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Thermodynamics of polyolefins

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Abstract. The thermodynamic properties of polyethylene, polydeuteroethylene, polypropylene, polybut-1-ene, polypent-1-ene, poly-3-methylbut-1-ene, polyhex-1-ene, polyisobutylene, poly-4-methylpent-1-ene, and polydec-1-ene as well as the thermodynamic parameters of their formation reaction in the temperature range 0–600 K are considered. The recommended thermodynamic quantities are presented. The characteristic feature of the variation of the thermodynamic properties and parameters of the formation reactions of polyolefins are described in terms of the compositions and structures of the initial monomers and polymers and their physical state and temperature at the standard pressure. The bibliography includes 115 references.

I. Introduction

The use of olefins of various composition and structure in polymerisation and copolymerisation reactions has led to considerable possibilities for the synthesis of polyolefins with new valuable operating properties.[1] Extensive theoretical and applied studies have been carried out in this connection on the synthesis of the initial monomers and on the properties of the polyolefins formed and their applications.[1–4] One of the dominant aspects of such studies at the present time is the search for appropriate catalytic systems, the study of the kinetics and mechanisms of the polymerisation and copolymerisation reactions, and the determination of the influence of the method of synthesis of polyolefins on their physical properties.[1–5] The effectiveness of the theoretical and applied developments is significantly improved if use is made of the advances in the thermodynamics of polymers and polymerisation. In the foreword to the American edition of H Sawada's book 'Thermodynamics of Polymerisation', the Editor, Prof. O'Driscoll, noted justifiably that any description of polymerisation which does not include thermodynamics is incomplete and the solution of certain problems is altogether impossible without a thermodynamic analysis.[6] It is noteworthy that the role of thermodynamics in the understanding of polymerisation processes has now been recognised and the thermodynamic aspects of polymerisation have been used systematically for the solution of current problems in polymer chemistry. Unfortunately, suitable data on the thermodynamic properties of polymers and the corresponding monomers are not always available. These data may be obtained mainly as a result of specific and laborious precise calorimetric studies. The majority of such studies have not been systematic. Because of this, the results obtained are scattered through scientific periodicals. The thermodynamic foundations of the technology of the synthesis of polymers may be used in theoretical and applied developments (see, for example, Lebedev and coworkers[7,8]). The discovery of the dependence of the thermodynamic properties and parameters of reactions on the compositions and structures of the reactants is particularly valuable because they can be used successfully for the estimation of the corresponding quantities for polymers and polymerisation reactions which have not yet been investigated (for example, those described by Vasil'ev[9] and Lebedev and Yevstropov[10]).

The aim of the present review is the analysis, critical selection, and survey of the thermodynamic properties of polyolefins and the parameters of their formation reactions over a wide temperature range and the determination of the dependences of the above properties and reaction parameters on the compositions and structures of the reactants and their physical states and on temperature at the standard pressure.

General information about the polymers considered in this review is presented in Table 1. All polyolefins are high-molecular-mass compounds, which rules out influence of molecular mass on their thermodynamic properties and on the parameters of the polymerisation reactions of the initial monomers. The calculations and estimations of the thermodynamic properties refer to 1 mole of the monomer repeat units of the macromolecules. In the tables of the thermodynamic properties and processes, the values quoted usually refer to the amorphous and crystalline states; if necessary, they can be readily estimated for any degree of crystallinity.

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Table 1. General information about the polyolefins under consideration.

Name	Monomer repeat unit		Microstructure (tacticity)
	formula	mass	
Polyethylene	$-C_2H_4-$	28.054	–
Polydeutero-ethylene	$-C_2D_4-$	32.086	–
Polypropylene	$-C_3H_6-$	42.080	Atactic, isotactic, syndiotactic
Polybut-1-ene	$-C_4H_8-$	56.104	Isotactic
Polyisobutylen[a]	$-C_4H_8-$	56.104	–
Polypent-1-ene	$-C_5H_{10}-$	70.134	Isotactic
Poly-3-methyl-but-1-ene	$-C_5H_{10}-$	70.134	"
Polyhex-1-ene	$-C_6H_{12}-$	84.163	"
Poly-4-methyl-pent-1-ene	$-C_6H_{12}-$	84.163	"
Polydec-1-ene	$-C_{10}H_{20}-$	140.268	"

[a] Amorphous specimen; in all the remaining cases, the specimens were partly crystalline.

II. Elements of the thermodynamics of polymerisation and polymers

In any physical state, real polymers exist in a state of metastable thermodynamic equilibrium,[11] so that the methods for the investigation of classical thermodynamics[12] are applicable to them, as well as other metastable systems. In particular, the theory of the occurrence of chemical reactions and their equilibria based on the Second Law of Thermodynamics is fully applicable to polymerisation processes.[13,14] The following characteristics are the thermodynamic parameters of polymerisation reactions: the thermodynamic constant of the polymerisation-depolymerisation process K°_{pol} and the equilibrium concentration of the monomer $[M]^\circ_e$ in the equilibrium reaction mixture; the enthalpy $\Delta_{pol}H^\circ$, the entropy $\Delta_{pol}S^\circ(T)$, and the Gibbs free energy $\Delta_{pol}G^\circ(T)$ of polymerisation; the upper (T°_{ceil}) and lower (T°_{low}) limiting polymerisation temperatures.[6,13-15] The circle in the superscript position indicates that the thermodynamic parameters of the polymerisation process occurring at the standard pressure $p^\circ = 101.325$ kPa are considered.

The Law of Mass Action is expressed by the following relation for the polymerisation reaction:

$$K^\circ_{pol} = \frac{1}{[M]^\circ_e}. \quad (1)$$

In their turn, K°_{pol} and $[M]^\circ_e$ are related to the standard Gibbs free energy of polymerisation by the van't Hoff equation.

The equilibrium concentration of the monomer can be expressed in terms of the enthalpy and entropy of polymerisation:

$$\ln [M]^\circ_e = \frac{\Delta_{pol}H^\circ(T)}{RT} - \frac{\Delta_{pol}S^\circ(T)}{R},$$

where R is the gas constant.

This equation is frequently used to obtain the values of $\Delta_{pol}H^\circ(T)$ and $\Delta_{pol}S^\circ(T)$, assuming that the enthalpy and entropy are independent of temperature in the experimental range of the latter. Subject to this condition, $\ln[M]^\circ_e$ is plotted against $1/T$ on the basis of the values of $[M]^\circ_e$ measured at several temperatures. This is usually a straight line, so that

$$\Delta_{pol}H^\circ(\Delta T) = -R \operatorname{tg} \alpha,$$

$$\Delta_{pol}S^\circ(\Delta T) = R \lim_{(1/T)\to 0} (\ln [M]^\circ_e),$$

where α is the slope of the straight line. The enthalpy and entropy of polymerisation are the averages of the quantities in the temperature range of measurement of $[M]^\circ_e$.

The temperature variations of K°_{pol} and $[M]^\circ_e$ are expressed by the van't Hoff equation of the reaction isobar.

The influence of temperature on $[M]^\circ_e$ is determined by the numerical value and sign of the enthalpy of polymerisation. The greater the numerical value of $\Delta_{pol}H^\circ$, the more marked is the variation of $[M]^\circ_e$, and, if $\Delta_{pol}H^\circ < 0$, then $[M]^\circ_e$ increases with increasing temperature and conversely. All the formation reactions of polyolefins are exothermic, so that the equilibrium yield of the polymer produced by them increases with decrease in temperature.

The influence of pressure on the polymerisation-depolymerisation equilibrium constant K_N, expressed in terms of the mole fraction of the monomer in the reaction mixture, is described by the equation[11,16]

$$\left(\frac{\partial \ln K_N}{\partial p}\right)_T = -\frac{\Delta_{pol}V}{RT},$$

where $\Delta_{pol}V$ is the difference between the molar volumes of the polymer and the monomer at the specified temperature and pressure. For moderate pressure (p), one can use the approximate relation

$$\ln K_N = \ln K^\circ_N - \frac{\Delta_{pol}V^\circ p}{RT},$$

where $\Delta_{pol}V^\circ$ is the difference between the molar volumes of the polymer and the monomer at the standard pressure. Since $\Delta_{pol}V^\circ < 0$ in the polymerisation of olefins, an increase in pressure is favourable as regards the yield of the polymers. This equation is applicable to the case where the pressure amounts to tens and even hundreds of atmospheres.

The temperature dependences of the enthalpy, entropy, and Gibbs free energy are expressed by the Kirchhoff and Gibbs–Helmholtz equations.[16]

The influence of temperature on $\Delta_{pol}H^\circ(T)$ and $\Delta_{pol}S^\circ(T)$ is determined by the numerical values and signs of $\Delta_{pol}C^\circ_p(T)$ and $\Delta_{tr}H^\circ$, while its influence on $\Delta_{pol}G^\circ(T)$ is determined by the numerical value and sign of $\Delta_{pol}H^\circ(T)$. For the polymerisation reactions of olefins, $\Delta C^\circ_p(T)$ and $\Delta_{pol}H^\circ(T)$ are usually negative. As a result of this, the numerical values of $\Delta_{pol}H^\circ(T)$ and $\Delta_{pol}S^\circ(T)$ increase with increasing temperature but remain negative, while $\Delta_{pol}G^\circ(T)$ diminishes with a consequent decrease in the yield of the polymer corresponding to thermodynamic equilibrium; on the other hand, it increases with decrease in temperature.

The dependences of the enthalpy, entropy, and Gibbs free energy on pressure are expressed by the following equations:[17-20]

$$\Delta_{pol}H = \Delta_{pol}H^\circ + \int_{p^\circ}^{p} \Delta_{pol}V(p)\mathrm{d}p - T\int_{p^\circ}^{p}\left[\frac{\partial \Delta_{pol}V(p)}{\partial T}\right]_p \mathrm{d}p,$$

$$\Delta_{pol}S = \Delta_{pol}S^\circ - \int_{p^\circ}^{p}\left[\frac{\partial \Delta_{pol}V(p)}{\partial T}\right]_p \mathrm{d}p,$$

$$\Delta_{pol}G = \Delta_{pol}G^\circ + \int_{p^\circ}^{p} \Delta_{pol}V(p)\mathrm{d}p,$$

where p° is the standard pressure.

$\Delta_{pol}H^\circ(T)$ and $\Delta_{pol}S^\circ(T)$ for the polymerisation of olefins are negative, whilst the entropy factor $T\Delta_{pol}S^\circ(T)$ increases faster with temperature than $\Delta_{pol}H^\circ(T)$, so that at the upper limiting temperature T°_{ceil} the enthalpy and the entropy factor are equalised and $\Delta_{pol}G^\circ(T_{ceil}) = 0$. It can be shown that at moderate pressures

$$\ln T_{ceil} = \ln T^\circ_{ceil} + \frac{\Delta_{pol}V^\circ(T^\circ_{ceil})p}{\Delta_{pol}H^\circ(T^\circ_{ceil})}.$$

Pressure can amount to tens and in certain cases even thousands of atmospheres.[11] At $T < T^{\circ}_{ceil}$, the equilibrium in the polymerisation reaction is displaced towards the formation of the polymer, whereas at $T > T^{\circ}_{ceil}$ it is actually displaced towards the initial monomer. At temperatures close to T°_{ceil} and higher, the polymer rapidly depolymerises to the initial monomer under kinetic conditions.[13-15] Since $\Delta_{pol}V^{\circ}(T^{\circ}_{ceil})$ and $\Delta_{pol}V^{\circ}(T^{\circ}_{ceil})$ for the polymerisation reaction are negative, their ratio is positive and T°_{ceil} accordingly increases with increase in pressure. This leads to the expansion of the range of temperatures favouring polymerisation and to the thermodynamic stability of the polymer.

Heat capacity is one of the most important thermodynamic quantities entering into key thermodynamic relations.[16,21,22]

A series of quantum theories of the heat capacities of chain structures — linear polymers have now been developed: the Stockmayer–Hecht theory[23] based on the analysis of the vibrational spectrum of the lattice formed by the polymer chains; Tarasov's theory of the heat capacities of chain structures[24] based on the analysis of the vibrational spectrum of a one-dimensional continuum (rigid string); Lifshits's theory[25] also based on the consideration of the vibrational spectrum of a one-dimensional continuum. In contrast to Tarasov, Lifshits chose thin rods (needles) as the one-dimensional continuum. All the above theories of heat capacity have been analysed critically by Godovskii,[26] who demonstrated convincingly that Lifshits's theory of heat capacity has the greatest physical justification. However, Tarasov's theory has nevertheless found extensive practical application.[24] It is expressed analytically by the following equation:

$$C_{v1,3} = D_1\left(\frac{\theta_1}{T}\right) - \frac{\theta_3}{\theta_1}\left[D_1\left(\frac{\theta_3}{T}\right) - D_3\left(\frac{\theta_3}{T}\right)\right], \qquad (2)$$

where D_1 and D_3 are symbols for the Tarasov and Debye heat capacity functions respectively, θ_1 and θ_3 are the characteristic Tarasov and Debye temperatures, and θ_3/θ_1 expresses the degree of interaction of the chains. The generalised expression for the Tarasov and Debye heat capacity functions assumes the form[24]

$$C_{v\,m} = 3mR\left(\frac{T}{\theta_m}\right)^m \int_0^{\theta_m/T} \frac{(\theta_m/T)^{m+1}\exp(\theta_m/T)}{[\exp(\theta_m/T)-1]^3}\,d\frac{\theta_m}{T},$$

where $m = 1$ or 3.

Chernoplekov[27] compiled tables of the heat capacities of chain structures, which greatly facilitate practical calculations of the skeletal contribution to the heat capacities of chain polymers. The characteristic temperatures θ_1 and θ_3 are usually determined by an inverse calculation from the experimental measurements of the heat capacities of specific polymers over a temperature range. Eqn (2) has been used particularly fruitfully by Wunderlich and coworkers, for example, in two studies[28,29] for the calculation of the heat capacities of linear polymers over a wide temperature range (frequently from 0 to 1000 K). The contribution of atomic vibrations to the heat capacities of polymers has been calculated from vibrational spectroscopic data using the Einstein heat capacity function.

