Journal of Thermal Analysis, Vol. 54 (1998) 731-740

THERMODYNAMICS OF POLYVINYLACETATE FROM 0 TO 350 K

B. V. Lebedev and T. G. Kulagina

Chemsitry Institute, Nizhny Novgorod State University, Nizhny Novgorod, Russian Federation

(Received February 20, 1998)

Abstract

The temperature dependence of the heat capacity of vinyl acetate in the range 13 to 330 K and of polyvinylacetate between 4.9 and 330 K was determined by adiabatic vacuum calorimetry with an error of about 0.2%. Temperatures and enthalpies of physical transitions were measured. From the data obtained, the thermodynamic characteristics of melting of vinyl acetate and parameters of glass transition and glassy state of the monomer and polymer were calculated. The thermodynamic functions $H^{\circ}(T)-H^{\circ}(0)$, $S^{\circ}(T)$, $G^{\circ}(T)-H^{\circ}(0)$ were estimated for both materials from 0 to 350 K. The results of calculation and the literature value of enthalpy of bulk polymerization of vinyl acetate at T=350 K were used for the estimation of the thermodynamic parameters of its polymerization process $\Delta H^{\circ}_{\text{pol}}$, $\Delta S^{\circ}_{\text{pol}}$, $\Delta G^{\circ}_{\text{pol}}$ in the interval 0 to 350 K. A ceiling limiting temperature of polymerization T°_{ceil} was evaluated.

Keywords: enthalpy, entropy, Gibbs energy, heat capacity, limiting polymerization temperature, polyvinylacetate, temperature, thermodynamics of polymerization, vinyl acetate

Introduction

In spite of the wide practical application of vinyl acetate (VA) and polyvinylacetate (PVA), their thermodynamic properties and the parameters of the polymerization of VA have not been investigated in detail. In [1, 2] the temperature dependences of the heat capacity C_p° of the monomer and polymer were given only for the range from 60 to 330 K. It was established that PVA shows an anomaly in the temperature dependence of the heat capacity between 135 and 146 K, whose nature is not clear. Wunderlich *et al.* [3, 4] measured the C_p° values of PVA in the range 80 to 370 K. A plot of the temperature-dependent heat capacities of PVA over the range 80 to 400 K was shown elsewhere [5], but the polymer sample under study was not characterized. The standard enthalpy of formation of VA was calculated from data on the hydrogenation reaction of the monomer [6]. Joshi [7, 8] measured the enthalpy of the bulk polymerization of VA at T=350 K by direct calorimetry. No data are available on the relationship $C_p^{\circ}=f(T)$ for PVA and VA in crystalline and glassy states between 0 and 60 K. It is obvious that without these quantities one cannot make a precise estimation of the thermodynamic

1418–2874/98/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

functions of the monomer and polymer, particularly of the absolute magnitudes of their entropies which are essential in the calculation of the entropy of polymerization, Gibbs function and equilibrium monomer concentrations in a reaction mixture. The glass transition temperatures of PVA reported earlier [4, 5] differ by several degrees.

The goal of the present work was to obtain a complex of precise data on the properties of VA an PVA, viz. the heat capacity and thermodynamic characteristics of formation, the thermodynamic functions as well as thermodynamic parameters of the bulk polymerization of VA over the range 0 to 350 K. These data are necessary for the design of an expert-reference information system of the thermodynamic properties of polymers, monomers and polymerization processes on a personal computer the creation of which is supported by the grant of the Russian Foundation of Basic Research.

Experimental

The sample of VA was prepared from a commercial product used in the production of PVA; the main characteristics of the latter were described elsewhere [9]. It was additionally rectified under vacuum. As a result, on subsequent calorimetric determinations the total content of impurities in it was found to be $\chi_2 = 0.25\pm0.01$ mol%. The impurities were not identified. PVA was formed by the polymerization of a part of the monomer sample. The polymerization of the monomer was conducted in a sealed glass ampoule under the influence of 0.01 mol% of dicyclohexylperoxydicarbonate at 298 K. PVA was precipitated from the reaction mixture with thoroughly purified heptane and then it was twice dissolved in an equimolecular mixture of acetone and hexane with a further precipitation of the polymer with heptane. The polymer was dried under vacuum to constant mass at about 300 K. Elemental analysis indicated (mass%): C, 55.65; H, 7.39; O, 39.39; theoretical: C, 55.81; H, 7.01; O, 37.17. The viscosity-average molecular mass of PVA was determined to be $\overline{M}_v = 7.2\cdot10^5$ from the viscosity of solutions in acetone according to the procedure described earlier [10]. From X-ray analysis data (a Dron-3.0 device) the polymer sample is completely amorphous at room temperature.

