[RNHC_6H_4CH_2C_6H_4NHCOO(CH_2)_4OCONHC_6H_4CH_2C_6H_4NHCOO\text{-}]_n$

LPU

$R = [\text{-}O(CH_2)_4OCO(CH_2)_4OCO\text{-}]_9$

Samples **2**, **3**, and **4** were prepared according to a standard procedure.[5] The polycyclotrimerization of BADCE produces crosslinked PC, whose network contains triazine rings in the nodes.[6,16]





$$R = H_4C_6\text{-}\underset{Me}{\overset{Me}{C}}\text{-}C_6H_4$$

All samples were characterized by data of IR spectroscopy, elemental analysis, and other methods.[1—14] Selected characteristics of the substances under study are given in Table 1.

To study the temperature dependence of the heat capacity and to determine the temperatures of physical transformations in a region of 6—350 K, we used an automated BKT-3 adiabatic vacuum calorimeter.[17] Its measurement error for the heat capacities of substances at 6—15 K is ±2%, when the temperature increases to 40 K it is ±0.5%, and in a region of 40—350 K the error is ±0.2%. The main experimental details on measuring the heat capacities of LPU and semi-IPNs are presented in Table 2.

**Table 2.** Selected experimental details on measuring the heat capacity

| Sample | $m^a$/g | $T^b$/K | $N^c$ |
|---|---|---|---|
| **1** | 0.4129 | 6.5—349.5 | 148 |
| **2** | 0.4470 | 6.2—350 | 120 |
| **3** | 0.4142 | 6.8—349.9 | 140 |
| **4** | 0.5311 | 6.0—349.7 | 199 |

[a] Weight of a sample placed into a calorimetric ampule.

[b] Temperature region of measuring the heat capacity.

[c] Number of experimental points.

The heat capacity ($C_p°$) of an LPU sample was 50—35% of the total $C_p°$ of the calorimeter with the substance, and the $C_p°$ values of all the semi-IPNs ranged from 45 to 25%. In all cases, these ratios decreased with the temperature increase. The experimental $C_p°$ values were averaged on a computer. The root-mean square deviation of $C_p°$ from the corresponding smoothened curves $C_p° = f(T)$ for LPU and semi-IPNs in an interval of 7—100 K was ±0.20%, and that in the region from 100 to 340 K was ±0.06%.

The energies of combustion of LPU and semi-IPNs were measured in a V-08 modernized calorimeter with an isothermal shell and a static bomb.[18,19] The combustion of succinic acid, which was synthesized at the D. I. Mendeleev Research Institute of Metrology (St. Petersburg, Russia), gave the standard enthalpy of combustion of the acid coinciding with the passport value (error 0.017%). The energies of combustion of LPU and semi-IPNs were determined under calorimetric-bomb conditions at 298.15 K (Table 3). The combustion was complete in all cases. Usual thermochemical corrections were introduced when calculating $\Delta_c\bar{U}$. The $\Delta_c\bar{U}$ and $\Delta_cU°$ values are given with the double root-mean-square error calculated by the formula

$$\delta = 2[\Sigma x^2/n(n-1)]^{1/2}, \quad (1)$$

where $x$ is the deviation of each value from the average value, and $n$ is the number of entries.

**Table 3.** Data of experiments on the combustion of LPU and semi-IPNs at $T = 298.15$ K

| Sample | Number of entries | $m$/g | $-Q$/J | $(m_{\text{exp}}/m_{\text{calc}}) \cdot 100$ (%) | $-\Delta_c\bar{U}$ | $-\Delta_c U^\circ$ |
|---|---|---|---|---|---|---|
| | | | | | kJ mol$^{-1}$ | |
| **1** | 6 | 0.2051—0.2603 | 13452.0—16367.8 | 100.2—100.8 | 68429.7±12.5 | 68388.7±12.5 |
| **2** | 7 | 0.3626—0.4293 | 17054.4—21192.8 | 100.1—100.9 | 47128.2±44.9 | 47095.1±44.9 |
| **3** | 5 | 0.2050—0.2632 | 15170.5—16988.3 | 99.80—100.8 | 36692.0±27.6 | 36669.8±27.6 |
| **4** | 6 | 0.3661—0.4264 | 18434.2—18982.8 | 99.62—99.73 | 30142.4±15.9 | 30121.0±15.9 |

*Note.* $Q$ is the total amount of energy evolved upon combustion of substances in experiments; $\Delta_c\bar{U}$ and $\Delta_c U^\circ$ are the molar energies of combustion under the calorimetric-bomb conditions at $p = 30$ and 1 atm, respectively; $m_{\text{exp}}/m_{\text{calc}}$ is the ratio of the weight of $CO_2$ found in the combustion products to the weight calculated from the chemical formula of the compound.