The absolute value of the entropy $S^{\circ}(T)$ of a polymer is expressed by the following equation:

$$S^{\circ}(T) = S^{\circ}(0) + \int_0^T C_p^{\circ}(T)\,d\ln T + \sum \Delta_{tr}S^{\circ},$$

where $S^{\circ}(0)$ is the zero-point (residual) entropy of the polymer at $T = 0$ K, $C_p^{\circ}(T)$ is the temperature dependence of the heat capacity, and $\Delta_{tr}S^{\circ}$ is the entropy of phase transitions.

For vitreous and partially crystalline polymers, $S^{\circ}(0)$ is nonzero owing to the imperfection of the crystals, the thermodynamically nonequilibrium configurations of the macromolecules frozen at the glass transition temperature of the polymer T_g°, and certain other possible factors. The attempts at a theoretical estimation of $S^{\circ}(0)$, undertaken in a number of studies,[30-32] usually lead to values ranging from 10 to 20 J mol^{-1} K^{-1}. Strictly speaking, the zero-point entropy of a crystalline polymer is nonzero also owing to the imperfection of the crystals and because the polymer is a mixture of macromolecules having different masses.[11,33] However, it has been shown[31] that the corresponding entropy of mixing of polymers in any physical state is close to zero in cases where the average degree of polymerisation is greater than 100. It has been suggested that the quantity $S^{\circ}(0)$ could be neglected without significant error for polymers with a degree of crystallinity of 100%.

A number of investigators[34-36] developed a method for the estimation of $S^{\circ}(0)$ for polymers in the amorphous state from calorimetric measurements for partially crystalline polymers. The values of $S^{\circ}(0)$ for more than 100 vitreous polymers of different chemical composition and structure have now been obtained from the results of the corresponding calorimetric measurements. These results have largely confirmed the theoretical estimates. It was found that in most cases $S^{\circ}(0)$ is ~10% of S° (298.15 K) for the corresponding polymers in the amorphous state. It is also of interest that $S^{\circ}(0)$ amounts to between 10% and 80% (in most cases ~50%) of the entropies of fusion of the corresponding polymers with $\alpha = 100\%$.[11,13] It is not permissible to neglect $S^{\circ}(0)$ in accurate thermodynamic calculations.

It has been established[37-39] that the configurational entropy S°_{conf} makes the main contribution to $S^{\circ}(0)$ and that frequently we have $S^{\circ}_{conf} \simeq S^{\circ}(0)$. It has also been shown that S°_{conf} can be readily estimated from the formula[37]

$$S^{\circ}_{conf} = \int_{T_2^{\circ}}^{T_g^{\circ}} \Delta C_p^{\circ}(T_g^{\circ})\,d\ln T, \qquad (3)$$

where $\Delta C_p^{\circ}(T_g^{\circ})$ is the increase in heat capacity on devitrification of the polymer at T_g°, while T_2° is the Kauzmann temperature[37,40] and $T_g^{\circ}/T_2^{\circ} \simeq 1.29$. The quantities in Eqn (3) may be determined experimentally.

Thus the methods developed for the estimation of $S^{\circ}(0)$ made it possible to overcome the significant difficulties in the calculations of $S^{\circ}(T)$ and $\Delta_{pol}S^{\circ}(0)$, which in its turn opened a way to the full employment of calorimetric data for the calculation of the polymerisation–depolymerisation equilibrium.

III. Calorimetric research methods

1. Combustion calorimetry

The enthalpies of polymerisation of olefins have been calculated mainly from the experimental combustion energies of the monomers and the corresponding polymers. The reactants were combusted in bomb calorimeters.[41-45] Typical conditions in the measurements of combustion energies have been published.[46] A calorimeter with an isothermal jacket and a static bomb was used. The design of the calorimeter and the experimental method were similar to those described by Skuratov et al.[42]

2. Adiabatic vacuum calorimetry

The temperature dependences of the heat capacity and of the temperatures and enthalpies of physical transformations at low and moderate temperatures have been investigated in adiabatic vacuum calorimeters.[47-51] A number of olefins and polyolefins have been investigated in an adiabatic fully automated vacuum calorimeter, the design and method of employment of which have been described.[51-53]

3. Dynamic calorimetry

An automated differential calorimeter, working in accordance with the triple thermal bridge principle, is usually employed for measurements by dynamic calorimetry.[54] The design and method of employment of the calorimeter have been described.[55,56] A characteristic feature of the measurements of C_p° in this calorimeter is that it is calibrated for each individual measurement.

The sensitivity of the calorimeter has been raised to 1.3×10^{-2} J K^{-1} and the error of the heat capacity measurements has been reduced to 1%–4%. However, since in the experiments of Lebedev et al.[57] the heat capacities of the test substances in the temperature range 250–340 K were measured in an adiabatic vacuum calorimeter subject to an error of 0.2% and the conditions of the measurements in a dynamic calorimeter were chosen so that the values of C_p° obtained in the above temperature range were the same in both calorimeters, it was assumed[57] that, at $T > 340$ K, C_p° measured in the dynamic calorimeter is subject to an error within the range 0.5%–1.5%.

It was shown that the temperature and method of measurement make it possible to obtain C_p° for solid and liquid substances with an error up to 1%, the temperatures of physical transformations can be measured with an error up to 1.0 K, while the enthalpies of the transformations are subject to an error up to 0.8%.[30]

IV. Heat capacity

The heat capacities C_p° of polyolefins in the range from 5–10 to 350 K have been investigated as a rule in adiabatic vacuum calorimeters, while those at $T > 350$ K have been determined in dynamic calorimeters. In adiabatic vacuum calorimeters, between 90 and 150 experimental C_p° values were obtained in 10–25 series. The calorimeter tube was charged with between 2 and 6 g of the test substance. The heat capacity of the specimens was 50%–70% relative to the overall heat capacity of the calorimeter tube with the test substance. The experimental values of C_p° were averaged by the method of least squares. The scatter of the points around the corresponding averaging curves was 0.7% in the range 5–30 K, 0.07% in the range 30–150 K, and 0.02% in the range 150–340 K. In the study of substances in the dynamic calorimeter, the C_p° measurements were performed under the conditions of continuous heating of the calorimeter with the test substance. The rate of heating was varied from 16.7×10^{-3} to 8.3×10^{-3} K s^{-1} for the same substance in different series. The duration of a single measurement was ~ 20–25 s.

All the polyolefins investigated are partly crystalline polymers with the exception of the fully amorphous polyisobutylene and polyhex-1-ene.

Figure 1 presents a typical temperature dependence of the heat capacity of a partly crystalline polymer. Evidently, the heat capacity of a mixture of the vitreous and crystalline polymers increases smoothly in the range from the temperature at the beginning of the measurements from 6 K to the temperature of the onset of devitrification of the amorphous part of the specimen of 260 K (*AR*). In the range of devitrification temperatures, C_p° increases comparatively sharply with increase in temperature (*RN*) and then rises smoothly up to the temperature of the onset of the fusion of the crystalline part of the polymer (*NQ*). The fusion of the crystals is responsible for the anomalous variation of the heat capacity in the fusion range (*QSHUE*). The heat capacity of the polymer melt increases with increasing temperature (*EF*). Before proceeding to the analysis of the published data on the heat capacities of polyolefins, we shall make several remarks concerning the methods for the determination of the degree of crystallinity of polymers.

The degree of crystallinity of polyolefins α is determined as a rule from calorimetric data with the aid of the following equations:[26, 58, 59]

$$\alpha = 100\left(1 - \frac{\Delta C_p^\circ(\alpha)}{\Delta C_p^\circ(\alpha = 0)}\right), \quad (4)$$

$$\alpha = 100\,\frac{\Delta_{fus}H^\circ(\alpha)}{\Delta_{fus}H^\circ(\alpha = 100\%)}, \quad (5)$$

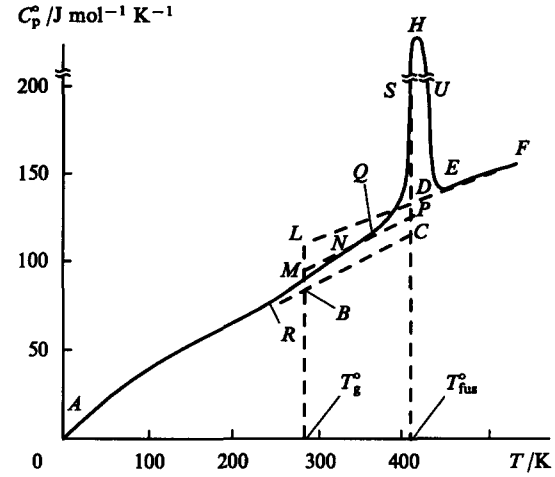


Figure 1. Typical temperature variation of the heat capacity of a partly crystalline polymer for isotactic polybut-1-ene as an example.[69–71] State of the polymer: *ABC* — crystalline, $\alpha = 100\%$, *AB* — vitreous, *LD* — highly elastic, *DEF* — liquid, *AR* — partly crystalline (form I, $\alpha \approx 77\%$; amorphous component in the vitreous state), *RNQ* — ditto, but with the amorphous component of the polymer in the highly elastic state; *QSHUE* — apparent heat capacity in the melting range of the crystals of form I.

where $\Delta C_p^\circ(\alpha)$ and $\Delta C_p^\circ(\alpha = 0)$ are respectively the increase in the heat capacity at the glass transition temperature T_g° of the partly crystalline and fully amorphous ($\alpha = 0$) polymer, while $\Delta_{fus}H^\circ(\alpha)$ and $\Delta_{fus}H^\circ(\alpha = 100\%)$ are the enthalpies of fusion of the polymer with a degree of crystallinity α and of the fully crystalline polymer.

$\Delta C_p^\circ(\alpha)$ and $\Delta C_p^\circ(\alpha = 0)$ were obtained graphically (sections *BM* and *BL* in Fig. 1). Point *B* was found by the linear extrapolation of the temperature dependence of the heat capacity of the partly crystalline polymer between $T < T_g^\circ$ and T_g°. Point *B* corresponds to the heat capacity of a mixture of the vitreous and crystalline materials, but C_p° is assumed to be equal at this point to the heat capacity of the polymer in the vitreous state. This is based on the experimentally observed equality of the heat capacities of the same polymer in the vitreous, partly crystalline, and even fully crystalline states at $T < T_g^\circ$ within the limits of the error of the measurements (differences between the values of C_p° less than 0.2%).[36, 60] Point *M* corresponds to the heat capacity of the same mixture of crystals with the amorphous component of the polymer in the highly elastic state. It was obtained by extrapolating the $C_p^\circ = f(T)$ relation (section *NQ*) between the end of the devitrification of the amorphous component and the onset of the prefusion of the crystalline component of the polymer. The increase in C_p° (section *B*) is associated with the devitrification of the amorphous component of the polymer. Point *L* was found by the linear extrapolation of the relation $C_p^\circ = f(T)$ for the liquid polymer (*EF*) into the region of its T_g°. Section *BL* corresponds to the increase in heat capacity owing to the segmental mobility of the macromolecules, which appeared in the course of the devitrification of the polymer in the amorphous state (the α-transition).[61]

On slow stepwise cooling, it is possible to measure the heat capacities of certain polymers in the range from point *E* to *L* (for example the heat capacity of the polymer in the highly elastic state in Fig. 1), whereupon the deviations of the C_p° points from the corresponding straight line *DL* are comparable to the error of the measurements of the heat capacity. Depending on the cooling conditions, the polymers are obtained in both amorphous and partly crystalline states. It is sometimes possible to measure C_p° in both states,[62, 63] whereupon the $C_p^\circ = f(T)$ relation for the polymer in the highly elastic state is located as a rule on the prolongation of the temperature variation of the heat capacity of the liquid (*FE*) to point *L*. Clearly the ratio of the sections *BM*/*BL* is equal to the fraction of the amorphous component of the polymer, while the

difference $1-BM/BL$ represents the fraction of the crystalline component of the polymer. The degrees of crystallinity of the polymers found from calorimetric and X-ray diffraction data agree subject a discrepancy which is usually within the limits of 3%–5%.[64]

In conclusion, we may note that the calorimetric method for the determination of the degree of crystallinity from the increase in the heat capacity at T_g° yields satisfactory results for low and moderate degrees of crystallinity, but may lead to significant errors for higher values of α.[26]

Polyethylene (PE) is one of the most thoroughly investigated polymers. Approximately 50 studies have been published in which the results of calorimetric investigations on ~100 polyethylene specimens having linear and branched structures, different molecular masses (from 2.5×10^4 to 8×10^6), and different degrees of crystallinity (from 25% to 97%) have been published for temperatures ranging from 0.16 to 570 K. All the published investigations have been thoroughly analysed and surveyed by Wunderlich and coworkers.[65] They obtained as a result the temperature variations of the heat capacity of PE in the crystalline, vitreous, highly elastic, and liquid states at temperatures in the range 0–600 K. It was shown that C_p° for crystalline PE increases smoothly with increase in temperature in the range from 0 to 360 K, after which there is a sharp rise in heat capacity owing to the onset of fusion, which occurs in the range 360–414 K. An anomalous $C_p^\circ = f(T)$ relation corresponds to the fusion process.

The heat capacity of vitreous PE also increases smoothly with increase in temperature from 0 to 200 K, after which the rise of C_p° becomes appreciably faster owing to devitrification, which is completed at 250 K. In the highly elastic and liquid states, the heat capacity of PE is a linear function of temperature. In the region of very low temperatures, C_p° of crystalline PE obeys the Debye T^3 law (in the range 1–9 K), while C_p° of vitreous PE is described by the equation

$$C_p^\circ = aT^3 + bT,$$

where a and b are constants. A similar relation is characteristic also of other amorphous solids. At temperatures in the ranges from 0 to 60 K and from 150 to 414 K, the heat capacities of amorphous and crystalline PE differ markedly, that of amorphous PE being higher. An additive dependence of the heat capacity on the degree of crystallinity of PE is manifested. In the range 60–150 K, the heat capacities of crystalline and amorphous PE are close: the differences do not exceed ±2%. The heat capacity of branched PE is always slightly higher than that of the linear polymer. Differences between the heat capacities were not discovered in a study of PE specimens having different molecular masses (from 6×10^4 to 1×10^6) in the same physical state.