Adiabatic vacuum calorimeters TAU-1 and UUNT were employed in the experiments. The calorimeter design and the operation were described elsewhere ([11] and [12], respectively). The reliability of the calorimeter operation was tested by measuring the C_p^o of standard corundum and benzoic acid as well as *n*-heptane. It was established that the apparatus and the procedure allow to obtain the C_p^o values of the substances in a condensed state with an uncertainty of about 1% at $T<25$ K and, mainly, 0.2% at $T>25$ K, to measure temperatures of physical transitions within ≈0.01 K in accordance with ITS-90 and to determine enthalpies of physical transitions within 0.3%.

The heat capacity of VA was measured in the range 12 to 330 K and of PVA between 5 and 330 K. The mass of VA and PVA placed in the calorimeter was

$9.778\cdot10^{-3}$ kg and $3.6425\cdot10^{-3}$ kg, respectively. The heat capacity of the samples was everywhere from 45 to 60% of the total heat capacity of the calorimetric ampoule and the substance. For VA, 144 experimental values of C_p^o were obtained in 12 series of measurements, and for PVA, 117 points of C_p^o in 9 series. The averaging of the experimental points was made on a computer. The root-mean-square scatter of the points from the corresponding averaged curves $C_p^o=f(T)$ for the monomer did not exceed ±0.40% between 13 and 80 K, ±0.20% from 80 to 250 K and ±0.075% in the range 250 to 330 K; for the polymer ±0.25% from 4 to 60 K, ±0.50% between 60 and 190 K and ±0.09% in the interval 190 to 330 K. The experimental C_p^o points and the smoothed curves for VA and PVA are illustrated in Figs 1 and 2, respectively.

Results and discussion

Heat capacity

In the temperature range studied VA exists in crystalline, glassy, supercooled liquid and liquid states (Fig. 1). On cooling from T=200 K at a rate of $9\cdot10^{-2}$ K s^{-1}, liquid VA was always supercooled and then vitrified. On further heating during C_p^o measurements in the range 115 to 120 K VA was devitrified. In the process of a subsequent heating at about 122 K, its spontaneous crystallization followed by heat evolution began. A complete crystallization occurred in about a day. After the crystallization, the heat capacity of VA is represented by curve AC. A sharp increase in C_p^o and a subsequent break of the plot $C_p^o=f(T)$ (Fig. 1, curve FJK) are caused by the melting of crystals. The heat capacity of liquid VA gradually increases with rising temperature. On slow cooling of the calorimetric ampoule with liquid VA (at a rate of about $6.6\cdot10^{-2}$ K s^{-1}) we succeeded in measuring C_p^o of the monomer in the supercooled liquid state to a temperature about 20 K below T_m^o. Stopping the cooling in the range 120 and 160 K always led to crystallization of VA. Such a temperature interval is characteristic of many organic liquids [13].

In the temperature range under study PVA is in glassy and high-elastic states. In both these states its C_p^o smoothly increases with increasing temperature. A relatively rapid growth of the C_p^o values between 270 and 305 K (Fig. 2, curve CGD) is connected with the devitrification of the polymer.

The difference between the C_p^o values of PVA we obtained and those given in [4] at T<100 K and T>300 K is approximately 1%, however, in the range 100 to 300 K it is somewhat greater.