The reaction of LPU combustion is given as an example:

$$C_{123}H_{176}N_4O_{51}\,(\text{h.e}) + 141.5\,O_2\,(\text{g}) = 123\,CO_2\,(\text{g}) + 88\,H_2O\,(\text{liq}) + 2\,N_2\,(\text{g}). \quad (2)$$

Physical states of the reactants are presented in parentheses: h.e is highly elastic, g is gaseous, and liq is liquid.

## Results and Discussion

**Heat capacity.** The temperature plots of $C_p{}^\circ$ for LPU, semi-IPNs, and PC are given in Fig. 1. The heat capacity of LPU (see Fig. 1, curve *1*) increases smoothly with the temperature increase in an interval of 6—230 K. Then it increases sharply due to the beginning devitrification process that occurs in an interval of 230—270 K. The $C_p{}^\circ$ values for samples **2** and **3** increase smoothly with the temperature increase (see Fig. 1, curves *2* and *3*), and then the devitrification of these samples occurs in intervals of 250—310 K and 280—320 K, respectively. No devitrification was observed for sample **4** (see Fig. 1, curve *4*), and its heat capacity increases smoothly with the temperature increase in the whole region under study. As for the poly(cyanurate)—poly(urethane) IPNs,[15,20] $C_p{}^\circ$ depends proportionally on $T$ in the temperature interval from 60 K to the temperature of devitrification onset. The heat capacities of the semi-IPN samples increase in the following order of samples: **4**, **3**, **2** (see Fig. 1, curves *2—4*). An increase in the PC content in the semi-IPNs, as for the fully IPNs,[15] favors, most likely, an enhancement of rigidity of the vibrating framework, resulting in the observed changes: a decrease in $C_p{}^\circ$ at the same temperature. The earlier obtained[16] temperature plot of the heat capacity of PC is also presented in Fig. 1 (curve *5*).

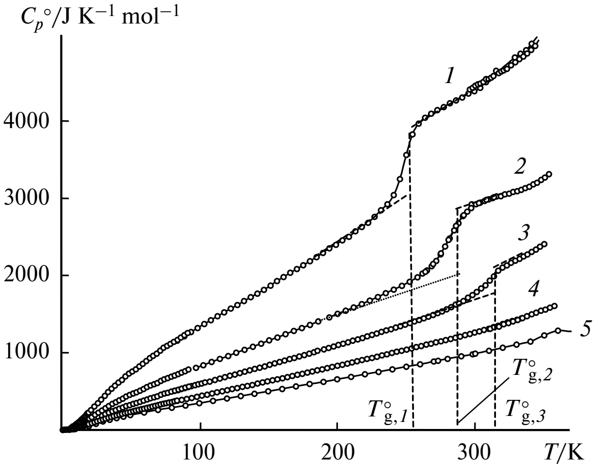


**Fig. 1.** Temperature plots of the heat capacity of samples **1** (*1*), **2** (*2*), **3** (*3*), and **4** (*4*) and PC (*5*)[16]; $T_g{}^\circ$ are glass transition temperatures.

**Glass transition parameters.** The glass transition parameters for LPU and semi-IPNs obtained by our calorimetric data are given in Table 4.