Polydeuteroethylene (PDE). The results of the study of the temperature variation of C_p° of polydeuteroethylene have been published.[66,67] Rabinovich et al.[66] investigated in an adiabatic vacuum calorimeter a PDE specimen with a degree of deuteration of 93% and a degree of crystallinity of 72% in the range 80–310 K. The molecular mass of the polymer is not indicated. The results of experimental measurements of C_p° were extrapolated to 100% crystallinity on the basis of the proportionality of the differences between the heat capacities of the polymer in the amorphous and crystalline states. The values of C_p° of the fully crystalline PDE were in their turn extrapolated to 100% degree of deuteration assuming that the difference between the heat capacities of PDE and PE at a specified temperature is proportional to the deuterium content. The heat capacity of PDE has been investigated[67] in adiabatic vacuum and dynamic calorimeters in the temperature ranges 5–330 and 330–450 K respectively. The degree of deuteration of the test specimen was 98%, its degree of crystallinity was ~92%, and its molecular mass was 2×10^5. The error of the measurements was ~0.2% in adiabatic vacuum calorimeters[66,67] and from 0.5 to 1.5% in a dynamic calorimeter.[67] The results obtained by Lebedev and Smirnova[67] are presented in Fig. 2. Evidently there are several characteristic

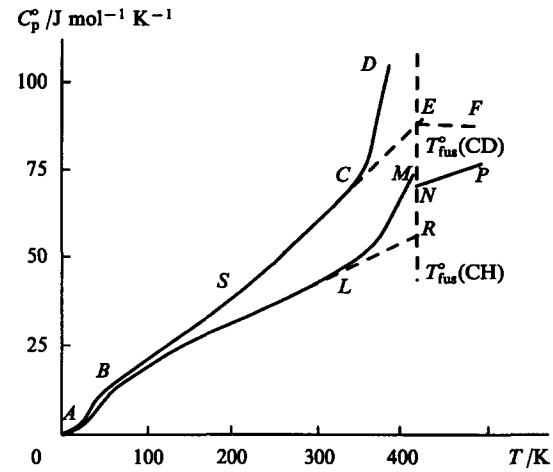


Figure 2. Heat capacities of polydeuteroethylene (*ABSCEF*)[67] and polyethylene (*ALMNP*).[65]
State of the polymer: *ABSC* — crystalline, α = 92%, *EF* — liquid, *CD* — apparent heat capacity in the melting range; *AL* — crystalline, α = 100%, *NP* — liquid, *LMN* — apparent heat capacity in the melting range; $T_{fus}^\circ(CD)$ and $T_{fus}^\circ(CH)$ — melting points of polydeuteroethylene and polyethylene respectively, *RN* — increase in heat capacity on fusion of polyethylene; for the explanation of the remaining symbols, see text.

sections on the $C_p^\circ = f(T)$ curve corresponding to the variation of the heat capacity with increasing temperature: 0–60 K (*AB*) — along this section, C_p° increases rapidly; 60–200 K (*BS*) — the range in which C_p° is a linear function of temperature, which occurs for all chain polymers; 200–350 K (*SC*) — the section along which the rate of change of C_p° is higher than along the preceding section, which may be associated with the devitrification of the amorphous component of the specimen; $T > 350$ K (*CD*) — along this section, C_p° increases sharply owing to the fusion of the polymer crystals. The heat capacity of the polymer melt (*EF*) is a linear function of temperature and a very weak one at that.

Comparison of the heat capacities C_p° found in the above two investigations[66,67] shows that, according to the data of Lebedev and Smirnova,[67] the heat capacity in the range 20–220 K is 3%–10% higher than in the study of Rabinovich et al.,[66] in the temperature range 220–260 K the heat capacities virtually coincide, while in the range 260–310 K the heat capacities are 3%–6% lower according to the data of Rabinovich et al.[66] The above discrepancies between the values of C_p° are apparently a consequence of the different degrees of deuteration and crystallinity of the test specimens and also of the above assumptions in the extrapolations.

Polypropylene (PP). More than 25 studies have been published in which the results of calorimetric measurements of the heat capacities of 34 specimens of atactic, isotactic, and syndiotactic PP are presented. Specimens with molecular masses from 8.9×10^3 to 6.4×10^5 and degrees of crystallinity from 10% to 65% were investigated. The heat capacity was determined in the temperature range 0.5–600 K. Atactic PP specimens are amorphous, while those of isotactic and syndiotactic PP are partly crystalline. All the published results have been thoroughly analysed and surveyed by Gaur and Wunderlich.[68]

The heat capacity of vitreous atactic PP increases smoothly with increasing temperature in the range from 0 to 230 K; at 230 K, a more rapid rise of the heat capacity is observed, apparently owing to the onset of devitrification. The heat capacity of crystalline PP also increases smoothly with temperature in the range 0–280 K. At $T > 280$ K, the growth of C_p° accelerates, which may be associated with the onset of the fusion of the polymer. In the highly elastic and liquid states, C_p° is a linear function of temperature.

In the crystalline state, the heat capacities C_p° of isotactic and syndiotactic PP are virtually identical; in the liquid state, the heat capacities of atactic, isotactic, and syndiotactic PP are identical in the experimental temperature range.

The heat capacity of vitreous PP is higher throughout than that of crystalline PP. In the range from 20 to 150 K, the difference between the values of C_p° diminishes from 30% to 5%, in the range 150–200 K it is within the limits of 5%, while in the range 260–460 K the difference between the C_p° of highly elastic and crystalline PP is 25%. In the range 20–150 K and also between the glass transition temperature and the melting point, C_p° of partly crystalline PP is linear function of the degree of crystallinity. The heat capacity of a partly crystalline specimen is higher the lower its degree of crystallinity.

Polybut-1-ene. The temperature variation of C_p° of isotactic polybut-1-ene specimens in the partly crystalline and liquid states has been investigated in the range 5–630 K.[69–71] The degree of isotacticity of the test specimens was ~90% and the degree of crystallinity of the polymer varied from 44% to 83% depending on the crystallisation conditions. The crystalline component of polybut-1-ene formed under these conditions consisted of one crystalline modification or a mixture of two or three possible crystalline modifications: rhombohedral, tetragonal, and hexagonal structures, which are designated as forms I, II, and III respectively.[72]

Lebedev and coworkers[69] investigated a specimen of isotactic polybut-1-ene with a degree of crystallinity of 77%. The crystalline component of the specimen consisted of form I. The heat capacities of the specimen were measured in the temperature ranges 6–35 and 200–304 K. Dainton et al.[47] investigated C_p° of a polybut-1-ene specimen with a degree of crystallinity of 44%, the crystalline component of the polymer consisting of a mixture of two crystalline modifications: 37% of form I and 7% of form II. The heat capacity measurements were performed in the range 22–310 K. Bares and Wunderlich[71] published C_p° data for polybut-1-ene in the vitreous, highly elastic, and liquid states in the temperature range 10–600 K.

Wilski and Grewer [70] investigated C_p° of the polymer in the range 250–430 K, but do not quote numerical values, confining themselves to a plot of the temperature variation of C_p°.

A common feature of all the polybut-1-ene specimens investigated is the equality of the heat capacities virtually within the limits of the errors of measurement at temperatures below T_g° for the polymer. The values of C_p° of the melt, found by Lebedev and coworkers,[69] also agree with those published by Bares and Wunderlich.[71] In the range 22–33 K, the data of Dainton et al.[47] and Lebedev et al.[69] differ only within the limits of 1%, but in the range 0–22 K the heat capacities are significantly higher according to the results of Dainton et al.[47] However, one should bear in mind that Dainton et al.[47] obtained then by extrapolating the dependence of the measured values of C_p° on T in accordance with the Debye heat capacity function. In the range 200–220 K, which precedes the devitrification of the amorphous part of the polymer, the heat capacity according to the results of Lebedev et al.[69] is ~1.5% smaller than that measured by Dainton et al.[47] This can apparently be accounted for by the influence of the difference between the degrees of crystallinity (44% and 77%) on the heat capacity of polybut-1-ene in the given temperature range and, in particular by the difference between the effects of the reinforcement[11,73] of the vitreous component of the polymer by the crystals which hinder the excitation of the segmental mobility of the macromolecules. Overall, the temperature dependence of the heat capacity of polybut-1-ene is a typical $C_p^\circ = f(T)$ relation for partly crystalline polymers.

In order to obtain the temperature dependence of the heat capacities of polybut-1-ene in the crystalline and amorphous states from the experimental heat capacities of a partly crystalline polymer, use was made of the method described in detail by Lebedev.[11,60] This method is based on the fact that the C_p° of partly crystalline polymers at $T < T_g^\circ$ virtually agrees with the heat capacity of the polymers in the vitreous and crystalline states within the limits of the error of the measurement; the linear relation $C_p^\circ = f(T)$ in the range from 50–60 K up to the glass transition temperature is observed for all the chain polymers investigated hitherto.[26] The authors assumed that the extrapolation of C_p° of a partly crystalline polymer from T_g° to T_{fus}° correctly reflects the heat capacity of the polymer in the crystalline state, while the linear extrapolation of the heat capacity of the polymer in the liquid state to T_g° describes correctly, in its turn, the heat capacity of the polymer in the highly elastic state. All the above extrapolations are presented in Fig. 1. In order to obtain the temperature dependence of the heat capacity of the polymer in the highly elastic state (*EDL*), Bares and Wunderlich[71] extrapolated the temperature dependence of the heat capacity of liquid polybut-1-ene (*FE*) to T_g°.

Polyisobutylene. The results of calorimetric studies on the temperature dependence of the heat capacity of polyisobutylene in the vitreous and highly elastic states have been published by Ferry and Parks[74] and Furukawa and Reilly.[75] The measurements of C_p° were performed in adiabatic vacuum calorimeters. Ferry and Parks[74] studied the C_p° of a low-molecular-mass ($M_n = 49 \times 10^3$) polymer specimen in the range 118–295 K. Furukava and Reilly[75] investigated a high-molecular-mass ($M_n = 1.35 \times 10^6$) polymer with a narrow molecular mass distribution ($M_w/M_n = 1.16$). Comparison shows that the heat capacity of the low-molecular-mass polyisobutylene is always 1%–2% higher than that of the high-molecular-mass polymer, apparently as a consequence of the difference between the molecular masses of the test specimens (by a factor greater than 3000). The nature and characteristics of the variation of the heat capacities of the low- and high-molecular-mass polyisobutylenes do not exhibit any differences: the heat capacities C_p° of the polymer in the vitreous and crystalline states increase smoothly with increase in temperature; in the vitrification ranges, $C_p^\circ = f(T)$ varies in the usual way.[11] Wunderlich and Baur[21] averaged the values of C_p° quoted by Ferry and Parks[74] and Furukawa and Reilly[75] and published a table of the heat capacities of polyisobutylene in the range 0–380 K.

Polypent-1-ene. The temperature variation of the heat capacity of isotactic polypent-1-ene has been investigated by Wunderlich and coworkers[76] in the range 220–430 K and by Lebedev et al.[77] in the range 9–500 K. The degree of isotacticity of the test polymer specimens was 80%–95% and their degree of crystallinity was 0%[76] and 60%.[77] The experimental values of C_p° quoted in the above studies[76,77] agree to within 1%. The temperature variation of the heat capacity of polypent-1-ene is typical for partly crystalline polymers. In the range 220–260 K, the amorphous component devitrifies, whilst in the range 330–390 K the crystalline component melts. The heat capacities of the polymer in the crystalline and amorphous states were found by extrapolation, as for polybut-1-ene (see above).

Poly-3-methylbut-1-ene. The temperature variation of the heat capacity of isotactic poly-3-methylbut-1-ene has been investigated by Lebedev and coworkers[78] in the range 8.5–650 K. The degree of isotacticity of the test specimen was ~95% and its degree of crystallinity 70%. On cooling melts of the initial specimen, the degree of crystallinity changed from 50% to 88% during their crystallisation and annealing. The amorphous component of the polymer devitrified in the range 300–370 K and the crystalline component melted in the range 500–610 K. Some irregularity in the temperature variation of C_p° in the range 370–500 K is probably associated with the recrystallisation processes during the heating of the polymer. The temperature variation of the heat capacity in the range 8.5–300 K exhibits no singularities of any kind: C_p° increases smoothly with increasing temperature. Immediately after the end of fusion, small endothermic effects were noted on the temperature variation of the heat capacity. For example, such an effect occurred for the initial poly-3-methylbut-1-ene specimen in the range 605–620 K. The maximum heat capacity $C_{p,max}^\circ = 230.0$ J mol^{-1} K^{-1} corresponds to 612 K. The

deviation of the heat capacity from its normal value at this temperature is ~8 J mol^{-1} K^{-1}.

It is noteworthy that the disposition of the $C_p^\circ = f(T)$ curves for the melt depended on the previous history of the specimens. This can apparently be accounted for by the retention of a certain amount of structure in the polymer after the fusion of its crystalline component and its subsequent decomposition, which requires an energy expenditure. A similar phenomenon has been observed also for poly-4-methylpent-1-ene.

Polyhex-1-ene. Bourderiat et al.[49] published the results of a study of the temperature variation of the heat capacity of polyhex-1-ene in the range 20–300 K. The measurements were performed in an adiabatic vacuum calorimeter. The test polymer specimen exists in the above temperature range in the vitreous and highly elastic states (Fig. 3). Devitrification occurs in the range 200–225 K. In other respects, the temperature dependence of the heat capacity of polyhex-1-ene exhibits no singularities, increasing smoothly with temperature. The error of the measurements of C_p° was 0.2%–0.4%. We may note that this type of $C_p^\circ = f(T)$ relation is typical for fully amorphous polymers.