Thermodynamics of melting

The thermodynamic parameters of melting of VA are listed in Table 1. For 100% purity VA the thermodynamic equilibrium melting temperature was determined graphically by means of Rossini's method from the dependence of the

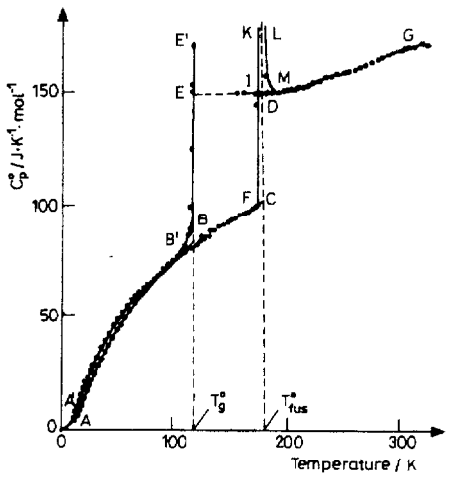


Fig. 1 Heat capacity of vinyl acetate: ABC is for crystalline VA, A'B' – glassy, ED – supercooled liquid, DG-liquid, FJKLM is the apparent heat capacity in the melting region, B'EE' is the heat capacity in the glass transition region, BE is the increase in heat capacity on devitrification, CD is the increase in heat capacity on melting; T_g^0 and T_m^0 are temperatures of glass transition and melting, respectively

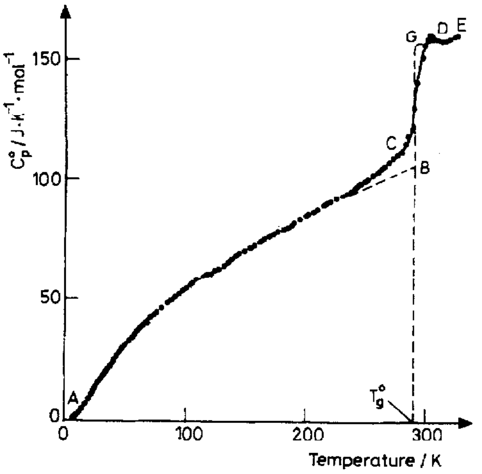


Fig. 2 Heat capacity of polyvinylacetate: AB is for glassy polymer, DE – high-elastic, BD is the heat capacity in the glass transition region, BG is the increase in heat capacity on devitrification, T_g^0 is glass transition temperature

equilibrium temperatures of triple points T_F^s on the fraction melted F measured in the calorimeter [14]. The relationship T_F^s *vs.* F is a straight line satisfactorily described by the following equation:

$$T_F^s = T_0^s - F^{-1}(T_0^s - T_{1.0}^s) \qquad (1)$$

where T_0^s and $T_{1.0}^s$ denote triple-point temperatures of 100% purity VA and the sample studied, respectively. By extrapolating the plot T_F^s *vs.* F^{-1} to F^{-1}=0 and F^{-1}=1 they were determined to be $T_{1.0}^s$ = 180.56 K and T_0^s = 180.64 K. The values of T_0^s and $T_{1.0}^s$ were assumed to be equal to thermodynamic-equilibrium melting temperatures of VA of 100% purity and the sample under study. The grounds for this assumption were demonstrated, for example, in [14]. The deviation of the experimental T_F^s points from the straight line (Eq. (1)) is not greater than 0.04%.

Table 1 Thermodynamic parameters of melting of vinyl acetate*, p=101.325 kPa

T_m^o / K	ΔH_m^o / kJ mol^{-1}	ΔS_m^o / J K^{-1} mol^{-1}	$\Delta C_p^o(T_m^o)$ / J K^{-1} mol^{-1}
180.64±0.01	8.460±0.02	46.84±0.10	49.7

*T_m^o, ΔH_m^o, ΔS_m^o are temperature, enthalpy and entropy of melting of vinyl acetate, respectively, $\Delta C_p^o(T_m^o)$ is the increase in heat capacity on melting of vinyl acetate

The enthalpy of melting ΔH_m^o for VA was measured by the method of continuous energy input described in detail earlier [12]. Table 1 lists the arithmetic mean of three measurements of ΔH_m^o: 8457, 8433 and 8491 J mol^{-1}. The entropy of melting ΔS_m^o was calculated from the values of the enthalpy and temperature of melting for VA. An increase was found graphically in the heat capacity on melting, ΔC_p^o (T_m^o) (Fig. 1, section CD).