The glass transition temperatures $T_g{}^\circ$ were determined using an earlier described method[21] from the inflection point in the temperature plot of the entropy $S^\circ(T) = f(T)$ in the glass transition interval. The error of determination of $T_g{}^\circ$ by this method usually does not exceed 0.5—1.0 K. An increase in the heat capacity upon devitrification was determined graphically by the extrapolation of the normal run of the heat capacity of the samples under study in the highly elastic and glassy states below $T_g{}^\circ$. The configurational entropy was estimated by the equation[22] $S^\circ_{\text{conf}} = \Delta C_p{}^\circ \ln(1.29\pm0.14)$. The $S^\circ_{\text{conf}}$ value was found[23] to be close to the zero entropy $S^\circ(0)$ of the glassy polymers. That is why we accepted $S^\circ_{\text{conf}} = S^\circ(0)$ and used for the estimation of the absolute entropies of LPU and semi-IPNs in the amorphous state during calculation of

**Table 4.** Parameters of glass transitions of LPU and the semi-IPNs

| Sample | $T_g{}^{\circ\,a}$ /K | $\Delta C_p{}^{\circ\,b}(T_g{}^\circ)$ | $S^\circ{}_{\text{conf}}{}^c$ |
|---|---|---|---|
| | | J K$^{-1}$ mol$^{-1}$ | |
| **1** | 248 | 1032 | 263 |
| **2** | 280 | 717 | 183 |
| **3** | 306 | 303 | 77 |

[a] Glass transition temperature.
[b] Increase in the heat capacity upon devitrification.
[c] Configurational entropy.

the thermodynamic parameters of preparation of the semi-IPNs.

**Thermodynamic functions.** The values of heat capacity $C_p{}^\circ$, enthalpy $H^\circ(T) - H^\circ(0)$, entropy $S^\circ(T) - S^\circ(0)$, and Gibbs function $G^\circ(T) - H^\circ(0)$ for the LPU and semi-IPNs under study are given in Table 5. To calculate the thermodynamic functions, the $C_p{}^\circ$ values were extrapolated from $T = 7$—9 K (lower limit of measurements of $C_p{}^\circ$) to 0 K from the heat capacity Debye function

$$C_p{}^\circ = nD(\theta_D/T), \tag{3}$$

using specially selected parameters $n$ and $\theta_D$. The $n$ and $\theta_D$ parameters are presented in Table 6.

When calculating the thermodynamic functions, we accepted that Eq. (3) reproduces the $C_p{}^\circ$ with the same error in the temperature interval from 0 to (7—9) K. The enthalpy and entropy were determined by the numerical integration of the dependences of $C_p{}^\circ$ on $T$ and $C_p{}^\circ$ on $\ln T$, and the Gibbs energy was calculated using the enthalpy and entropy at the corresponding temperatures. The procedure of calculation of the function is described, for instance, in Ref. 24. We believe that the error of the calculated functions is 1—2% at $T < 30$ K, 0.5% in the 30—80 K interval, and 0.2—0.3% in a range of 80—350 K.

