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Application of precise calorimetry in study of polymers and polymerization processes

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Abstract

The peculiarities of polymers as objects of calorimetric studies were discussed and the calorimetric apparatus used at author's laboratory was characterized. Some main results of calorimetric studies of heat capacity, temperatures and enthalpies of physical transitions in polymers as well as thermodynamic parameters of polymerization reactions were reported. © 1997 Elsevier Science B.V.

1. Introduction

The fact that the conversion of many up-to date monomers into the corresponding polymers is not thermodynamically favourable is not obvious, and therefore, the investigation of polymerization should be started, in principle, from a thermodynamic analysis [1–3]. An important goal of such analysis is to establish a principal feasibility of the conversion of a monomer into a polymer and its degree under particular physicochemical conditions. A spontaneous transformation of the monomer into the polymer is only possible provided a decrease of Gibbs function, $\Delta_{\mathrm{pol}}G^{\mathrm{p}}<0$, or at its standard values characterizing an equilibrium $\Delta_{\mathrm{pol}}G^{\circ}<40$ kJ mol^{-1} [4]. The thermodynamic analysis also allows one to obtain the thermodynamic parameters of polymerization reactions, viz. enthalpy $\Delta_{\mathrm{pol}}H^0$, entropy $\Delta_{\mathrm{pol}}S^0$, thermodynamic constant of polymerization–depolymerization equilibrium K^0_{pol}, equilibrium monomer concentration $[M]^0_e$ in an equilibrium reaction mixture and limiting polymerization temperatures T^0_{cell} and T^0_{low}. The availability of temperature dependences of heat capacity, temperatures and enthalpies of physical transitions of monomers and the corresponding polymers in a wider temperature range the lower limit of which close to 0 K is also of importance. The total combination of these data is the thermodynamic principles of polymer production technology. It is clear that the results cited can be obtained only by using a complex of various calorimetric apparatus.

2. Experimental

2.1. *Peculiarities of polymers as objects of calorimetric studies*

As objects of calorimetric studies, polymers show a number of known peculiarities [3,5]: they are a mixture of macromolecules of different size mass; monomeric units in the macromolecules can differ in the

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type of their bonding ("head-to-tail", "head-to-head"). If multiple bonds are available in the macromolecules, cis- and trans-units are present at various ratios. Depending on the kind of catalysts used in the polymer synthesis, the polymers can exhibit a different microtacticity. The variation in units is possible, the polymers are, as a rule, either amorphous or partially crystalline. All the above should be taken into consideration in the course of calorimetric studies. To make direct calorimetric measurements of polymerization enthalpies it is necessary to estimate thoroughly a conversion degree of the monomer into the polymer and to identify a final state of the polymer.

2.2. Calorimetric apparatus

To measure the temperature dependence of heat capacity, temperatures and enthalpies of physical transitions in the range of 5– 340 K vacuum adiabatic calorimeters TAU-1 (completely automatic) and an UNTNT calorimeter (semi-automatic) described in detail in [6,7] were employed, and between 220 and 700 K an ADKTTM automatic differential calorimeter operating by the principle of triple thermal-bridge was used [8].

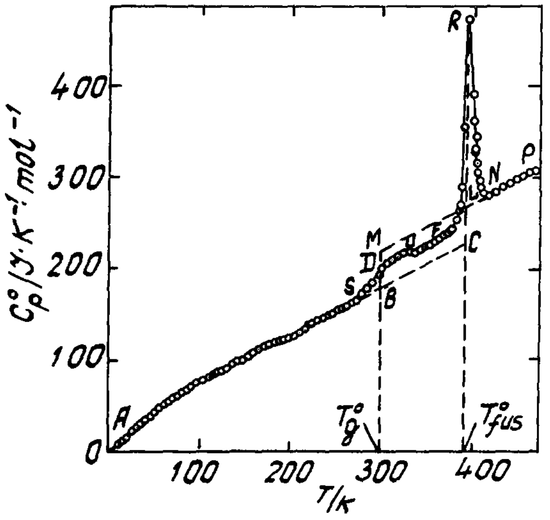

Fig. 1. Heat capacity of poly-2,2-dimethyltrimethylene carbonate: ABC, crystalline; AB, glassy; ML, high-elasticity; AS, mixture of 48% crystals and 52% glass; UF, mixtures of crystals and polymer in high-elasticity state in the above ratio; FRN, apparent heat capacity in melting interval; NP, liquid.