Determination of the total impurity content in the monomer

A decrease in the melting temperature $\Delta T_m^o = (T_0^s - T_{1.0}^s)$ = 0.08 K indicates the presence of impurities in the VA sample. For calculating the total impurity content χ_2, Rossini's equation was used [14]:

$$-\ln(1-\chi_2) = A\Delta T_m^o(1 + B\Delta T_m^o) \qquad (2)$$

where A and B are the first and the second cryoscopic constants of VA: $A = \Delta H_m^o / R(T_m^o)^2 = (0.03118 \pm 0.0002)\ \mathrm{K}^{-1}$,
$B = \{((T_m^o)^{-1} - \Delta C_p^o(T_m^o) / 2\Delta H_m^o)\} = (0.002596 \pm 0.000001)\ \mathrm{K}^{-1}$

By solving Eq. (2) for χ_2, it was found that χ_2 = (0.0025±0.0005) mole.

The total content of impurities was also estimated by us from premelting by means of Tamman's method using expression (3):

$$\chi_2 = \{Q - <C_p^o> (T_f^o - T_i^o)\}\mathrm{M}(T_m^o - T_i^o)(T_m^o - T_f^o) / \{\mathrm{m}R(T_m^o)^2(T_f^o - T_i^o)\} \qquad (3)$$

Here Q denotes the energy necessary to raise the temperature of the mass m of the monomer sample from the initial temperature T_i^o = 178 K to the final temperature $T_f^\circ = 179$ K in the premelting region; $< C_p^\circ > = 110.6$ J K^{-1} mol^{-1} is the average apparent heat capacity in the interval from T_i° to T_f°; T_m° is the melting temperature of absulutely pure VA; M is the molar mass of the monomer and R is the universal gas constant. It was found that $\chi_2 = (0.0025 \pm 0.0001)$ mole. It is seen that the impurity contents found by the methods of Rossini and Tamman coincide within the error of measurements. This implies that the impurities do not form solid solutions with the main substance [14].

Parameters of glass transition and glassy state

The parameters of glass transition and glassy state of VA and PVA are given in Table 2. The glass transition temperature T_g° was determined from the inflection of the corresponding plots $S^\circ = f(T)$ of the monomer and polymer by the method of Alford and Dole [15]. Our value of T_g° for PVA differs from that cited in [5] and [16] by approximately 10 K. Perhaps, this can be explained by the fact that in the above works a dynamic calorimeter with a fairly high heating rate was employed to estimate T_g° and no correction was made to extrapolate T_g° to zero heating rate. The temperature of Kauzman T_2° was found from the entropy diagram of the monomer (Fig. 3).

Table 2 Thermodynamic parameters of glass transition of vinyl acetate and polyvinylacetate*, p=101.325 kPa

Compound	T_g° / K	T_2°/ K	$\Delta C_p^\circ(T_g^\circ)$/	S_{conf}° /	$S_{gl}^\circ(0)$/	$H_{gl}^\circ(0) - H_{cr}^\circ(0)$ /
			J K^{-1} mol^{-1}			kJ mol^{-1}
VA	120±1	93	65.9	15±1	15±1	4.660±0.50
PVA	219±1	–	51	13±1	–	–

*T_g° – glass transition temperature, T_2° – Kauzman temperature of vinyl acetate from [17], $\Delta C_p^\circ(T_g^\circ)$ – the increase in heat capacity on the devitrification of the sample, S_{conf}° – configurational entropy, $S_{gl}^\circ(0)$ – zero entropy of vinyl acetate, $H_{gl}^\circ(0) - H_{cr}^\circ(0)$ – is the difference of zero enthalpies of glass and crystal at 0 K.

The increase in the heat capacity on the devitrification of the monomer and polymer $\Delta C_p^\circ(T_g^\circ)$ was obtained graphically (Figs 1 and 2, sections BE and BG, respectively).