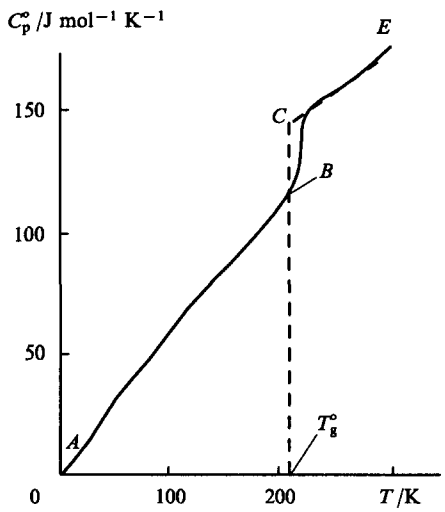


Figure 3. Typical temperature dependence of the heat capacity of an amorphous polymer for isotactic polyhex-1-ene as an example.[49]
State of the polymer: *AB* — vitreous, *CE* — highly elastic; *BC* — increase in heat capacity on devitrification.

Poly-4-methylpent-1-ene. The temperature variation of the heat capacity of isotactic poly-4-methylpent-1-ene was investigated by Karasz et al.[48] in the range 77–540 K, by Melia and Tyson[79] in the range 80–320 K, and by Lebedev et al.[80] in the range 7–670 K. The degree of isotacticity of the test specimens was ~95 and the degree of crystallinity was 30%,[48] 65%,[79] and between 35% and 40%.[80] The experimental values obtained by Lebedev et al.[80] in the range 77–300 K are smaller by ~1% than the data published by Karasz et al.[48] and higher by 0.5%–1.7% than the results quoted by Melia and Tyson,[79] the scatter of the experimental points being ~2%.

Figure 4 presents the temperature variation of the heat capacity of poly-4-methylpent-1-ene. The amorphous component of the polymer devitrified in the range 270–320 K and the crystalline component melted in the range 470–557 K for the initial specimen and 450–550 K for specimens obtained on cooling and crystallisation of the initial specimen.

Apart from devitrification and fusion, two additional anomalies in the heat capacity were manifested on the $C_p^\circ = f(T)$ curve for the initial polymer specimen: one in the range 360–390 K (between the glass transition temperature and the melting point) and the other in the range 575–600 K (at temperatures above the melting temperature range, i.e. in the polymer melt). In all the

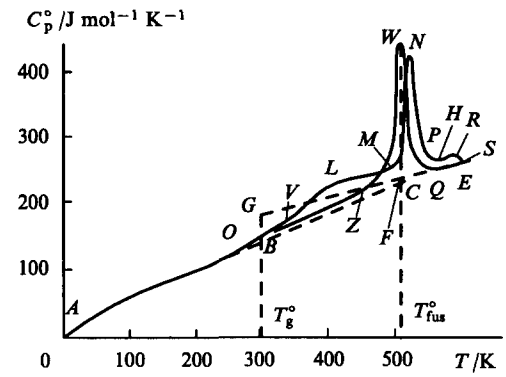


Figure 4. Heat capacity of isotactic poly-4-methylpent-1-ene.[48,79,80]
State of the polymer: *ABC* — crystalline, α = 100%, *AB* — vitreous, *GF* — highly elastic, *FQE* — liquid (isotropic melt). *AOVLMNPHRS* — heat capacity of the initial specimen (after synthesis and purification): *AB* — partly crystalline, α = 35%, amorphous component of the polymer in the vitreous state; *OVLM* — partly crystalline, α = 35%, amorphous component in the highly elastic state; *MNP* — apparent heat capacity in the melting range; *PHRS* — heat capacity of a melt containing condis-crystals, *HRS* — apparent heat capacity in the melting range of the condis-crystals, *AOZ* — heat capacity of the polymer with α = 40% (obtained by cooling the melt of the initial specimen), amorphous component of the polymer in the vitreous state from 0 K to T_g°, amorphous component of the polymer in the highly elastic state from T_g° to 440 K (point *Z*); *ZWQ* — apparent heat capacity in the melting range.

subsequent experiments, these anomalies were not reproduced. The dependences of the heat capacity in the temperature range corresponding to the end of devitrification and up to the temperature of the onset of fusion coincided within the limits of 1.5%. The errors of the measurements were approximately the same. In each of the experiments, the heat capacity of the melt increased smoothly with rising temperature from T_{fus}° to 610–670 K, but the positions of the $C_p^\circ = f(T)$ curves relative to one another fell systematically from experiment to experiment becoming stabilised only in the fourth–fifth experiments (*QE*). At 600 K, C_p° decreased by ~5.5% from the first to the fourth and fifth experiments. The anomaly in the heat capacity in the range $T_g^\circ - T_{fus}^\circ$ was discovered by Karasz et al.[48] Its appearance was attributed to the presence in the poly-4-methylpent-1-ene specimens, together with the main crystalline modification, of a small amount of another crystalline modification formed in the synthesis of the polymer. Hitherto five different crystalline modifications are known for this polymer.[81,82] The anomaly in C_p° in the poly-4-methylpent-1-ene melt is apparently caused by the presence in the latter of mesomorphic formations,[83] which gradually decompose from experiment to experiment during the measurements of the heat capacities of the melts. In the fourth and fifth experiments,[80] the melt probably becomes fully isotropic.

Polydec-1-ene. The temperature variation of the heat capacity of isotactic polydec-1-ene has been investigated in adiabatic vacuum and dynamic calorimeters in the range 5–450 K.[78,84] The degree of isotacticity of the test polymer was 90% and its degree of crystallinity was 35%. Approximately 200 experimental values of C_p° were obtained in 20 series reflecting the sequence of the measurements. The averaged $C_p^\circ = f(T)$ curves are presented in Fig. 5. The amorphous component of the polymer devitrified in the temperature range 190–230 K (*NP*).

The fusion of the crystalline component of polydec-1-ene was observed in the to range 240–315 K; it occurred in two stages, to each of which corresponded an apparent temperature variation of the heat capacity: *RZQM* and *MUSF*. It was found that polyolefins with bulky side substituents form crystals, like other polymers with a similar structure,[85] as a result of the crystallisation of the main polymer chains and the crystallisation of the side substituents;[86] for polydec-1-ene, they are designated by crII and

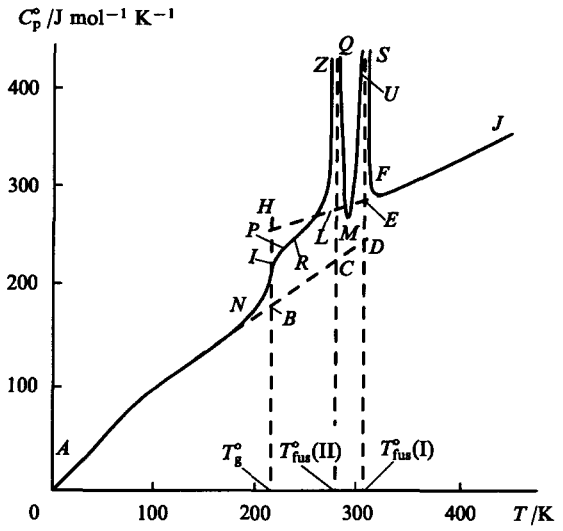


Figure 5. Heat capacity of isotactic polydec-1-ene. [84]
State of the polymer: *ABC* — crII and crI crystals, *CD* – crI crystals; *AB* — vitreous, *HLE* — highly elastic, *EJ* — liquid; *ANPR* — partly crystalline (α = 35%): the amorphous component of the polymer in the vitreous state along section *AN* and in the highly elastic state along section *PR*; *NP* — heat capacity in the vitrification range; *RZQM* — apparent heat capacity in the melting range of crII crystals; *MUSF* — apparent heat capacity in the melting range of crI crystals.

crI respectively. On slow cooling of the polymer melt, it was possible to measure its heat capacity in the supercooled (highly elastic) state between 270 K and a temperature below the melting points of crII and crI crystals. The attempts at a more extensive supercooling terminated in each case by the spontaneous crystallisation of the polymer with the simultaneous formation of crI and crII crystals, after which the heat capacity was described by the *RZQMUSF* curve (Fig. 5). The temperature variation of the heat capacity of the polymer in the partly crystalline (*AN*), supercooled liquid (*LE*), and liquid (*EFJ*) states exhibits no singularities of any kind: it increases smoothly with increasing temperature.

V. Thermodynamic parameters of fusion

The thermodynamic parameters of fusion have been obtained for all the polyolefins investigated (Table 2) with the aid of dynamic calorimeters. The temperature corresponding to the maximum apparent heat capacity in the melting range of the polymer was adopted as the melting point T_{fus}°. For example, for polybut-1-ene this is the temperature at point *H* in Fig. 1. The results of experiments with the lowest rate of heating of the calorimeter with the test substance ($< 2.7 \times 10^{-2}$ K s^{-1}) were normally employed for this purpose in accordance with the recommendations of Bernshtein and Egorov.[87] The enthalpies of fusion $\Delta_{fus}H^\circ(\alpha)$ were measured as a rule in three experiments and the average result with an arithmetical mean deviation was adopted as $\Delta_{fus}H^\circ(\alpha)$. In a separate experiment, $\Delta_{fus}H^\circ(\alpha)$ was calculated as the difference between the integrals of the temperature variations of C_p° in the melting range, obtained from the apparent (*QSHUT*) and normal (*QPDE*) heat capacity curves (Fig. 1). All the polymers investigated were partly crystalline with the exception of the fully amorphous polyisobutylene and polyhex-1-ene. The enthalpies of fusion $\Delta_{fus}H^\circ(\alpha)$ were obtained in experiments for a degree of crystallinity α. The molar enthalpies of fusion of the fully crystalline polymers were calculated from the formula [88]

$$\Delta_{fus}H^\circ(\alpha = 100\%) = 100\,\frac{\Delta_{fus}H^\circ(\alpha)}{\alpha}. \qquad (6)$$

The entropy of fusion $\Delta_{fus}S^\circ(\alpha = 100\%)$ was calculated from the values of $\Delta_{fus}H^\circ(\alpha = 100\%)$ and T_{fus}° by the formula

$$\Delta_{fus}S^\circ(\alpha = 100\%) = \frac{\Delta_{fus}H^\circ(\alpha = 100\%)}{T_{fus}^\circ}. \qquad (7)$$

We shall now consider the characteristic features of the behaviour of certain polyolefins on fusion and crystallisation. Depending on the conditions in the crystallisation of polybut-1-ene (the nature of the solvent, the rate of cooling of the melts, etc.), crystals of forms I, II, and III are produced. On heating, the crystals usually melt without interconversions, but Clampitt and Hughes [89] observed a spontaneous transition of the crystals of form II into those of form I, which occurred at ~300 K in the course of seven days. The temperatures and enthalpies of fusion of crystals of forms I–III, measured calorimetrically, have been published by Lebedev et al.[69] and those of crystals of forms I and II have been published by Wilski and Grewer.[70]

As an example, we shall consider the results of an experiment designed to determine the thermodynamic parameters of the fusion of polybut-1-ene published by Lebedev et al.[69] Fig. 6 presents the temperature variations of the heat capacity of the initial polymer specimen (curve *1*) and the specimens obtained by crystallising its melt directly in the calorimeter on cooling from 500 to 200 K at different rates: 5×10^{-2} (curve *2*) and 1.5×10^{-2} K s (curve *3*). The initial specimen was crystallised from solution in isooctane during its precipitation with isopropyl alcohol, whereupon the crystalline form III was formed. Crystals of form III melted in the range 280–385 K and their fusion was completed by the onset of the crystallisation of the melt in form II. This is indicated by an exothermic process which completes the

Table 2. Thermodynamic parameters of the fusion of polyolefins.

Polymer	Crystal[a]	T_{fus}°/K	$\Delta_{fus}H^\circ$ /kJ mol^{-1}	$\Delta_{fus}S^\circ$ /J mol^{-1} K^{-1}	$\Delta C_p^\circ(T_{fus}^\circ)$ /J mol^{-1} K^{-1}	Ref.
Polyethylene	cr	414.6	8.8±0.1	21.2±02	–	65, 83
Polydeuteroethylene	cr	415	–	–	–	67
Polypropylene	cr	460.7	9.2±0.8	20.0±1.6	–	68, 83
Polybut-1-ene	crI	406.8	7.11	17.5	15.7	69, 70
	crII	393.0	3.68	9.36	–	69, 70
	crIII	374.0	2.67	7.14	–	69
Polypent-1-ene	cr	388	5.58	14.4	16.1	77, 83
Poly-3-methylbut-1-ene	cr	584	6.04	10.4	1.5	78
Poly-4-methylpent-1-ene	cr	508	10.2	19.5	11.5	80
Polydec-1-ene	crII	276	6.43	23.3	–	84
	crI	301	7.23	24.0	39.0	78

[a] crI – crIII are different crystalline forms.