Enthalpies of monomer polymerization were measured in a differential automatic microcalorimeter DAK-1-1 [9] and a calorimeter of Mathews type with boiling carbon tetrachloride [10].

Combustion energies of monomers and polymers were measured in an improved calorimeter V-08 with an isothermal shield and a static bomb [11]. From calibration and test data, maximum errors of experimental values were found to be for C_p^0 about 1% in the range 5–30 K, 0.5% from 30–50 K, 0.2–0.3% between 50 and 330 K and 0.5–2.5% in the interval 330–700 K; for T_{tr}^0 0.01 K from 0 to 330 K, 0.1 K between 330 and 700 K. As to uncertainties of $\Delta_{tr}H^0$, they were estimated to be 0.3 and 0.8% in the same temperature ranges, respectively; with $\Delta_{comb}U$, an error was 0.02–0.04% at 298.15 K and for $\Delta_{pol}H^0$ 1–2% between 298 and 350 K.

3. Results and discussion

3.1. Heat capacity

In Fig. 1 a typical temperature dependence of heat capacity is shown for a partially crystalline polymer. In $C_p^0 = f(T)$ curves the glass transition of an amorphous polymer fraction and the fusion of crystalline ones are distinctly seen. For a number of polymers we established transitions of "order ⇄ disorder" and "crystal ⇄ crystal" types.

From the experimental data it is followed that in the temperature range from 60 K to the temperature of devitrification beginning C_p^0 of polymers is a linear function of temperature $C_p^0 \sim T^{-1}$. Besides, at T below T_g^0 the C_p^0 values of polymers in glassy, partially crystalline and crystalline states coincide within measurement errors, i.e. they do not practically depend upon the crystallinity degree α and only at very low temperatures a noticeable relation between heat capacity and α is observed [12]. The dependence of C_p^0 on α shows itself markedly in the range $T_g^0 - T_{fus}^0$. For polymers in liquid and overcooled liquid states the variation of C_p^0 with T is close to linear. The heat capacities of cis- and trans-isomers and stereoisomers in the same physical states are similar: the differences do not usually exceed 1–2%. The heat capacity of deuteropolymers is always larger than that of the corresponding hydrogen analogs (in the case of a complete substitution of hydrogen for deuterium it is greater by 15–20%).

3.2. *Thermodynamics of fusion*

A stable equilibrium, when the formation of perfect crystals of a certain kind occurs, the chemical potential of which is influenced only by T and p, is not achieved for kinetic reasons on the polymer crystallization. As a result, a set of various metastable crystalline formations of ultramicroscopic and microscopic sizes with different chemical potentials is formed. In this case the Gibbs function G of crystal surface is a substantial part of their total Gibbs function. At a temperature below a thermodynamic-equilibrium melting temperature G(cr) < G(l) and at the melting temperature $\Delta G=0$. This condition is realized for crystals of different size at various temperatures: the smaller the crystals are the lower their T^0_{fus}. This leads to a nonisothermality of fusion that is observed in experiments on the measurement of fusion processes. It was revealed that for many polymers the fusion begins practically at once after the devitrification of an amorphous fraction of a sample and takes place in a wide temperature interval (up to 100 K). In Fig. 2 are shown typical integral and differential curves of fusion reflecting the crystal distribution by melting temperatures. It is seen that the fusion of most mass of crystals (about 70%) occurs in a relatively narrow temperature range: for a sample of polytetrahydrofuran (PTHF) of 54% crystallinity in 12 K interval and of 65% crystallinity polymer in 4 K range. Temperatures of the beginning and the end of fusion and the temperature at which a maximum quantity of crystals melts are similar for both samples of PTHF.

For a lot of polymers studied by us the plots T^0_F vs. F^{-1} are straight lines well described by the equation

$$T^0_F = T^0_0 - F^{-1}(T^0_0 - T^0_1), \quad (1)$$

where T^0_F is thermodynamic-equilibrium melting temperature at the polymer fraction melted F; T^0_0 and T^0_1 are thermodynamic-equilibrium melting temperatures of the sample under study and a hypothetical perfect crystal of the same polymer for $F^{-1}=1$ and $F^{-1}=0$, respectively.