Configurational entropies S_{conf}° were calculated by the following equation [17]:

$$S_{conf}^\circ = \int_{T_2^\circ}^{T_m^\circ} \Delta C_p^\circ(T_g^\circ)\,\mathrm{d}\ln T \tag{4}$$

in addition, according to [18], for PVA the value of the ratio T_g°/T_2° was taken to be 1.29. The zero-temperature entropy of VA in the glassy state was calculated by Eq. (5) [19]:

$$S^{\circ}_{\mathrm{gl}}(0) = \int_{0}^{\mathrm{T}^{\circ}_{\mathrm{m}}}[C^{\circ}_{\mathrm{p}}(\mathrm{cr}) - C^{\circ}_{\mathrm{p}}(\mathrm{a})]\mathrm{d}\ln T + \Delta S^{\circ}_{\mathrm{m}} \tag{5}$$

The difference of zero enthalpies of VA in the glassy and crystalline state was estimated by using expression (6) [19]:

$$H^{\circ}_{\mathrm{gl}}(0) - H^{\circ}_{\mathrm{cr}}(0) = \int_{0}^{\mathrm{T}^{\circ}_{\mathrm{m}}}[C^{\circ}_{\mathrm{p}}(\mathrm{cr}) - C^{\circ}_{\mathrm{p}}(\mathrm{a})]\mathrm{d}T + \Delta H^{\circ}_{\mathrm{m}} \tag{6}$$

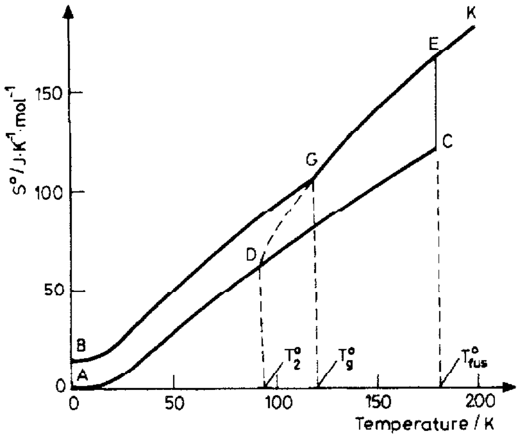


Fig. 3 Entropy diagram of vinyl acetate: ADC is the entropy of crystalline vinyl acetate, BG – of glass, AB is the zero (residual) entropy of glass, DG – of hypothetical glassy state, GE – of supercooled liquid, EK – of liquid, CE is the entropy of melting, T°_{2} is the Kauzman temperature, T°_{g} and T°_{m} are temperatures of glass transition and melting, respectively

Thermodynamic functions

To calculate the thermodynamic functions of VA and PVA (Table 3), the temperature dependence of C°_{p} of the monomer was extrapolated from 12 K and that of the polymer from 5 K to 0 K by Debye's function for heat capacity (7):

$$C^{\circ}_{\mathrm{p}} = nD(\Theta_{\mathrm{D}} / T) \tag{7}$$

where D is the symbol for the Debye function, n and Θ_{D} are specially selected parameters. For crystalline VA n=6 and Θ_{D}=125.5 K, for glassy VA 6 and 113.7, respectively, and for PVA n=2, Θ_{D}=76.24 K. With these parameters, Eq. (7) describes the experimental values of the heat capacity of the monomer between 12 and 18 K and of the polymer in the interval 5 to 12 K with an error of 1%. While calculating the functions, it was assumed that for VA at T<12 K and for PVA at

$T<5$ K Eq. (7) reproduces the C_p^o values at the same precision. The functions $H^o(T)-H^o(0)$, $S^o(T)$, $G^o(T)-H^o(0)$ were calculated from the temperature-dependent C_p^o, temperatures and enthalpies of physical transitions by means of the known procedures [20].

Table 3 Thermodynamic functions of vinyl acetate $\{M(C_4H_6O_2)=86.09$ g mol$^{-1}\}$ and polyvinylacetate (per mole of a repeating unit $C_4H_6O_2$; $M=86.09$ g mol^{-1})}*, $T=298.15$ K and $p=101.325$ kPa

Substance	Physical state**	C_p^o/ J K^{-1} mol^{-1}	$H^o(T)-H^o(0)$/ kJ mol^{-1}	$S^o(T)$/ J K^{-1} mol^{-1}	$-[G^o(T)-H^o(0)]$/ kJ mol^{-1}
VA	*l*	167.1	37.96	244.8	35.08
PVA	*h.e.*	156.5	19.59	151.6	25.61