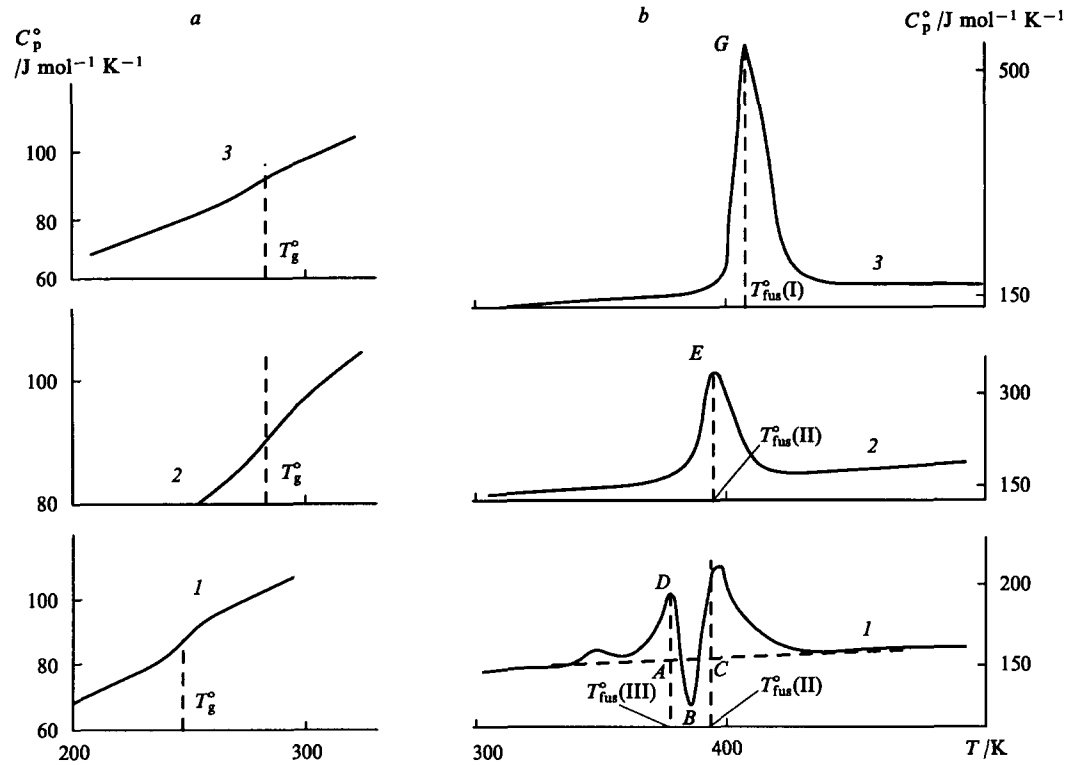


Figure 6. Heat capacity of isotactic polybut-1-ene in the temperature ranges 200–300 K (*a*) and 300–600 K (*b*) (according to dynamic calorimetric data, heating rate 1.7×10^{-2} K s^{-1}).
(*1*) Specimen containing 65% of crystals of form III (with a hexagonal structure) and after their fusion and crystallisation of the amorphous component — crystals of form II (with a tetragonal structure); (*2*) specimen containing 83% of crystals of form II; (*3*) specimen containing 77% of crystals of form I (with a rhombohedral structure).

fusion of crystals of form III and precedes the fusion of crystals of form II (the *ABC* exotherm in Fig. 6*b*, curve *1*). The crystals of form II produced melted in the range 340–420 K (the endotherm in the same figure). We may note that, on crystallisation from solution, the initial specimen had a degree of crystallinity of 65% (crystals of form III).

On cooling of the melt at a rate of 5×10^{-2} K s^{-1}, crystals of form II, constituting 83% of the mass of the specimen, were formed. Crystals of form II melted in the range 340–420 K (Fig. 6*b*, curve *2*), as for the initial polybut-1-ene specimen (curve *1*). When the melt was cooled at a rate of 1.5×10^{-2} K s^{-1} (approximately three times lower than in the previous case), crystals of form I were produced, the degree of crystallinity amounting to 77%. The crystals melted in the range 350–450 K (curve *3*). We may note that at this or slightly higher rate of cooling of the melt, a mixture of crystals of forms I and II was formed (10% and 40% respectively). This has also been observed by Dainton et al.:[47] on slow cooling of the melt, a mixture consisting of 7% of crystals of form I and 37% of those of form II was obtained. The degree of crystallinity of the test polymer specimens was determined by Eqn (4) from the values of $\Delta C_p^\circ(\alpha)$ at the glass transition temperature. The values of $\Delta C_p^\circ(\alpha)$ were found graphically from the curves describing the temperature variation of the heat capacity and incorporating devitrification regions (Fig. 6**a**, curves *1–3*). $\Delta C_p^\circ(T_g^\circ)$ is 9.7 J mol^{-1} K^{-1} for the specimen containing crystals of form III, 4.3 J mol^{-1} K^{-1} for the specimen with crystals of form II, and 58 J mol^{-1} K^{-1} for the specimen with crystals of form I. The increase in heat capacity on devitrification of polybut-1-ene in the amorphous state is $\Delta C_p^\circ(\alpha = 0) = 27.5$ J mol^{-1} K^{-1} (section *BL* in Fig. 1).

The melting temperature ranges were determined graphically as the temperatures of the onset and end of the anomalous changes in heat capacity caused by fusion (apparent heat capacity endotherms in Fig. 6*b*, curves *1–3*). The temperatures corresponding to the maximum heat capacity in the melting range were adopted as the melting points (points *D*, *E*, and *G* on curves *1–3*). The enthalpies of fusion $\Delta H^\circ(\alpha)$ were determined by the method involving the continuous injection of energy: for the crystalline forms II and I in three experiments in each case and for form II in one experiment. This yielded $\Delta H^\circ(\alpha = 65\%) = 1.735$ kJ mol^{-1} for form III, $\Delta H^\circ(\alpha = 83\%) = 2.754$ kJ mol^{-1} for form II, and $\Delta H^\circ(\alpha = 77\%) = 5.475$ kJ mol^{-1} for form I. The molar enthalpies of fusion of each form were calculated by Eqn (5) from the corresponding values of $\Delta H^\circ(\alpha)$ and α. The entropies of fusion were calculated by Eqn (6) from the enthalpies of fusion and the melting points. All the thermodynamic parameters of fusion are listed in Table 2. The data of Lebedev et al.[69] and Wilski and Grewer [70] agree satisfactorily. Judging from the entropy of fusion, the crystalline form I (rhombohedral crystals) is most ordered, while form III is least ordered. Wilski and Grewer [70] established that form III is thermodynamically least stable. We may note that form III cannot be obtained under the conditions of calorimetric experiments on crystallisation of melts of isotactic polybut-1-ene. Furthermore, the determination of the melting temperature range for crystals of form III, crystallised from solution, is complicated by the onset of the crystallisation of the melt in form II, which masks the termination of the fusion of form III. All these factors preclude accurate measurements of the enthalpy of fusion of form III. The enthalpy and entropy of fusion of form III listed in Table 2 must therefore be regarded as only estimates.

According to data quoted by Andrianova [72] and Raff and Doak,[90] polypent-1-ene can exist in two crystalline modifications: I (crystals with a monoclinic lattice) and II (crystals with an orthorhombic lattice). It was established that polypent-1-ene usually exists in the crystalline modification I, while modification II is formed extremely rarely. The melting points of modifications I and II are respectively 403 and 348 K. The enthalpies of fusion of

the polymer have been published.[48,76,77] Their numerical values vary from 3.98 to 6.28 kJ mol^{-1}. The results of calorimetric measurements of the thermodynamic parameters of fusion[77] are listed in Table 2.

The thermodynamic characteristics of the fusion of poly-3-methylbut-1-ene were determined in four experiments.[78] In all the experiments, the fusion of the polymer began in the range from 500 to 540 K and ended at 610 K. The melting temperatures corresponding to the maximum apparent heat capacity varied in the melting range from 576.8 to 584.9 K from experiment to experiment. The rates of heating of the calorimeter with the test substance increased under these conditions from 1.7×10^{-2} to 3.3×10^{-2} K s^{-1}. Table 2 lists the value of T°_{fus} for the initial specimen (heating rate 1.7×10^{-2} K s^{-1}). For poly-3-methylbut-1-ene specimens with degrees of crystallinity of 50%, 70%, 81%, and 88%, the values of $\Delta_{fus}H^{\circ}(\alpha)$ = 3.04, 4.23, 4.91, and 5.31 kJ mol^{-1} respectively were obtained. They were recalculated for the polymer with 100% crystallinity by Eqn (6). The melting range of poly-3-methylbut-1-ene has been published as 513–583 K.[91] Minsker et al.[92] give T°_{fus} = 545 K for a specimen of isotactic poly-3-methylbut-1-ene with a degree of crystallinity of 90.5%.

Lebedev et al.[80] carried out five experiments on the fusion of poly-4-methylpent-1-ene (heating rate $\sim 3 \times 10^{-2}$ K s^{-1}) and obtained a series of melting points ranging from 521.7 K in the first experiment for the initial specimen to 508.5 K in the fifth experiment. A decrease in T°_{fus} from experiment to experiment was noted. In the fourth and fifth experiments, the values of T°_{fus} virtually coincided. A similar phenomenon has also been observed by Andrianova.[72] The arithmetical mean of the values of T°_{fus} found in the fourth and fifth experiments was adopted as T°_{fus} for poly-4-methylpent-1-ene (Table 2). The enthalpy of fusion of the crystalline component of the specimen, obtained in the first experiment, is lower than in the fourth and fifth experiments (in the latter experiments the values of $\Delta_{fus}H^{\circ}$ are virtually identical). The value found by Karasz et al.[48] was adopted as the enthalpy of fusion of the polymer with a crystallinity of 100%.

The apparent heat capacities in the melting range of crystals of forms II and I of isotactic polydec-1-ene were measured with continuous heating of the calorimeter containing the test substance at a rate of 8×10^{-3} K s^{-1}.[84] The temperature corresponding to the maximum apparent heat capacity $C^{\circ}_{p,max}$ = 555.3 J mol^{-1} K^{-1} in the melting range was adopted as the melting point T°_{fus}(II) of the crystals formed by the main chains; the temperature corresponding to $C^{\circ}_{p,max}$ = 495.3 J mol^{-1} K^{-1} in the melting range of crystals of form I was adopted as the melting point $C^{\circ}_{p,max}$ = (I) of the crystals formed by the side substituents. The enthalpies of fusion were found to be $\Delta_{fus}H^{\circ}(\alpha = 35\%; \text{II})$ = 2.25 kJ mol^{-1} and $\Delta_{fus}H^{\circ}(\alpha = 35\%; \text{I})$ = 2.53 kJ mol^{-1}. These values were recalculated for 100% crystallinity. The degree of crystallinity was calculated by Eqn (4) from calorimetric data:[84] $\Delta C^{\circ}_{p}(T^{\circ}_{g};\ \alpha = 0) = 60$ and $\Delta C^{\circ}_{p}(T^{\circ}_{g};\ \alpha) = 39$ J mol^{-1} K^{-1}. In the calculations of the degree of crystallinity, it was assumed that the value α found refers to crystals of both form II and I. This means that, on crystallisation of the main chains of the polymer, the corresponding amount of side substituents crystallises simultaneous. In several consecutive measurements of $\Delta_{fus}H^{\circ}$(II) and $\Delta_{fus}H^{\circ}$(I) for different degrees of crystallinity α, it was found that the ratio

$$\frac{\Delta_{fus}H^{\circ}(\text{II})}{\Delta_{fus}H^{\circ}(\text{I})} = 0.7 \pm 0.2.$$

is approximately constant.

VI. Parameters of vitrification and of the vitreous state

The parameters of the vitrification and the vitreous state of the polyolefins investigated are listed in Table 3. The glass transition temperature T°_{g} was determined from the point of inflection in the plots of the temperature variation of the entropy $S^{\circ}(T) = f(T)$ in the vitrification range. The error of the determination of T°_{g} by this method is usually 0.5–1.0 K.

The availability of the relations $C^{\circ}_{p} = f(T)$ for the amorphous and crystalline states and also of the temperatures and enthalpies of the physical transformations made it possible to estimate the differences between the enthalpies of the polymers in the vitreous and crystalline states $H^{\circ}_{g}(0) - H^{\circ}_{cr}(0)$ at T = 0 K and the residual (zero-point) entropy in the vitreous state $S^{\circ}_{g}(0)$. The corresponding calculations were performed by means of published equations,[11,33,93] which assumed the following form for polyolefins:

$$H^{\circ}_{g}(0) - H^{\circ}_{cr}(0) = \int_{0}^{T^{\circ}_{fus}} [C^{\circ}_{p}(\text{cr}) - C^{\circ}_{p}(\text{g})]\mathrm{d}T + \Delta_{fus}H^{\circ},$$

$$S^{\circ}_{g}(0) = \int_{0}^{T^{\circ}_{fus}} [C^{\circ}_{p}(\text{cr}) - C^{\circ}_{p}(\text{g})]\mathrm{d}\ln T + \Delta_{fus}S^{\circ},$$

where C°_{p}(cr) and C°_{p}(g) are the temperature functions of the heat capacities of the polymer in the crystalline and vitreous states respectively.

The configurational entropy S°_{conf} of the vitreous polymer was calculated by Eqn (3). The Kauzmann temperature T°_{2} was found graphically from the entropy diagram, as had been done, for example, for polybut-1-ene (Fig. 7). The ratio $T^{\circ}_{g}/T^{\circ}_{2}$ for the polymeric and monomeric glasses is usually 1.29,[37,38] so that S°_{conf} was estimated from the formula[37]

$$S^{\circ}_{conf} = \Delta C^{\circ}_{p}(T^{\circ}_{g}) \ln 1.29.$$

It is especially convenient for the estimation of S°_{conf} for vitrifying but not crystallising polymers.

According to dynamic calorimetric data,[69] the devitrification of polybut-1-ene specimens (Fig. 6) with degrees of crystallinity of 65%, 77%, and 83% occurred in the temperature ranges 230–255 K, 265–270 K, and 270–295 K respectively. The glass transition temperatures of these specimens were found to be 249 K for the first and 282 K for the other two. A dependence of

Table 3. Parameters of the vitrification process and of the vitreous state of polyolefins.

Polymer	T°_{g} /K	$\Delta C^{\circ}_{p}(T_{g})$	$S^{\circ}_{g}(0)$	S°_{conf}	$H^{\circ}_{g}(0) - H^{\circ}_{cr}(0)$	Ref.
		J mol^{-1} K^{-1}			/kJ mol^{-1}	
Polyethylene	237	21.0	5.4	3.2	5.0	65
Polypropylene	260	19.2	1.1	4.4	4.2	68
Polybut-1-ene	249	27.5	6.7	7.0	3.7	69
Polyisobutylene	200	22.6	–	5.7	–	76
Polypent-1-ene	238	21	3.8	2.3	2.4	77
Poly-3-methylbut-1-ene	327	32.1	0	8.2	1.9	78
Polyhex-1-ene	216	29	–	7.4	–	49,96
Poly-4-methylpent-1-ene	300	33.6	8	8.6	5.6	80
Polydec-1-ene	208	60	26	15.3	8.4	84

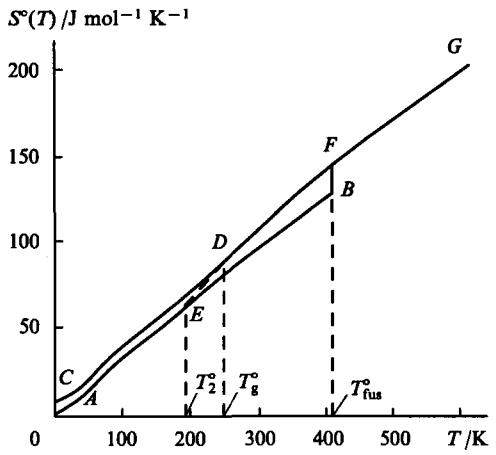


Figure 7. Entropy diagram for polybut-1-ene.
State of the polymer: *AEB* — crystalline, *CD* — vitreous, *DF* — highly elastic, *FG* — liquid, *ED* — hypothetical glass; *AC* — residual (zero-point) entropy of the glass, *BF* — entropy of fusion.