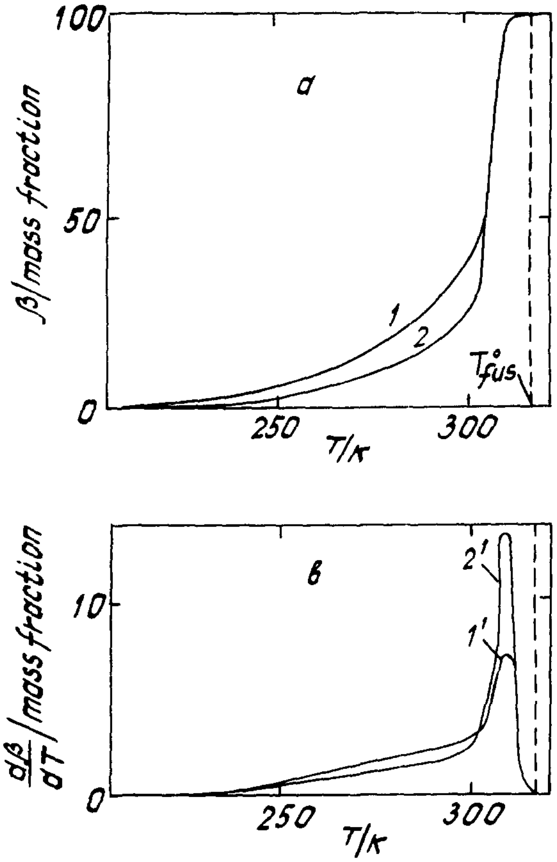

Fig. 2. Integral (a) and differential (b) curves of melting of polytetrahydrofuran: 1 and 1′- sample of 54% crystallinity; 2 and 2′- of 65% crystallinity.

The molar enthalpies of melting $\Delta_{fus}H^0(\alpha)$ for the polymer samples studied were measured by the method of continuous energy input [3], usually in three and more experiments. The average obtained was re-calculated for 100% crystallinity by the equation

$$\Delta_{fus}H^0(\alpha = 100) = 100\Delta_{fus}H^0(\alpha)/\alpha. \quad (2)$$

The entropy of melting $\Delta_{fus}S^0(\alpha=100)$ was estimated from the values of $\Delta_{fus}H^0(\alpha=100)$ and T^0_{fus}. An increase in the heat capacity at T^0_{fus} on the polymer transition from a crystalline state to a liquid one was determined graphically (section CL, Fig. 1).

The comparison of the thermodynamic quantities of fusion of various polymers shows that there is no correlation between T^0_{fus} and $\Delta_{fus}H^0(\alpha=100)$. A number of high-fusible polymers have small values of melting enthalpy and, on the contrary, polymers with a low melting temperature possess relatively large values of melting enthalpies. It follows that T^0_{fus} is determined both by $\Delta_{\mathrm{fus}}H^0(\alpha{=}100)$ and $\Delta_{\mathrm{fus}}S^0(\alpha{=}100)$.

3.3. *Parameters of glass transition and other relaxation transitions*

Parameters of glass transition and glassy state are ΔT^0_{g}, a temperature range of glass transition, $\Delta C^0_{\mathrm{p}}(T^0_{\mathrm{g}})$, the increase in heat capacity on devitrification, S^0_{conf}, a configurational entropy, $S^0_{\mathrm{gl}}(0)$, a zero entropy, $H^0_{\mathrm{gl}}(0) - H^0_{\mathrm{cr}}(0)$, differences in enthalpies of the polymer in glassy and crystalline states at 0 K and T^0_2, Kauzman temperature.