* C_p^o – heat capacity, $H^o(T)-H^o(0)$ – the change of enthalpy of the substances on heating from 0 K to T, $S^o(T)$ – the absolute value of entropy of the substances at T, $G^o(T)-H^o(0)$ – the change of Gibbs function on heating of the substances;
** *l* – liquid, *h.e.* – high-elastic

In the calculation of the entropy of the polymer, its S_{conf}^o was regarded to be equal to the zero entropy of the polymer in the glassy state $S_{conf}^o=S^o(0)$.

Thermochemical parameters of formation

In Table 4 are given the thermochemical parameters of formation of VA and PVA. They correspond to the following processes at $T=298.15$ K and $p=101.325$ kPa:

for VA $4C_{(gr)}+3H_{2(g)}+O_{2(g)} \rightarrow C_4H_6O_{2(l)}$

and for PVA $4nC_{(gr)}+3nH_{2(g)}+nO_{2(g))} \rightarrow [X_4H_6O_2]_{(h.e.)}$

where *gr* is graphite, *g* – gaseous, *l* – liquid and *h.e.* – high-elastic.

The enthalpy of formation ΔH_f^o of VA was determined elsewhere [6]. The value of ΔH_f^o for the polymer in the high-elastic state was calculated by using Eq. (8) which is a consequence of the first principle of thermodynamics:

$$\Delta H_f^o(\mathrm{PVA}) = \Delta H_{pol}^o - \Delta H_f^o(\mathrm{VA}) \qquad (8)$$

where ΔH_{pol}^o is the enthalpy of polymerization of liquid VA into PVA in the high-elastic state at $T=298.15$ K and $p=101.325$ kPa, being calculated from Joshi's results [8] and the data listed in Table 4 by using Kirchhoff's formula [21]. The entropy of formation ΔS_f^o of VA and PVA was calculated on the basis of the data in Table 3 and the values of entropy of formation of $C_{(gr)}$, $H_{2(g)}$ and $O_{2(g)}$ cited in [21].

Table 4 Thermochemical parametersof formation of vinyl acetate and polyvinylacetate*, T=298.15 K, p=101.325 kPa

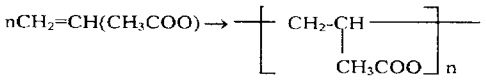
Substance	Physical state**	$-\Delta H_f^o$/ kJ mol^{-1}	$-\Delta S_f^o$/ J K^{-1} mol^{-1}	$-\Delta G_f^o$/ kJ mol^{-1}	$\ln K_f^o$
VA	*l*	349.8 [6]	374.8	238.1	96.0
PVA	*h.e.*	437.1	467.9	297.6	120.0

*ΔH_f^o, ΔS_f^o, ΔG_f^o – enthalpy, entropy and Gibbs energy of formation, respectively, $\ln K_f^o$ – logarithm of the equilibrium constant of the formation reaction of VA and PVA;
** *l* liquid, *h.e.* – high-elastic

The Gibbs function of formation ΔG_f^o was estimated from the values of ΔH_f^o and ΔS_f^o. The thermodynamic equilibrium constants of the reactions of formation of liquid VA and high-elastic PVA from simple substances were calculated from the ΔG_f^o values by using van't Hoff's equation.

Thermodynamic parameters of polymerization

VA is polymerized according to the scheme:



$$nCH_2{=}CH(CH_3COO) \rightarrow \left[CH_2\text{-}\underset{CH_3COO}{CH} \right]_n \tag{9}$$

The thermodynamic parameters of process (9) are given in Table 5. The enthalpy of bulk polymerization ΔH_{pol}^o of liquid VA into amorphous PVA was measured according to Joshi [7, 8] in six experiments at T≅350 K. At other temperatures the ΔH_{pol}^o values (Table 5) were calculated by Kirchhoff's formula [20] using the enthalpies of reagents. The entropies of polymerization ΔS_{pol}^o were estimated from the absolute magnitudes of entropies of the reagents calculated on the basis of our calorimetric data. The Gibbs functions ΔG_{pol}^o were evaluated from the enthalpies and entropies of the processes at corresponding temperatures. Since for the reaction VA) → PVA one can see that always $\Delta H_{pol}^o<0$ and $\Delta S_{pol}^o<0$,