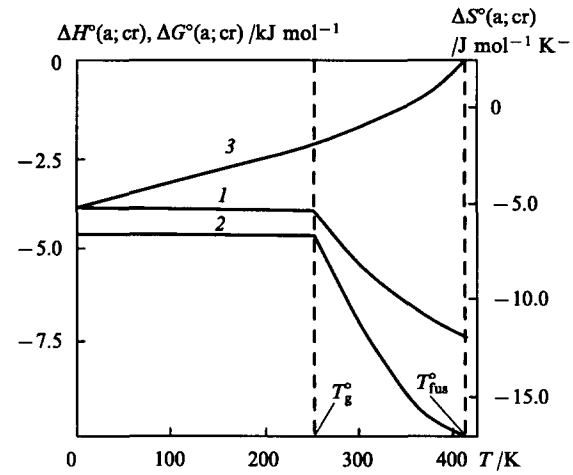


Figure 8. Temperature dependences of the enthalpy (*1*), entropy (*2*), and Gibbs free energy (*3*) of the transition of polybut-1-ene from the amorphous to the crystalline state in the temperature range from 0 K to T°_{fus}.

the vitrification temperature ranges and of the glass transition temperatures on the degree of crystallinity of the test specimens was traced. The higher the values of α, the higher the temperature range to which the temperature range of vitrification and T_g° are displaced. This is apparently caused by the effect due to the reinforcement of the vitreous component of the polymer by crystals,[73] as a consequence of which difficulties arise in the excitation of the segmental mobility of the polybut-1-ene macromolecules. The temperature T_g° obtained for poly-3-methylbut-1-ene agrees satisfactorily with $T_g^\circ = 327$ K published by Andrianova.[72] It is of interest that the zero-point entropy of this polymer in the vitreous state was found to be zero. Strictly speaking, within the limits of experimental error and the errors associated with the assumptions made in calculations, it is equal to the zero-point entropy of the polymer in the crystalline state. It has been shown[11,93] that $S^\circ_{cr}(0) = 0$ for polymers in the crystalline state. Apparently, the same features are characteristic of poly-3-methylbut-1-ene as for poly-4-methylpent-1-ene.[80] With decrease in the degree of crystallinity, the density of the amorphous part of the polymer increases, i.e. short-range order becomes more marked with decrease in the long-range order in the disposition of the units of the macromolecules in the crystal lattice.[80] As a result of the operation of these two effects (the increase in entropy on breakdown of long-range order and its diminution on enhancement of short-range order), the entropy changes are compensated because the above factors act in opposition.

For polyolefins at 0 K, the difference between the enthalpies of the vitreous and crystalline states varies from 1.9 kJ mol^{-1} (for poly-3-methylbut-1-ene) to 8.4 kJ mol^{-1} (for polydec-1-ene). The error in the values of $H^\circ_g(0) - H^\circ_{cr}(0)$ is $\sim 10\%$. Vitreous polymers, which are in principle capable of crystallising, exist in a metastable state owing to the high activation energy for the rearrangement and the extremely long relaxation times associated with this fact. Clearly the difference between the Gibbs free energies of the vitreous and crystalline states ΔG°(a; cr) constitutes an estimate of the metastability of the amorphous polymer under the given conditions. For the temperature range between 0 K and T°_{fus}, the above quantity may be calculated from the difference between the enthalpies ΔH°(a; cr) and the entropies ΔS°(a; cr) of the amorphous and crystalline states at any temperature within the above range by the formula[11]

$$\Delta G^\circ(\text{a; cr}) = \Delta H^\circ(\text{a; cr}) - T\Delta S^\circ(\text{a; cr}),$$

ΔH°(a; cr) and ΔS°(a; cr) can be readily calculated in their turn from the values of $H^\circ_g(0) - H^\circ_{cr}(0)$ and ΔS° and the temperature variations of the heat capacities of the polymer in the amorphous (vitreous and highly elastic) and crystalline states in the above temperature range, as has been done, for example, in the studies of Lebedev and coworkers.[7,94] Typical temperature variations of ΔG°(a; cr), ΔH°(a; cr), and ΔS°(a; cr) are presented in Fig. 8 in relation to polybut-1-ene.

VII. Thermodynamic functions

The thermodynamic functions of polyolefins in the range 0–600 K have been calculated with the aid of their experimental heat capacities and the temperatures and enthalpies of the physical transformations. For this purpose, the heat capacity of the polymer was usually extrapolated from 5–10 to 0 K using the Debye function[59]

$$C_p^\circ = nD\left(\frac{\theta_D}{T}\right), \qquad (8)$$

where n and θ_D are specially selected parameters. They are usually chosen so that Eqn (8) describes the experimental heat capacities C_p°, or the average heat capacities for the range 5–15 K obtained from them, subject to an error not exceeding 1%–1.5%. In the calculation of the functions, it was assumed that at $T < 5$–10 K the above equation reproduces the heat capacity of the polymer with the same error. Wunderlich[95] usually employed the two-parameter Tarasov heat capacity function [see Eqn (2)] to extrapolate the heat capacities of polymers. For example, the corresponding characteristic temperatures for polyethylene in the crystalline state are $\theta_1 = 519$ K and $\theta_3 = 158$ K.

The heat capacity of polyhex-1-ene was extrapolated from 20 to 0 K in terms of the specially selected equation[96]

$$C_p^\circ = 0.0258T + 0.02950\,T^2 + 0.000417\,T^3.$$

Since virtually all the polymers investigated are partly crystalline with the exception of polyisobutylene and polyhex-1-ene, their thermodynamic functions were calculated by the method which makes it possible to evaluate the functions of the polymers in the fully amorphous and crystalline states from the experimental data on properties of the partly crystalline polymers.[11,36]

The functions (Table 4) were calculated on a computer by means of the equations[11,94]

$$H^\circ(T) - H^\circ(0) = \sum \int_0^T C_p^\circ(T)\,dT + \sum \Delta_{fus}H^\circ,$$

$$S^\circ(T) = \sum \int_0^T C_p^\circ(T)\,d\ln T + \sum \Delta_{fus}S^\circ,$$

Table 4. Thermodynamic functions of polyolefins under standard pressure.

T/K	$C_p^\circ(T)$	$H^\circ(T) - H^\circ(0)$	$S^\circ(T)$	$-[G^\circ(T) - H^\circ(0)]$
Polyethylene [65]				
Crystalline state				
5	0.0249	0.000032	0.0084	0.00001
10	0.1931	0.000488	0.0654	0.000176
15	0.6336	0.002416	0.2158	0.000821
20	1.459	0.007468	0.5008	0.00255
25	2.446	0.01718	0.9306	0.00609
30	3.676	0.03242	1.482	0.01205
40	6.376	0.08226	2.898	0.03366
50	9.046	0.1598	4.618	0.07106
100	18.91	0.8808	14.22	0.5410
150	25.74	2.004	23.24	1.481
200	31.14	3.428	31.40	2.850
250	37.10	5.128	38.96	4.610
298.15	43.40	7.070	46.04	6.656
350	49.32	9.474	53.46	9.238
400	54.76	12.08	60.40	12.08
414.6	56.32	12.89	62.40	12.98
Liquid state				
414.6	71.70	21.66	83.58	12.98
450	74.76	24.27	89.56	16.03
500	79.08	28.16	97.68	20.72
550	83.41	32.17	105.4	25.80
600	87.74	36.44	112.9	31.26
Vitreous state				
0	0	0	5.4	0
5	0.1133	0.000139	5.44	0.0270
10	0.7418	0.002046	5.68	0.0547
15	1.756	0.0082	6.26	0.0857
20	2.804	0.01966	6.81	0.1165
25	3.978	0.03574	7.56	0.1525
30	5.210	0.0595	8.396	0.1924
40	7.800	0.1245	10.24	0.2854
50	10.29	0.2150	12.26	0.3979
100	19.49	0.9766	22.45	1.269
150	28.12	2.162	31.94	2.629
200	37.20	3.796	41.28	4.460
Highly elastic state				
250	57.44	6.034	51.18	6.761
298.15	61.62	8.900	61.66	9.484
350	66.12	12.21	71.88	12.95
400	70.44	15.63	81.00	16.77
414.6	71.70	16.66	83.58	17.99
Polydeuteroethylene [67]				
Crystalline state				
5	0.6056	0.00035	0.0748	0.000023
10	0.4884	0.00180	0.2752	0.000949
15	1.293	0.00610	0.6116	0.003080
20	2.392	0.01521	1.128	0.007353
25	3.750	0.03044	1.802	0.01461
30	5.270	0.05301	2.621	0.02561
40	8.315	0.1209	4.553	0.06120
50	11.51	0.2198	6.745	0.1144
100	21.33	1.076	18.22	0.7457
150	29.15	2.335	28.32	1.913
200	37.89	4.007	37.88	3.569
250	46.16	6.104	47.20	5.697
298.15	54.13	8.518	56.02	8.183
300	54.52	8.619	56.35	8.287
350	62.92	11.55	65.38	11.33
400	71.25	14.91	74.34	14.82
415	74.00	16.04	77.12	16.01

T/K	$C_p^\circ(T)$	$H^\circ(T) - H^\circ(0)$	$S^\circ(T)$	$-[G^\circ(T) - H^\circ(0)]$
Polypropylene [68]				
Crystalline state				
10	0.5538	0.001099	0.1342	0.000242
20	3.572	0.02043	1.354	0.006638
30	7.065	0.04381	3.470	0.03028
40	10.20	0.1605	5.942	0.07718
50	13.02	0.2768	8.526	0.1494
100	26.25	1.258	21.60	0.9022
150	37.57	2.862	34.46	2.306
200	47.63	4.994	46.66	4.336
298.15	65.17	10.56	69.05	10.03
350	73.94	14.16	80.16	13.90
400	82.42	18.07	90.61	18.17
450	90.90	22.40	100.8	22.96
460.7	92.72	23.39	103.0	24.05
Liquid state				
460.7	112.7	32.59	123.0	24.05
500	118.6	37.14	132.5	29.10
Vitreous state				
0	0	0	1.1	0
10	1.076	0.002311	1.39	0.0116
20	5.077	0.03262	3.33	0.0340
30	8.721	0.1021	6.10	0.0810
40	11.89	0.2054	9.05	0.1571
50	15.01	0.3398	12.03	0.2617
100	28.51	1.445	26.83	1.238
150	39.48	3.152	40.52	2.926
200	49.63	5.374	53.24	5.274
260	64.92	8.792	68.09	8.911
Highly elastic state				
260	82.29	8.792	68.09	8.911
298.15	88.07	12.05	79.76	11.73
350	95.91	16.81	94.48	16.26
400	103.5	21.80	107.8	21.32
450	111.0	27.16	120.4	27.02
460.7	112.7	28.36	123.0	28.31
Polybut-1-ene [69]				
Crystalline state (crI)				
5	0.1943	0.00023	0.0585	0.00005
10	1.350	0.0037	0.4883	0.0012
15	3.272	0.0150	1.382	0.0057
20	5.480	0.0368	2.620	0.0156
25	7.790	0.0699	4.091	0.0323
30	10.11	0.1147	5.714	0.0567
40	14.86	0.2396	9.272	0.1313
50	19.26	0.4105	13.07	0.2428
100	37.78	1.848	32.26	1.378
150	53.37	4.138	50.62	3.455
200	67.39	7.167	67.95	6.423
250	80.36	10.86	84.39	10.23
298.15	92.85	15.03	99.61	14.67
300	93.33	15.20	100.2	14.85
350	106.3	20.19	115.5	20.25
400	119.3	25.83	130.6	26.40
406.8	121.0	26.65	132.6	27.29
Liquid state				
406.8	136.7	33.76	150.1	27.29
450	144.7	39.83	164.3	34.08
500	153.9	47.29	179.9	42.69
550	163.1	55.22	195.1	52.07
600	172.3	63.61	209.7	62.19

Table 4 (continued).