Because of high sensitivity of adiabatic vacuum calorimeters one succeeds in registering accurately the beginning and the end of devitrification from the change in the heat capacity. As a rule, ΔT^0_{g} lies in the range 20–60 K that 2–3 times as large as the values recorded by other methods. The glass transition temperature T^0_{g} approaches usually an average temperature of a glass transition range. The most precise methods of T^0_{g} estimation are the determination of an inflection point of a plot $C^0_{\mathrm{p}} = \mathrm{f}(T)$ or a bend of plot $S^0{=}\mathrm{f}(T)$ in the glass transition range. It should be noted that due to a relaxation character of the glass transition process and a difference of time scales of experimental methods, slightly distinguishing values of T^0_{g} are obtained. The increase in heat capacity on the devitrification is determined graphically (section BM, Fig. 1). The value of $\Delta C^0_{\mathrm{p}}(T^0_{\mathrm{g}})$ is included in the expression for the re-calculation of a configurational entropy of glass S^0_{conf} [13]

$$S^0_{\mathrm{conf}} = \Delta C^0_{\mathrm{p}}(T^0_{\mathrm{g}}).\ln T^0_{\mathrm{g}}/T^0_2, \qquad (3)$$

where T^0_2 is Kauzman temperature, i.e. a hypothetical temperature when on cooling an amorphous polymer, an equilibrium glassy state whose entropy is equal to that of a crystalline-state polymer can be achieved. T^0_2 is determined from an entropy diagram (Fig. 3) or the ratios $T^0_{\mathrm{g}}/T^0_2 \approx 1.30$ and $T^0_{\mathrm{g}} - T^0_2 \approx 55$ [13]. Besides, S^0_{conf} is an important value since its magnitude is close to the zero entropy $S^0_{\mathrm{gl}}(0)$ of the glassy polymer. The evaluation of $S^0_{\mathrm{gl}}(0)$ makes it possible to calculate absolute values of entropies of amorphous polymers. The calculations of $S^0_{\mathrm{gl}}(0)$ from the calorimetric data are made by using the equation

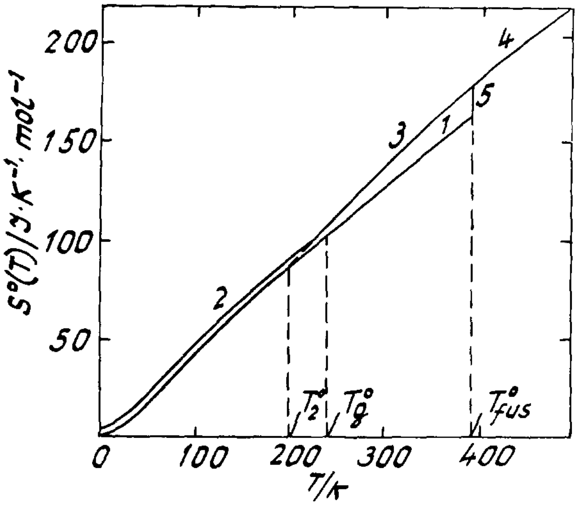

Fig. 3. Entropy diagram of polybutene-1: 1′ - entropy of crystalline polymer; 2′ - glassy; 3 - high-elasticity; 4 - liquid, 5 - entropy of melting.

$$S^0_{\mathrm{gl}}(0) = \int_0^{T^0_{\mathrm{fus}}} [C^0_{\mathrm{p}}(\mathrm{cr}) - C^0_{\mathrm{p}}(\mathrm{a})]\mathrm{d}\ln T + \Delta_{\mathrm{fus}}S^0(\alpha = 100), \qquad (4)$$

where $C^0_{\mathrm{p}}(\mathrm{cr})$ and $C^0_{\mathrm{p}}(\mathrm{a})$ are temperature-dependent heat capacities of crystalline (cr) and amorphous (a) polymers (curves AC and ABMLNP, respectively, Fig. 1). The substantiation of the calculation procedure is reported earlier [14]. An error of the $S^0_{\mathrm{gl}}(0)$ values is within $\pm 2\ \mathrm{J\ K^{-1}\ mol^{-1}}$. Until now $S^0_{\mathrm{gl}}(0)$ was estimated for approximately 70 polymers distinguished by the composition and structure. The values of $S^0_{\mathrm{gl}}(0)$ were found to be 3–100 $\mathrm{J\ K^{-1}\ mol^{-1}}$. In most cases, the $S^0_{\mathrm{gl}}(0)$ values are about 10% of $S^0(298.15\ \mathrm{K})$ of the corresponding polymers in the amorphous state or from 10 to 80% (more often not 50%) of the melting entropy of the corresponding 100% crystalline polymers.