Table 5 Thermodynamic characteristics of the bulk polymerization reaction of vinyl acetate*, p=101.325 kPa

T/ K	Physical state of monomer and polymer**	$-\Delta H_{pol}^o$/ kJ mol^{-1}	$-\Delta S_{pol}^o$/ J K^{-1} mol^{-1}	$-\Delta G_{pol}^o$/ kJ mol^{-1}
0	*cr; gl*	68.9	−13	68.9
100	*cr; gl*	69.9	2.4	69.7
200	*l; gl*	81.5	69.9	67.5
298.15	*l; h.e.*	87.3	93.0	59.5
350	*l; h.e.*	87.9	94.9	54.7

*T – temperature, ***cr* – crystalline, *gl* – glassy, *h.e.* – high-elastic, *l* – liquid

process (9) has a ceiling limiting temperature T^{o}_{ceil}. According to the estimation by Dainton's method [22], T^{o}_{ceil} is equal to 926 K. It is clear that it is much higher than the temperature of the onset of the thermal polymer destruction which is about 440 K as cited in [9].

* * *

The study was performed with a financial support of the Russian Foundation of Basic Research (project 96-07-89026) and the Ministry of Science and Technology of Russian Federation.

References

1 B. V. Lebedev, Chem. Cand. Thesis, Gorky State University, Gorky 1967.
2 B. V. Lebedev and I. B. Rabinovich, Trudy po Khimii i Khimicheskoi Tekhnologii, 2 (1972) 68.
3 U. Gaur, B. B. Wunderlich and B. Wunderlich, J. Phys. Chem., Ref. Data, 12 (1983) 29.
4 H. S. Bu, W. Aycock, S. Z. D. Cheng and B. Wunderlich, Polymer, 29 (1988) 1485.
5 M. S. Sheiman, I. B. Rabinovich and Yu. V. Ovchinnikov, Vysokomol. Soed., A14 (1972) 377.
6 M. A. Dolliver, T. L. Gresham, G. B. Kistiakowsky, E. A. Smith and W. E. Vaughan, J. Am. Chem. Soc., 60 (1938) 440.
7 R. M. Joshi, J. Polymer Sci., 56 (1962) 313.
8 R. M. Joshi, Makromolekulare Chem., 66 (1963) 114.
9 Encyclopedia of Polymers, Sov. Encyclopediya, Moscow, 2 (1972) 384.
10 Polymer Handbook, Ed. J. Braudrup, E. H. Immergut, Wiley, N. Y. 1975.
11 V. I. Kosov, V. M. Malyshev, G. A. Milner, E. L. Sorkin and V. F. Shibakin, Izmeritelnaya Tekhnika, 11 (1985) 56.
12 B. V. Lebedev and V. Ya. Lityagov, Termodin. Org. Soedin., 5 (1976) 89.
13 B. V. Lebedev, Chem. D. Thesis, Moscow State University, Moscow 1979.
14 Yu. I. Alexandrov, Precise Cryometry of Organic Compounds, Khimiya, Leningrad 1975, p. 70.
15 S. Alford and M. Dole, J. Am. Chem. Soc., 77 (1955) 4774.
16 M. S. Sheiman, Chem. Cand. Thesis, Gorky State University, Gorky 1971.
17 G. Adam and J. H. Gibbs, J. Chem. Phys., 43 (1965) 139.
18 A. B. Bestul and S. S. Chang, J. Chem. Phys., 40 (1964) 3731.
19 B. V. Lebedev and I. B. Rabinovich, Dokl. AN SSSR, 237 (1977) 691.
20 B. V. Lebedev, Thermodynamics of Polymers, Gorky State University, Gorky 1989.
21 Handbook 'Thermal Constants of Substances', Ed. V. P. Glushko, Viniti, Moscow, issue 1, part I, 1965–1972.
22 F. S. Dainton and K. I. Ivin, Quart. Rev., 12 (1958) 61.