T/K	$C_p^\circ(T)$	$H^\circ(T) - H^\circ(0)$	$S^\circ(T)$	$-[G^\circ(T) - H^\circ(0)]$
Polybut-1-ene [69]				
Vitreous state				
0	0	0	6.7	0
50	19.26	0.4105	19.7	0.576
100	37.78	1.848	38.9	2.04
150	53.37	4.138	57.3	4.46
200	67.39	7.167	74.6	7.76
249	80.10	10.78	90.7	11.8
Highly elastic state				
249	107.6	10.78	90.7	11.8
298.15	116.7	16.29	110.9	16.8
300	117.0	16.51	111.6	17.0
350	126.2	22.59	130.4	23.1
400	135.5	29.13	147.9	30.0
406.8	136.7	30.06	150.1	31.0
Polyisobutylene				
Vitreous state				
0	0	0	5.70	0
5	0.129	0.000084	5.74	0.02861
10	1.010	0.00254	6.04	0.0579
15	3.007	0.01243	6.81	0.0896
20	4.662	0.03167	7.91	0.1264
25	6.300	0.05918	9.12	0.1689
30	7.838	0.09448	10.41	0.2177
40	10.76	0.1877	13.07	0.3350
50	13.68	0.3098	15.78	0.4793
100	30.97	1.411	30.36	1.625
150	48.59	3.406	46.29	3.538
200	64.50	6.234	62.45	6.257
Highly elastic state				
200	87.11	6.234	62.45	6.257
250	97.79	10.84	82.97	9.901
298.15	109.3	15.82	101.2	14.34
300	109.7	16.03	101.8	14.53
350	122.4	21.83	119.7	20.07
380	130.2	25.61	130.1	23.82
Polypent-1-ene [77]				
Crystalline state				
5	0.266	0.00033	0.081	0.00007
10	1.765	0.00488	0.649	0.0016
15	3.815	0.0185	1.722	0.0074
20	6.881	0.0447	3.209	0.0195
25	10.93	0.0891	5.171	0.0402
30	14.24	0.1524	7.473	0.0717
40	20.06	0.3244	12.38	0.1708
50	25.48	0.5524	17.44	0.3198
100	49.15	2.447	42.75	1.828
150	67.95	5.392	66.38	4.565
200	85.90	9.248	88.44	8.441
250	104.1	14.00	109.6	13.39
298.15	121.5	19.43	129.4	19.15
300	122.2	19.66	130.2	19.39
350	140.4	26.22	150.4	26.40
388	154.1	31.82	165.5	32.39
Liquid state				
388	170.2	37.40	179.9	32.39
400	173.8	39.46	185.1	34.60
450	188.5	48.52	206.5	44.39
500	203.2	58.31	227.1	55.23
Vitreous state				
0	0	0	3.8	0
5	0.266	0.00033	3.9	0.0192
10	1.765	0.00488	4.5	0.0401
15	3.815	0.0185	5.5	0.064
20	6.881	0.0447	7.0	0.095
25	10.93	0.0891	9.0	0.1359
30	14.24	0.1524	11.3	0.1866
40	20.06	0.3244	16.2	0.3236
50	25.48	0.5524	21.2	0.5076
100	49.15	2.447	46.6	2.213
150	67.95	5.392	70.2	5.135
200	85.90	9.248	92.2	9.200
238	105.0	12.78	108.4	13.02
Highly elastic state				
238	126.0	12.78	108.4	13.02
250	129.6	14.32	114.7	14.36
298.15	143.8	20.90	138.8	20.48
300	144.4	21.17	139.6	20.71
350	159.1	28.75	163.0	28.30
388	170.2	35.01	179.9	34.79
Poly-3-methylbut-1-ene [78]				
Crystalline state				
5	0.564	0.000738	0.190	0.00021
10	2.874	0.00902	1.241	0.00339
15	4.873	0.02875	2.813	0.01345
20	7.390	0.05992	4.582	0.03172
25	10.35	0.1056	6.608	0.05965
30	13.18	0.1641	8.736	0.09795
40	18.84	0.3253	13.33	0.2080
50	23.60	0.5383	18.07	0.3650
60	28.24	0.7966	22.76	0.5691
70	32.78	1.102	27.46	0.8203
80	37.45	1.453	32.14	1.118
90	41.92	1.850	36.81	1.463
100	46.08	2.290	41.45	1.854
150	64.65	5.068	63.72	4.490
200	81.70	8.729	84.67	8.204
250	99.00	13.26	104.8	12.94
298.15	116.2	18.47	123.8	18.44
300	117.0	18.69	124.5	18.67
350	132.8	24.94	143.8	25.38
400	148.5	31.97	162.5	33.04
450	163.9	39.78	180.9	41.62
500	179.4	48.36	199.0	51.12
550	194.5	57.71	216.8	61.52
584	204.7	64.50	228.7	69.09
Liquid state				
584	206.0	70.54	239.1	69.09
600	210.0	73.87	244.7	72.97
640	216.2	82.40	258.5	83.03
Vitreous state				
0	0	0	0	0
5	0.564	0.000738	0.190	0.00021
10	2.874	0.00902	1.241	0.00339
15	4.873	0.02875	2.813	0.01345
20	7.890	0.05992	4.582	0.03172
25	10.35	0.1056	6.608	0.05965
30	13.18	0.1641	8.736	0.09795
40	18.84	0.3253	13.33	0.2080

Table 4 (continued).

T/K	$C_p^\circ(T)$	$H^\circ(T) - H^\circ(0)$	$S^\circ(T)$	$-[G^\circ(T) - H^\circ(0)]$
Poly-3-methylbut-1-ene [78]				
Vitreous state				
50	23.60	0.5383	18.07	0.3650
60	28.24	0.7966	22.76	0.5691
70	32.78	1.102	27.46	0.8203
80	37.45	1.453	32.14	1.118
90	41.92	1.850	36.81	1.463
100	46.08	2.290	41.45	1.854
150	64.65	5.068	63.72	4.490
200	81.70	8.729	84.67	8.204
250	99.00	13.26	104.8	12.94
298.15	116.2	18.47	123.8	18.44
300	117.0	18.69	124.5	18.67
327	125.9	21.97	135.0	22.16
Highly elastic state				
327	158.0	21.97	135.0	22.16
350	161.7	25.64	145.8	25.39
400	171.2	33.97	168.0	33.25
450	180.6	42.76	188.7	42.17
500	189.9	52.03	208.3	52.10
584	206.0	68.65	239.1	70.90
Polyhex-1-ene [77,96]				
Vitreous state				
0	0	0	7.3	0
10	2.803	0.0104	9.0	0.0798
20	9.092	0.0684	12.8	0.188
30	16.42	0.1939	17.8	0.340
40	23.68	0.3954	23.6	0.5467
50	30.17	0.6648	29.6	0.8128
60	36.69	1.000	35.6	1.138
70	42.68	1.398	41.8	1.527
80	48.28	1.853	47.9	1.974
90	53.76	2.364	53.8	2.480
100	59.08	2.929	59.7	3.048
150	84.94	6.513	88.6	6.783
200	111.3	11.44	116.8	11.92
215.5	119.2	13.20	125.2	13.78
Highly elastic state				
215.5	147.7	13.20	125.2	13.78
250	159.6	18.46	147.8	18.49
298.15	177.5	26.59	177.5	26.33
300	178.5	26.92	178.6	26.66
Poly-4-methylpent-1-ene [80]				
Crystalline state				
5	0.483	0.0006	0.1458	0.0001
10	3.250	0.0090	1.194	0.0030
15	6.900	0.0343	3.196	0.0136
20	10.78	0.0784	5.706	0.0357
25	14.60	0.1421	8.532	0.0712
30	18.00	0.2236	11.49	0.1212
40	24.30	0.4364	17.57	0.2665
50	29.85	0.7075	23.60	0.4725
60	35.10	1.032	29.50	0.7381
70	40.35	1.410	35.31	1.062
80	45.70	1.840	41.05	1.444
90	50.90	2.323	46.73	1.883
100	55.90	2.857	54.36	2.379
150	77.55	6.206	79.22	5.677
200	97.25	10.58	104.2	10.27
250	118.7	15.98	128.2	16.08
Crystalline state				
298.15	139.2	22.18	150.9	22.80
350	161.0	29.98	174.9	31.24
400	183.0	38.58	197.8	40.56
450	204.0	48.24	220.6	51.02
500	225.0	58.97	243.2	62.62
508	228.0	60.78	246.8	64.58
Liquid state				
508	239.5	71.02	267.0	64.58
550	248.9	84.31	292.1	76.36
600	256.5	96.93	314.1	91.52
Vitreous state				
0	0	0	8	0
5	0.483	0.0006	8.1	0.0399
10	3.250	0.0090	9.2	0.0830
15	6.900	0.0343	11.2	0.1336
20	10.78	0.0784	13.7	0.1957
25	14.60	0.1421	16.5	0.2712
30	18.00	0.2236	19.5	0.3611
40	24.30	0.4364	25.6	0.5864
50	29.85	0.7075	31.6	0.8725
60	35.10	1.032	37.5	1.218
70	40.35	1.410	43.3	1.622
80	45.70	1.840	49.1	2.084
90	50.90	2.323	54.7	2.603
100	55.90	2.857	60.4	2.797
150	77.55	6.206	87.2	6.877
200	97.25	10.58	112.2	11.86
250	118.7	15.98	136.2	18.07
300	140.0	22.44	159.7	25.47
Highly elastic state				
300	173.6	22.44	159.7	25.47
350	189.4	31.52	187.7	34.16
400	205.3	41.38	214.0	44.22
450	221.1	52.04	239.1	55.56
500	237.0	63.50	263.2	68.10
508	239.5	65.40	267.0	70.24
Polydec-1-ene [84]				
Crystalline state (crII and crI)				
5	0.600	0.000836	0.214	0.000236
10	3.810	0.01013	1.392	0.00379
15	8.750	0.04105	3.830	0.01639
20	14.67	0.09925	7.136	0.04347
25	21.24	0.1888	11.11	0.08882
30	27.82	0.3117	15.57	0.1553
40	39.64	0.6484	25.17	0.3585
50	51.39	1.104	35.28	0.6605
60	62.48	1.673	45.64	1.065
70	72.25	2.348	56.02	1.573
80	80.91	3.115	66.25	2.185
90	88.45	3.962	76.22	2.898
100	96.09	4.885	85.94	3.709
150	137.3	10.73	132.8	9.186
200	174.2	18.52	177.3	16.95
250	211.2	28.17	220.2	26.89
276	230.1	33.90	242.0	32.90
Crystalline state (crI)				
276	230.1	40.33	265.3	32.90
298.15	246.1	45.61	283.7	38.97
301	249.0	46.31	286.0	39.79

Table 4 (continued).

T/K	$C_p^\circ(T)$	$H^\circ(T)-H^\circ(0)$	$S^\circ(T)$	$-[G^\circ(T)-H^\circ(0)]$	T/K	$C_p^\circ(T)$	$H^\circ(T)-H^\circ(0)$	$S^\circ(T)$	$-[G^\circ(T)-H^\circ(0)]$
Polydec-1-ene[84]					*Vitreous state*				
Liquid state					50	51.39	1.104	61.6	1.966
301	287.8	53.54	310.0	39.79	60	62.48	1.673	71.6	2.611
350	307.3	68.08	354.7	56.07	70	72.25	2.348	82.0	3.378
400	335.2	84.13	397.6	74.89	80	80.91	3.115	92.3	4.253
450	363.7	102.6	438.7	95.80	90	88.45	3.962	102.2	5.220
Vitreous state					100	96.09	4.885	111.9	6.285
0	0	0	26.0	0	150	137.3	10.73	158.8	13.06
5	0.600	0.000836	26.2	0.129	200	174.2	18.52	203.3	22.10
10	3.810	0.01013	27.4	0.2619	208	180.5	20.03	210.5	23.75
15	8.750	0.04105	29.8	0.4030	*Highly elastic state*				
20	14.67	0.09925	33.1	0.5587	208	260.5	20.03	210.5	23.75
25	21.24	0.1888	37.1	0.7340	250	270.0	31.01	258.5	33.62
30	27.82	0.3117	41.6	0.9302	298.15	286.1	44.36	307.3	47.26
40	39.64	0.6484	51.2	1.392	301	287.8	45.15	310.0	48.16

Note. The thermodynamic functions presented have the following dimensions: $C_p^\circ(T)$ and $S^\circ(T)$ — J mol^{-1} K^{-1}, $H^\circ(T)-H^\circ(T)$ and $G^\circ(T)-H^\circ(0)$ — kJ mol^{-1}.

$$G^\circ(T)-H^\circ(0)=[H^\circ(T)-H^\circ(0)]-TS^\circ(T),$$

where C_p° is the temperature variation of the heat capacities of the substances in the crystalline, vitreous, highly elastic, and liquid states (see, for example, Fig. 1). In the calculations of the entropy for polyisobutylene and polyhex-1-ene, it was assumed that their zero-point entropy is equal to the configurational entropy. The errors in the calculated functions are on average 1%–1.15% at $T<20$ K, 0.5% in the range 20–50 K, ~0.2% in the range 50–340 K, and 0.5%–2% in the range 340–600 K.

VIII. Thermochemical characteristics

The thermochemical characteristics of polyolefins are listed in Table 5. The enthalpies of combustion were obtained from the experimental combustion energies $\Delta_c U$ measured calorimetrically. Since all the polymers investigated were partly crystalline, the $\Delta_c U(\alpha)$ were found in the experiments. The results were recalculated for the standard state and the values of $\Delta_c U^\circ(\alpha)$ were obtained. They were used to calculate the enthalpies of combustion $\Delta_c H^\circ(\alpha)$. The enthalpies of combustion of the polymer in the crystalline and amorphous (vitreous or highly elastic) states were calculated in their turn from the values of $\Delta_c H^\circ(\alpha)$ and the molar enthalpy of fusion of the polymer with $\alpha = 100\%$ (calculated for $T = 298.15$ K) by means of the following relations:

$$\Delta_c H^\circ(\text{cr}) = \Delta_c H^\circ(\alpha) + (1-\alpha)\Delta_{fus}H^\circ(298.15\text{ K}),$$

$$\Delta_c H^\circ(\text{a}) = \Delta_c H^\circ(\alpha) - \alpha\Delta_{fus}H^\circ(298.15\text{ K}).$$

Here α is expressed as a fraction. The enthalpy of fusion of the polymer at 298.15 K was calculated by the equation

$$\Delta_{fus}H^\circ(298.15\text{ K}) = \Delta_{fus}H^\circ(T_{fus}^\circ) + \int_{T_{fus}}^{298.15\text{K}} [C_p^\circ(\text{a}) - C_p^\circ(\text{cr})]\,dT.$$

Table 5. Thermochemical characteristics of polyolefins at 298.15 K and the standard pressure.

Polymer	Physical state[a]	$-\Delta_c H^\circ$	$-\Delta_f H^\circ$	$\Delta_f G^\circ$	$\Delta_f S^\circ$	$\ln K_f^\circ$	Ref.
		/kJ mol^{-1}			/J mol^{-1} K^{-1}		
Polyethylene	cr	1289.8±0.3	58.9±0.3	5.2±0.9	215.0±1.3	0.912	45, 46, 107
	h.e	1306.6±0.3	52.1±0.3	10.8±0.9	210.9±1.3	1.889	
Polydeuteroethylene	cr	1304.9±0.9	74.6±0.9	−1.7±1.3	244.4±1.0	−0.298	46, 67
	h.e	1312.2±0.9	67.1±0.9	1.0±1.3	228.3±1.3	0.170	
Polypropylene	cr	1951.4±0.4	86.2±0.4	10.1±0.9	339.7±1.5	1.775	45, 46
	h.e	1957.1±0.4	80.4±0.4	17.7±0.9	329.0±1.5	3.096	
Polybut-1-ene	cr	2609.8±0.4	107.6±0.4	25.2±1.0	475.4±1.6	4.420	45, 69
	h.e	2614.7±0.4	102.7±0.4	26.8±1.0	434.1±1.6	4.518	
Polypent-1-ene	cr	3250.9±1.9	145.0±1.9	18.7±2.8	551.9±1.8	3.267	46, 77
	h.e	3254.8±1.9	145.0±1.9	19.7±2.8	542.3±1.8	3.449	
Poly-3-methylbut-1-ene	cr	3225.7±2.5	141.0±2.5	25.3±3.0	557.8±2.0	4.432	46, 78
	g	3257.2±2.5	139.5±2.5	26.8±3.0	557.5±2.0	4.695	
Poly-4-methylpent-1-ene	cr	3898.7±1.8	177.4±1.8	21.4±2.4	666.7±1.2	3.749	46, 80
	g	3901.4±1.8	174.7±1.8	24.1±2.4	666.7±1.2	4.222	

[a] The following designations of the states of the polymers have been adopted: cr — crystalline, g — vitreous (glassy), h.e. — highly elastic.