From the same experimental data the difference in enthalpies of polymers in glassy and crystalline states

$H^0_{\mathrm{gl}}(0) - H^0_{\mathrm{cr}}(0)$ is calculated by using the equation

$$H^0_{\mathrm{gl}}(0) - H^0_{\mathrm{cr}}(0) = \int_0^{T^0_{\mathrm{fus}}} [C^0_{\mathrm{p}}(\mathrm{cr}) - C^0_{\mathrm{p}}(\mathrm{a})]\mathrm{d}T + \Delta_{\mathrm{fus}}H^0(\alpha = 100) \qquad (5)$$

The values of $H^0_{\mathrm{gl}}(0) - H^0_{\mathrm{cr}}(0)$ are known for about 70 polymers of various composition and structure and they lie in the interval from 2.8 to 31 kJ mol^{-1}, their error being about 10%. The glassy polymers, in principle capable to crystallize, are in the metastable state due to a large energy of rearrangement activation and prolonged relaxation times associated with this. It is suggested that a difference in the Gibbs functions of glassy and crystalline states $G^0_{\mathrm{gl}}(T) - G^0_{\mathrm{cr}}(T) = \Delta G^0(\mathrm{a;cr})$ is the estimation of the amorphous polymer metastability under given conditions. From the values of $H^0_{\mathrm{gl}}(0) - H_{\mathrm{cr}}(0)$ and $S^0_{\mathrm{gl}}(0)$ and the relations of $C^0_{\mathrm{p}}(\mathrm{cr})$ and $C^0_{\mathrm{p}}(\mathrm{a})$ against T the values of $\Delta G^0(\mathrm{a;\,cr})$, $\Delta H^0(\mathrm{a;cr})$ and $\Delta S^0(\mathrm{a;cr})$ were calculated for 20 polymers at temperatures from 0 to T^0_{fus}. As an example, the calculation results are given for poly-ε-caprolactone (Fig. 4).

On studying the temperature dependence of heat capacity of glassy polymers it was established that some of them have relaxation transitions. For example, in the range of 15–20 K polyvinylbenzyldimethylsilane has an endotherm with maximal heat capacity at 17 K, transition enthalpy $\Delta_{\mathrm{tr}}H^0$=105 J mol^{-1}, transition entropy $\Delta_{\mathrm{tr}}S^0$=5.9 J K^{-1} mol^{-1} that is close to Rln2=5.76 J K^{-1} mol^{-1}. It was attributed by us to transitions of "order ⇄ disorder" type with the number of statistic disordering N=2 (in a given case, probably, because of benzyl radical position).

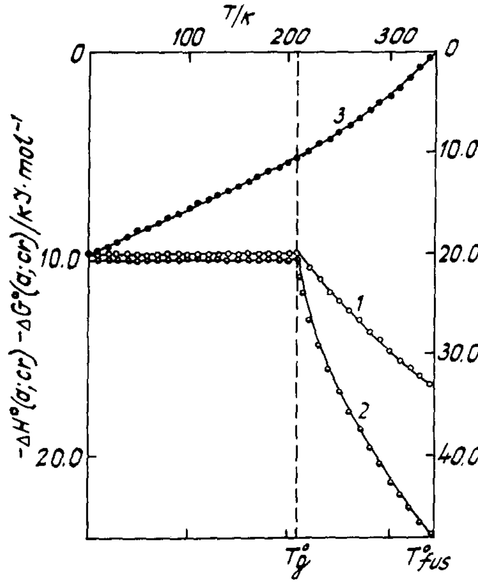

Fig. 4. Enthalpy (1), entropy (2) and Gibbs function (3) of transformation of amorphous poly-ε-caprolactone into crystalline.

For poly-1,1,3-trihydrotetrafluoropropyl-α-cyanacrylate the endothermic transformation of the same type was observed in the temperature interval of 384–525 K. The maximum heat capacity $C^0_{\mathrm{p,max}}$= 3400 J K^{-1} mol^{-1} at T^0_{tr}=480 K, $\Delta_{\mathrm{tr}}H^0$=69 kJ mol^{-1}, $\Delta_{\mathrm{tr}}S^0$= 144 J K^{-1} mol^{-1}. This transition is associated with the formation (on cooling) or destruction (on heating) of mesomorphic structure of the polymer [15,16].