**Standard enthalpies of combustion and thermodynamic characteristics of formation.** The enthalpies of combus-

**Table 5.** Thermodynamic functions of LPU and the semi-IPNs (based on one mole of repeating units, $p$ = 0.1 MPa)

| $T$/K | $C_p{}^\circ(T)$ | $S^\circ(T) - S^\circ(0)$ | $H^\circ(T) - H^\circ(0)$ | $-[G^\circ(T) - H^\circ(0)]$ |
|---|---|---|---|---|
| | J K$^{-1}$ mol$^{-1}$ | | kJ mol$^{-1}$ | |
| **Sample 1** | | | | |
| Glassy state | | | | |
| 5 | 9.19 | 3.07 | 0.011 | 0.00384 |
| 10 | 60.05 | 22.65 | 0.167 | 0.0593 |
| 15 | 139.8 | 61.12 | 0.655 | 0.2619 |
| 20 | 231.5 | 114.2 | 1.588 | 0.6963 |
| 25 | 323.5 | 175.7 | 2.975 | 1.417 |
| 30 | 417.1 | 242.9 | 4.826 | 2.461 |
| 40 | 594.3 | 387.9 | 9.908 | 5.609 |
| 50 | 738.7 | 536.5 | 16.59 | 10.23 |
| 100 | 1330 | 1244 | 69.34 | 55.04 |
| 150 | 1854 | 1882 | 149.0 | 133.4 |
| 200 | 2388 | 2490 | 255.3 | 242.8 |
| 248 | 2882 | 3056 | 381.9 | 376.0 |
| Highly elastic state | | | | |
| 248 | 3914 | 3056 | 381.9 | 376.0 |
| 250 | 3932 | 3087 | 389.7 | 382.1 |
| 298.15 | 4393 | 3818 | 589.8 | 548.6 |
| 300 | 4417 | 3846 | 598.0 | 555.7 |
| **Sample 2** | | | | |
| Glassy state | | | | |
| 5 | 6.99 | 2.342 | 0.009 | 0.00293 |
| 10 | 40.48 | 16.34 | 0.1197 | 0.04368 |
| 15 | 90.00 | 41.67 | 0.4399 | 0.1851 |
| 20 | 145.1 | 75.07 | 1.028 | 0.4731 |
| 25 | 202.4 | 113.6 | 1.896 | 0.9435 |
| 30 | 260.7 | 155.7 | 3.054 | 1.617 |
| 40 | 366.1 | 245.6 | 6.206 | 3.620 |
| 50 | 453.1 | 336.9 | 10.31 | 6.533 |
| 100 | 821.8 | 772.3 | 42.80 | 34.43 |
| 150 | 1154 | 1168 | 92.14 | 83.04 |
| 200 | 1500 | 1547 | 158.4 | 150.9 |
| 250 | 1868 | 1921 | 242.7 | 237.7 |
| 280 | 2092 | 2145 | 302.1 | 298.7 |
| Highly elastic state | | | | |
| 280 | 2809 | 2145 | 302.1 | 298.7 |
| 298.15 | 2915 | 2325 | 354.0 | 339.2 |
| 300 | 2925 | 2343 | 359.4 | 343.5 |
| 350 | 3216 | 2816 | 513.0 | 472.6 |
| **Sample 3** | | | | |
| Glassy state | | | | |
| 5 | 4.55 | 1.519 | 0.0061 | 0.002 |
| 10 | 29.78 | 11.32 | 0.084 | 0.029 |
| 15 | 66.52 | 30.26 | 0.3237 | 0.130 |
| 20 | 107.2 | 54.87 | 0.7561 | 0.341 |
| 25 | 148.7 | 83.24 | 1.396 | 0.685 |
| 30 | 189.2 | 113.9 | 2.241 | 1.177 |
| 40 | 264.1 | 179.0 | 4.519 | 2.640 |
| 50 | 324.8 | 244.6 | 7.471 | 4.759 |
| 100 | 594.7 | 556.9 | 30.78 | 24.91 |
| 150 | 839.0 | 843.8 | 66.57 | 59.99 |
| 200 | 1095 | 1120 | 114.9 | 109.1 |
| 250 | 1365 | 1393 | 176.3 | 171.9 |
| 298.15 | 1627 | 1656 | 248.4 | 245.3 |
| 300 | 1637 | 1666 | 251.4 | 248.4 |
| 306 | 1670 | 1699 | 261.3 | 258.5 |
| Highly elastic state | | | | |
| 306 | 1973 | 1699 | 261.3 | 258.5 |
| 350 | 2393 | 1991 | 357.3 | 339.6 |
| **Sample 4** | | | | |
| Glassy state | | | | |
| 5 | 3.28 | 1.097 | 0.004 | 0.001 |
| 10 | 21.25 | 8.094 | 0.060 | 0.022 |
| 15 | 47.55 | 21.63 | 0.2312 | 0.094 |
| 20 | 76.75 | 39.23 | 0.5406 | 0.2441 |
| 25 | 106.6 | 59.56 | 0.9991 | 0.4899 |
| 30 | 135.9 | 81.59 | 1.606 | 0.8423 |
| 40 | 190.3 | 128.4 | 3.245 | 1.891 |
| 50 | 234.8 | 175.8 | 5.375 | 3.412 |
| 100 | 437.1 | 403.2 | 22.37 | 17.95 |
| 150 | 631.8 | 617.2 | 49.09 | 43.49 |
| 200 | 830.2 | 825.8 | 85.58 | 79.58 |
| 250 | 1041 | 1034 | 132.3 | 126.1 |
| 298.15 | 1253 | 1235 | 187.5 | 180.7 |
| 300 | 1262 | 1242 | 189.8 | 183.0 |
| 350 | 1555 | 1458 | 259.8 | 250.4 |

**Table 6.** Results of selection of the $n$ and $\theta_D$ parameters for the calculation of $C_p°$ by Eq. (3)

| Sample | $n$ | $\theta_D$/K | $\Delta T$*/K | δ** (%) |
|---|---|---|---|---|
| **1** | 36 | 68.16 | 6—11 | 1.4 |
| **2** | 19 | 60.25 | 8—12 | 1.2 |
| **3** | 18 | 68.38 | 6—11 | 0.5 |
| **4** | 12 | 66.58 | 6—11 | 0.5 |

* Temperature interval for which the $n$ and $\theta_D$ parameters of Eq. (3) were selected.