3.4. *Thermodynamic functions*

From the data on the temperature dependence of heat capacity, temperatures and enthalpies of physical transitions of polymers the thermodynamic functions $H^0(T)$-$H^0(0)$, $S^0(T)$, $G^0(T)$-$H^0(0)$ were calculated for the amorphous and crystalline states in the range from 0 to (340–700) K, e.g. for poly-2,2-dimethyltrimethylene carbonate from the curves $C^0_{\mathrm{p}} = \mathrm{f}(T)$ (ABMLNP and ABC, respectively, Fig. 1). The extrapolation of experimental data of relation $C^0_{\mathrm{p}} = \mathrm{f}(T)$ from (5–10) K to 0 K was made by the Debye function for heat capacity $C^0_{\mathrm{p}} = nD(\Theta_D/T)$, where n and Θ_{D} are specially selected parameters. The equation describes the experimental data in the range 5–20 K within 0.5–1.0%. The entropy of amorphous polymers was estimated with taking into account $S_{\mathrm{gl}}(0)$. To evaluate the thermodynamic functions of the polymer having any crystallinity degree α, the method of linear extrapolation was used. For example, for the heat capacity

$$C^0_p(\alpha) = C^0_p(\alpha = 100) + [C^0_p(\alpha = 0) - C^0_p(\alpha = 100)] \cdot (100 - \alpha)/100.$$

3.5. *Enthalpy of combustion and thermochemical parameters of formation*

In an isothermal calorimeter with a bomb the combustion energies of polymers with crystallinity degree α, $\Delta_{comb}U(\alpha)$, were measured at T=298.15 K and then they were recalculated for the standard pressure to obtain $\Delta_{comb}U^0(\alpha)$. From the latter the combustion enthalpies $\Delta_{comb}\mathbf{H}^0(\alpha)$ were estimated at the same temperature and pressure and further recalculated for the polymers in the crystalline and amorphous states with using the data on $C_p^0 = f(T)$ relation of polymers in the above physical states and their melting enthalpies re-calculated from T_{fus}^0 to T=298.15 K. The values of $\Delta_{comb}H^0$(cr) and $\Delta_{comb}H^0$(a) were taken to estimate the enthalpies of polymer formation $\Delta_f H^0$(cr) and $\Delta_f H^0$(a) at the same T and p. Then after the entropies of formation $\Delta_f S^0$ (cr) and $\Delta_f S^0$(a) at T=298.15 K and p=101.325 kPa were obtained, the Gibbs functions of polymer formation $\Delta_f\mathbf{G}^0$(cr) and $\Delta_f\mathbf{G}^0$(a) were calculated for the same physical conditions. The calculation procedure and several results are published in [11].

3.6. *Thermodynamic parameters of polymerization reactions*

Polymerization enthalpies $\Delta_{pol}H^0$ of many classes of monomers were measured by direct calorimetry method or calculated from enthalpies of combustion or formation of polymers and the corresponding monomers. At other temperatures from 0 to (350–700) K the above values were determined from the experimental values of $\Delta_{pol}H^0$ and temperature dependences of heat capacities, temperatures and enthalpies of physical transformations of reagents by Kirchhoff's formula. On analyzing the values of $\Delta_{pol}H^0$ it was found that the polymerization enthalpy can be represented as the sum of the following contributions

$$\Delta_{pol}H^0(T) = \Delta E_{at} + \Delta E_{conj} + \Delta E_{int} + \Delta[H^0(T) - H^0(0)] \qquad (6)$$

where ΔE_{at} is the difference of average energies of atomic bonds breaking in the monomer and forming in the polymer during the polymerization process; ΔE_{conj} is the difference of energies of conjugation or hyperconjugation of atomic bonds in the monomer and the polymer; ΔE_{int} is the difference in energies of intermolecular interaction in the monomer and polymer at 0 K; $\Delta[H^0(T)$–$H^0(0)]$ is the difference of enthalpies of heating of the polymer and the monomer from 0 K to T. The importance of each term is considered in detail in work [3].

Depending on the physical states of the monomer and the polymer formed, the values of $\Delta_{pol}H^0$ are arranged in the following row: M(1)→ P(gl)< M(gl) → P(gl)< M(cr) → P(cr)≈ M(l) → P(gl) < M(l) → P(cr) < M(g) → P(gl) < M(g) → P(l or h.e.) < M(g)→ P(cr), where M is a monomer, P - a polymer; in brackets the physical states of reagents are given.

The polymerization entropy $\Delta_{pol}S^0$(T) was calculated from absolute entropies of monomers and corresponding polymers. It was turned out that $\Delta_{pol}S^0(T)$ depends relatively little upon composition and structure of reagents and is strongly influenced by their physical states. In the polymerization of gaseous vinyl monomers into amorphous polymers, the $\Delta_{pol}S^0(T)$ value is negative and varies from 160–180 J K^{-1} mol^{-1}, of liquid monomers between 85 and 105 J K^{-1} mol^{-1} and of crystalline ones from 10–300 J K^{-1} mol^{-1}. On varying temperature from 0 to 450 K, the variation interval of $\Delta_{pol}S^0$ for three – eight-membered cyclic monomers with a different composition is (96±4) J K^{-1} mol^{-1}. By the absolute magnitude $\Delta_{pol}S^0$ is maximal for the processes M(g)→P(cr). A detailed consideration of polymerization entropies is made elsewhere [3].

The Gibbs function of polymerization at standard pressure $\Delta_{pol}G^0(T)$ was calculated from the values of $\Delta_{pol}H^0(T)$ and $\Delta_{pol}S^0(T)$. When the value of $\Delta_{pol}G^0$ is mainly determined by the enthalpy contribution and the role of the entropic factor $T\cdot\Delta_{pol}S^0$ is relatively small, the dependence of $\Delta_{pol}G^0$ upon composition and structure of reagents is similar to that of $\Delta_{pol}H^0$. On the polymerization of cyclic monomers, the $\Delta_{pol}G^0$ values have both positive and negative magnitudes. Their dependence on temperature and physical states is described by Gibbs–Helmholtz equation

$$\partial(\Delta_{pol}G^0/T)/\partial T = -\Delta_{pol}H^0/T^2 \qquad (7)$$

The significance of this equation consists in that it allows to predict from the reaction enthalpy·how the increase in temperature affects the direction of reaction and how much efficiently the variation of temperature influences $\Delta_{pol}\mathbf{G}^0$. It is clear that with large values of $\Delta_{pol}H^0$, the change in temperature effects much the values of $\Delta_{pol}\mathbf{G}^0$; for exothermic reactions it leads to the increase of $\Delta_{pol}\mathbf{G}^0$ values and for endothermic ones to their decrease.

From the Gibbs functions of polymerization it is easy to calculate the thermodynamic constant of polymerization–depolymerization equilibrium K^0_{pol} and equilibrium concentrations of monomer $[M]^0_{\text{e}}$ and polymer $[P]^0_{\text{e}}$ in a reaction mixture at any temperature

$$\Delta_{\text{pol}}\text{G}^0 = -R \cdot T \cdot \ln K_{\text{pol}} \quad (8)$$

$$[M]^0_{\text{e}} = \exp(\Delta_{\text{pol}}\text{G}^0/RT); \quad (9)$$

with taking into account $[M]^0_{\text{e}} = 1/K^0_{\text{pol}}$,

$$[P]^0_{\text{e}} = 1 - \exp(\Delta_{\text{pol}}G^0/RT). \quad (10)$$

The polymerization processes have more often a ceiling limiting polymerization temperature T^0_{ceil}, rarely a lower limiting temperature T^0_{low} or have neither ceiling nor lower limiting temperature. They are determined from the intersection point of plots $\Delta_{\text{pol}}H^0=\text{f}(T)$ and $T\Delta_{\text{pol}}S^0=\text{f}(T)$. At the limiting temperature $\Delta_{\text{pol}}\text{G}^0=0$. Above the ceiling limiting temperature a spontaneous polymerization is thermodynamically prohibited and the polymer is stable relative to depolymerization at $T < T^0_{\text{ceil}}$. During the polymerization in solutions T^0_{ceil} depends on an initial monomer concentration $[\text{M}]_0$ [17] .

$$T^0_{\text{ceil}} = \Delta_{\text{pol}}H^0(T^0_{\text{ceil}})/\{\Delta_{\text{pol}}S^0(T^0_{\text{ceil}}) + R\ln[M]_0\} \quad (11)$$

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