** The error with which Eq. (3) describes the experimental $C_p°$ values with the selected $n$ and $\theta_D$ values in the temperature interval indicated.

tion $\Delta_c H°$ (Table 7) were calculated from the values of the energies of combustion $\Delta_c U°$ of the samples under standard pressure (see Table 3). The calculation procedure has been described in detail.[18] The standard enthalpies of formation $\Delta_f H°$ for the three semi-IPNs and LPU under study were calculated from $\Delta_c H°$ of compounds **1—4** and the enthalpies of formation of liquid water, gaseous carbon dioxide, and dinitrogen[25] at $T$ = 298.15 K and $p$ = 0.1 mPa. The entropies of formation $\Delta_f S°$ for samples **1—4** were calculated from the absolute values of their entropy $S°(T)$, which were obtained from their $S°(T) - S°(0)$ (see Table 5) and $S°(0)$ values accepted to be equal to the configurational entropies (see Table 4). For sample **4**, the entropy of formation was calculated ignoring $S°(0)$. The Gibbs functions of formation $\Delta_f G°$ of the LPU and semi-IPNs from simple substances at 298.15 K and standard pressure were calculated from $\Delta_f H°$ and $\Delta_f S°$ at 298.15 K.

All the values presented in Table 7 concern the processes of formation of compounds **1—4** from simple substances. The reaction of LPU formation is given below as an example.

$$123\ \mathrm{C\ (gr)} + 88\ \mathrm{H_2\ (g)} + 2\ \mathrm{N_2\ (g)} + 25.5\ \mathrm{O_2\ (g)} = \\ = \mathrm{C_{123}H_{176}N_4O_{51}\ (h.e)} \qquad (4)$$

gr is graphite

**Dependence of the thermodynamic properties on the composition of semi-IPNs.** Analysis of the thermodynamic functions (see Table 5) showed that they change linearly with a change in the composition of the semi-IPNs in the same physical state at the same temperature and under standard pressure. For example, for $C_p°$ at $T$ = 200 K for the semi-IPNs in the glassy state, this dependence is described by the equation

$$C_p°(200\ \mathrm{K}) = 2381.2 - 1726.1n, \qquad (5)$$

where $n$ is the mole fraction of PC in the semi-IPN. The heat capacity $C_p°$ (J K$^{-1}$ mol$^{-1}$) is based on a conditional mole of semi-IPN. Deviations of the experimental $C_p°$ values for the semi-IPNs and LPU under study from those calculated by Eq. (5) are ±0.5—1%.

Below we present the dependences of other thermodynamic functions of the semi-IPNs in the glassy state on the PC content in them expressed in molar fractions for $T$ = 298.15 K. Since at this temperature samples **1** and **2** exist in the highly elastic state and samples **3**, **4**, and **5** are glassy, the corresponding dependences were derived using the extrapolation of $C_p°$ values for **1** and **2**

$$H°(298.15) - H°(0) = 437.43 - 276.73n, \qquad (6)$$

$$S°(298.15) - S°(0) = 3702.6 - 2743.9n, \qquad (7)$$

$$-[G°(298.15) - H°(0)] = 427.96 - 272.48n, \qquad (8)$$

where $n$ is the number of mole fractions of PC in the semi-IPN composition. Deviations of the experimental values for the semi-IPNs from the corresponding straight lines for the enthalpy, entropy, and Gibbs function are at most 3.5, 1.7, and 4.6%, respectively. Equations (6)—(8) make it possible to calculate (with high accuracy) any thermodynamic function for glassy semi-IPNs of any composition in the temperature region from 60 to 300 K.

The plot of the standard enthalpy of combustion for the semi-IPN *vs.* mole fraction of PC in the semi-IPN composition based on a conditional mole of the glassy semi-IPNs at $T$ = 298.15 K is presented in Fig. 2. It can be seen that $\Delta_c H°$ increases linearly with an increase in

**Table 7.** Standard enthalpies of combustion ($\Delta_c H°$) and formation ($\Delta_f H°$), entropies ($\Delta_f S°$), and Gibbs functions ($\Delta_f G°$) of formation of LPU and the semi-IPNs ($T$ = 298.15 K)

| Sample | Molecular weight of repeating polymeric unit/g mol$^{-1}$ | $-\Delta_c H°$ | $-\Delta_f H°$ | $-\Delta_f S°$ /J K$^{-1}$ mol$^{-1}$ | $\Delta_f G°$ /kJ mol$^{-1}$ |
|---|---|---|---|---|---|
| | | kJ mol$^{-1}$ | | | |
| **1** | 2526.75 | 68429.3±12.5 | 5125.8±12.5 | 14022.0±8.4 | −946.5±2.9 |
| **2** | 1676.97 | 47121.0±44.8 | 2586.5±44.8 | 10524.9±5.2 | 551.5±9.8 |
| **3** | 1255.05 | 36688.2±27.6 | 1175.3±27.6 | 5767.9±3.7 | 544.3±13.1 |
| **4** | 1002.60 | 30135.3±15.9 | 645.3±15.9 | 4267.8±2.8 | 627.2±15.9 |
| PC[16] | 834.94 | 25819.5±22.5 | 251.0±22.5 | 3245.4±9.6 | 716.6±25.5 |

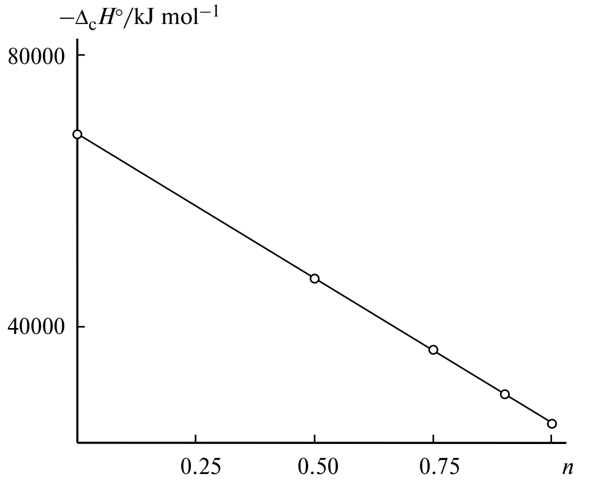


**Fig. 2.** Isotherm of the dependence of the standard enthalpies of combustion of the semi-IPNs on the mole fraction of crosslinked PC at $T = 200$ K for the samples in the glassy state.

the fraction of crosslinked PC in the semi-IPN. The dependence of $\Delta_cH°$ on $n$ is described by the equation

$$\Delta_cH° = -68442 + 42545n, \quad (9)$$

where $\Delta_cH°$ is expressed in kJ mol$^{-1}$, and $n$ is expressed in molar fractions of PC. Deviations of $\Delta_cH°$ of the semi-IPNs calculated by Eq. (9) from the experimentally measured values (see Table 7) do not exceed ±0.17%.

**Thermodynamic parameters of preparation of semi-interpenetrating polymeric networks of bisphenol A dicyanate ester and linear poly(urethane).** Semi-IPNs based on PC and LPU are formed by the polycyclotrimerization of BADCE in a medium of LPU. The quality of the network depends on the ratio of PC and LPU in the network of the semi-IPN. Calculations were performed for the process that can be presented by the following equation:

$$c\,\text{BADCE} + d\,\text{LPU} \rightarrow \text{PC—LPU}, \quad (10)$$

where $c$ and $d$ are the numbers of moles of BADCE and LPU, respectively, needed for the preparation of one conditional mole of PC—LPU. The enthalpy ($\Delta_rH°$), entropy ($\Delta_rS°$), and Gibbs function ($\Delta_rG°$) values for the synthesis of one mole of semi-IPNs **2—4** are given in Table 8 along with the mole ratios of the starting reactants that form in the reaction the corresponding conditional mole of a semi-IPN with the known composition. The enthalpies of the reactions at 298.15 K were calculated from the enthalpies of formation of the reactants (see Table 7) using published data for BADCE and PC,[16] and $\Delta_rH°$ for other temperatures were calculated by the Kirchhoff formula. The entropies of the reactions were determined from the entropies of the reactants (see Tables 4 and 5), BADCE, and PC.[16] The Gibbs functions of the reactions were calculated from the $\Delta_rH°$ and $\Delta_rS°$ values. For all the processes (see Table 8) in the temperature region under study, the $\Delta_rG°$ value is negative and its numerical values allow one to conclude about the thermodynamic stability of the semi-IPNs toward the starting components (BADCE and LPU). In this case, the semi-IPN (50 : 50, wt.) is the least thermodynamically unstable network toward PC and LPU.

**Table 8.** Thermodynamic characteristics* of formation of semi-IPNs **2—4** by reaction (10) based on one conditional mole of the semi-IPN; $p = 101.325$ kPa

| $T$/K | Physical state of reactant** | | | $-\Delta_rH°$ | $-\Delta_rG°$ | $-\Delta_rS°$ |
|---|---|---|---|---|---|---|
| | BADCE | LPU | semi-IPN | | | |
| | 1.5065 BADCE + 0.4978 LPU → **2** | | | | | |
| 100 | cr | gl | gl | 177 | 176 | 6.0 |
| 200 | cr | gl | gl | 183 | 186 | −12.0 |
| 298.15 | cr | h.e | h.e | 199 | 165 | 113 |
| 400*** | liq | h.e | h.e | 232 | 156 | 190 |
| | 2.2549 BADCE + 0.2484 LPU → **3** | | | | | |
| 100 | cr | gl | gl | 125 | 119 | 56.4 |
| 200 | cr | gl | gl | 131 | 111 | 101 |
| 298.15 | cr | h.e | gl | 148 | 99.1 | 162 |
| 400*** | liq | h.e | h.e | 201 | 78.7 | 307 |
| | 2.7024 BADCE + 0.0992 LPU → **4** | | | | | |
| 100 | cr | gl | gl | 403 | 342 | 608 |
| 200 | cr | gl | gl | 420 | 383 | 185 |
| 298.15 | cr | h.e | gl | 431 | 362 | 229 |
| 400*** | liq | h.e | gl | 509 | 306 | 507 |

* $\Delta_rH°$ and $\Delta_rG°$ in kJ mol$^{-1}$, $\Delta_rS°$ in J K$^{-1}$ mol$^{-1}$.

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

*** Obtained by extrapolation.

The standard Gibbs function of a process is determined by its enthalpy and entropy

$$\Delta_rG° = \Delta_rH° - T\Delta_rS°. \quad (11)$$

The enthalpy of formation of the semi-IPN for the completely occurring polycyclotrimerization process can be presented by the sum of two terms, namely, the enthalpy of polycyclotrimerization of BADCE ($\Delta H_1°$) and the enthalpy of interaction of the PC and LPU networks ($\Delta H_2°$): $\Delta_rH° = \Delta H_1° + \Delta H_2°$. Then

$$\Delta H_2° = \Delta_rH° - \Delta H_1°. \quad (12)$$

The thermodynamic parameters of BADCE polycyclotrimerization for the temperature region from 0 to 400 K have been calculated earlier[7] from the corresponding calorimetric data. For the reaction 3 BADCE (cr) → PC (gl) at 298.15 K, $\Delta H_1° = -576$ kJ mol$^{-1}$. Using Eq. (12) and taking into account the percent content of PC and LPU, we estimated $\Delta H_2°$ for the preparation of samples **2**, **3**, and **4** by the data in Table 7 and Ref. 7. At 298.15 K they were 92, 288, and 88 kJ mol$^{-1}$, respectively.

The estimation of $\Delta H_2°$ from Eq. (12) showed that polycyclotrimerization does not proceed completely. The estimated values of the enthalpy of interaction of LPU and PC (88—288 kJ mol$^{-1}$) are high for classical mixing of molecules. It is difficult to perform an unambiguous quantitative analysis of the interaction of molecules using the above values only. Possibly, the cyano groups in the systems considered are not completely involved in polycyclotrimerization. This agrees with the enthalpy values and model concepts of the interactions.[4]

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