We may note that the application of the Kirchhoff equation is possible subject to the condition that the calculation is performed for a constant pressure. In the present instance, it is carried out at the standard pressure (101.325 kPa).

The thermochemical parameters of the formation reaction (the enthalpies $\Delta_f H^\circ$, the entropies $\Delta_f S^\circ$, and the Gibbs free energies $\Delta_f G^\circ$) of the test compounds were calculated from their calorimetric enthalpies of combustion (Table 5) and the absolute entropies (Table 4) and also the enthalpies of formation of liquid water and gaseous carbon dioxide and the entropies of carbon in the form of graphite and gaseous hydrogen, published in handbooks.[97] The methods used for the corresponding calculations have been described.[42,57] For example, $\Delta_f H^\circ$, $\Delta_f S^\circ$, and $\Delta_f G^\circ$ for polybut-1-ene correspond to the following reaction occurring at 298.15 K and the standard pressure:[69]

$$4C(cr) + 4H_2(gas) = [-CH_2-CH(CH_2-CH_3)-] (cr) \text{ or (a)}.$$

The Gibbs free energy was calculated from the values of $\Delta_f H^\circ$ and $\Delta_f S^\circ$ by the equation

$$\Delta_f G^\circ = \Delta_f H^\circ - T\Delta_f S^\circ.$$

IX. Thermodynamic parameters of the formation reactions of polyolefins

The methods used to calculate the thermodynamic parameters of the polymerisation reactions from calorimetric data have been described.[11,13,80] The enthalpy of polymerisation $\Delta_{pol}H^\circ$ was calculated from the enthalpies of combustion of the monomer $\Delta_c H^\circ_M$ and the corresponding polymer $\Delta_c H^\circ_P$ at 298.15 K and 101.325 kPa.

$$\Delta_{pol}H^\circ = \Delta_c H^\circ_M - \Delta_c H^\circ_P .$$

For other temperatures, the enthalpies of polymerisation were found from the Kirchhoff equation:

$$\Delta_{pol}H^\circ(T) = \Delta_{pol}H^\circ(298.15\,K) + \Delta[H^\circ(T) - H^\circ(298.15\,K)], \quad (9)$$

where $\Delta[H^\circ(T)-H^\circ(298.15\ K)]$ is the difference between the enthalpies of heating of the polymer and monomer in the range 298.15 K – T.

The entropy of polymerisation $\Delta_{pol}S^\circ(T)$ was calculated from the entropies of the polymer $S^\circ_P(T)$ and the monomer $S^\circ_M(T)$ at the corresponding temperatures:

$$\Delta_{pol}S^\circ(T) = S^\circ_P(T) - S^\circ_M(T) .$$

The Gibbs free energy was calculated from the values of $\Delta_{pol}H^\circ(T)$ and $\Delta_{pol}S^\circ(T)$

$$\Delta_{pol}G^\circ(T) = \Delta_{pol}H^\circ(T) - T\Delta_{pol}S^\circ(T).$$

The concentrations of the monomer $[M]^\circ_e$ and the polymer $[P]^\circ_e$ in the equilibrium reaction mixture, corresponding to thermodynamic equilibrium, were estimated from the relations

$$[M]^\circ_e = \exp\frac{\Delta_{pol}G^\circ(T)}{RT},$$

$$[P]^\circ_e = 1 - \exp\frac{\Delta_{pol}G^\circ(T)}{RT}.$$

The limiting polymerisation temperatures T°_{ceil} of the processes investigated were found from the point of intersection of the relations

$$\Delta_{pol}H^\circ(T) = f(T) \quad (10a)$$

and

$$T\Delta_{pol}S^\circ(T) = f(T) \quad (10b)$$

or estimated by Dainton's method.[13]

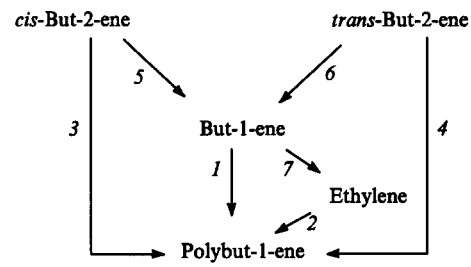
The results of the calculations are presented in Table 6. The standard enthalpy of polymerisation of gaseous ethene to partly crystalline polyethylene at 298.15 K, published by Sawada,[98] the thermodynamic functions of polyethylene,[65] the temperature dependence of the heat capacity, and the temperatures and enthalpies of the physical transformations of the monomer[99,100] were chosen as the initial data for the calculation of the thermodynamic parameters of the polymerisation of ethene. For propene, use was made of the value of $\Delta_{pol}H^\circ$(gas; cr and gas; a) at 298.15 K obtained by Joshi and Zvolinskii[45] and Richardson and Parks,[101] its thermodynamic functions[68] and $C^\circ_p = f(T)$, and the temperatures and enthalpies of the phase transitions.[102,103]

The enthalpies of the polymerisation of isobutene have been published.[104–107] In order to determine the thermodynamic parameters of the polymerisation, the value of $\Delta_{pol}H^\circ$(gas; a) at 298.15 K, given by Parks and Mocher,[107] was selected. All the other data necessary for the calculations were found in publications describing the temperature variations of the heat capacities and the temperatures and enthalpies of the physical transformations for polyisobutylene[74–76] and isobutene.[103,108]

The limiting polymerisation temperatures, estimated from Eqns (10), amounted to 670 K for ethene and 550 K for propene; the estimation of this parameter for isobutene by Dainton's method[13] yielded 390 K.

The thermodynamic parameters of the processes leading to the formation of isotactic polybut-1-ene (Scheme 1) for the temperature range 0–600 K under standard pressure have been published by Lebedev et al.[69] The enthalpies of the processes at 298.15 K and 101.325 kPa were calculated from the standard enthalpies of formation of the monomers, taken from Stull et al.,[103] and the enthalpies of formation of the polymer (Table 5). For other temperatures, the enthalpies of the processes $\Delta_r H^\circ$ were calculated from the temperature variation of the heat capacity and the temperatures and enthalpies of the phase transitions of the reactants quoted in the literature[69,109] and in Tables 2 and 5. The entropies of the processes $\Delta_r S^\circ$ were calculated from the absolute entropies of the reactants, while the Gibbs free energies $\Delta_r G^\circ$ were evaluated from the values of $\Delta_r H^\circ$ and $\Delta_r S^\circ$ for the corresponding temperatures.

Scheme 1



The upper limiting temperatures T°_{ceil} for the direct conversion of but-1-ene, *cis*- and *trans*-but-2-enes, and ethene into isotactic polybut-1-ene (processes *1*, *3*, *4*, and *2*) were estimated by Dainton's method[13] from the quantities $\Delta_r H^\circ$ and $\Delta_r S^\circ$ for the polymerisation reaction. They are respectively 520, 500, 490, and 640 K

The following relations hold at different temperatures:

$\Delta_r G^\circ < 0$ at $T < T^\circ_{ceil}$,

$\Delta_r G^\circ = 0$ at $T = T^\circ_{ceil}$,

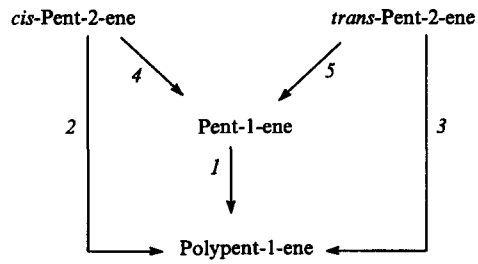
$\Delta_r G^\circ > 0$ at $T > T^\circ_{ceil}$.

This means that at $T < T^\circ_{ceil}$ the equilibria in the processes are displaced towards the formation of the polymer and the polymer produced is thermodynamically stable in relation to depolymerisation to the initial monomer; at $T > T^\circ_{ceil}$, the polymer is unstable in relation to the above monomers and rapidly depolymerises under kinetic conditions. In contrast to processes *3* and *4*, processes *5* and *6* have lower limiting temperatures — 830 and 910 K respectively. It has been shown[3,110] that isotactic polybut-1-ene can be obtained from *cis*- and *trans*-but-2-enes after their

isomerisation to but-1-ene, the yield of the polymer being low. This can be explained by the fact that, since $\Delta_r G^\circ$ for processes *5* and *6* is positive, the equilibrium concentration of but-1-ene in the reaction mixture is low. The reaction equilibrium is displaced towards an increase in the concentrations of but-1-ene with increase in temperature, since $\Delta_r G^\circ$ diminishes. This should increase the yield of polybut-1-ene.

The polypent-1-ene formation reactions may be represented by the Scheme 2:

Scheme 2



Chao and Hell [111] calculated the thermodynamic parameters of processes *1–5* for the temperature range 0–500 K from the results of Lebedev et al.[77] and the corresponding data on the initial monomers,[77,111] the enthalpies of the processes at 298.15 K from the enthalpies of formation of the reactants (see Table 5 and Lebedev et al.[77] and Chao and Hell [111]), and the enthalpies of the processes at other temperatures from the Kirchhoff formula [Eqn (9)]. The temperature variations of the heat capacities and the temperatures and enthalpies of the physical transformations of the reactants were used in the calculations (see Tables 2–4 and Lebedev et al.[77] and Chao and Hell [111]). The results show that the monomer ⇄ polymer equilibria in processes *1–3* are displaced towards the formation of polypent-1-ene: over the entire temperature range investigated, $\Delta_{pol}G^\circ < 0$; the absolute values of $\Delta_{pol}G^\circ$ for the processes decrease with increase in temperature. The enthalpies and entropies of these processes are also negative, which is the reason for the existence of the upper limiting polymerisation temperatures T°_{ceil}. Estimation by Dainton's method [13] yielded the following values: 590 K for process *1*, 560 K for process *2*, and 550 K for process *3*. Evidently, the thermodynamic characteristics of the polymerisation reactions of the isomeric pentenes diminish in the sequence pent-1-ene > *cis*-pent-2-ene > *trans*-pent-2-ene.

One should bear in mind that polypent-1-ene is not obtained directly in processes *2* and *3*;[3] its formation is preceded by the stage involving the conversion of *cis* and *trans*-pent-2-enes into pent-1-ene (processes *4* and *5*). The $\Delta_r G^\circ$ for these processes are positive. This means that the reaction equilibrium is displaced to the left. However, since at elevated temperatures the Gibbs free energies $\Delta_r G^\circ$ of the processes are small, the equilibrium reaction mixtures contain a certain amount of pent-1-ene formed from *cis* and *trans*-pent-2-enes. For example, at 500 K the mole fractions of pent-1-ene in the reaction mixture are ~0.20 (process *4*) and ~0.10 (process *5*). These concentrations were calculated from the thermodynamic equilibrium constants for these processes K°_r, which were in their turn evaluated from the equation of the van't Hoff isotherm.

As the temperature decreases, the equilibrium concentrations of pent-1-ene in the above processes also decrease. This is the reason for the low rates of conversion of *cis* and *trans*-pent-2-enes into polypent-1-ene and the low yield of the polymer during the reaction time. This situation may be altered as a result of the search for more effective isomerisation catalysts, an increase in the concentration of the catalyst in the reaction mixture, or the discovery of physicochemical conditions leading to the displacement of the equilibria *4* and *5* to the right. However, one should bear in mind that the increase of, for example, the pressure does not shift the equilibrium because reactions *4* and *5* proceed without change in the number of moles of the reactants. Variation of the solvent is also apparently relatively ineffective, since the physicochemical properties of the isomers are similar and the nature of their interaction with the solvent is virtually the same.

An increase in temperature may be comparatively effective. Extrapolation of the $\Delta_r H^\circ = f(T)$ and $T\Delta_r S^\circ = f(T)$ relations for the process under consideration leads to temperatures of 2800 and 1700 K at which the $\Delta_r G^\circ$ for processes *4* and *5* changes sign (from plus to minus). However, the upper limiting temperature of the polymerisation of pent-1-ene is only 590 K, so that the limits within which the temperature can be varied are restricted.

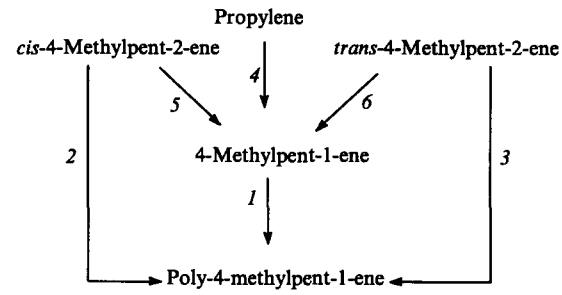
The thermodynamic parameters of the polymerisation of 3-methylbut-1-ene have no singularities of any kind:[78,111] $\Delta_{pol}H^\circ$ and $\Delta_{pol}S^\circ$ are negative throughout and their absolute values increase with increasing temperature; the Gibbs free energy of polymerisation is negative, diminishing with increase in temperature; the upper limiting polymerisation temperature is $T^\circ_{ceil} = 572$ K.

The enthalpy of the polymerisation of liquid hex-1-ene to highly elastic polyhex-1-ene at 298.15 K and 101.325 kPa is -101 kJ mol^{-1}. This value was obtained by the author of the present review from the enthalpies of formation of the liquid monomer $\Delta_f H^\circ(298.15\text{ K}) = -72.38$ kJ mol^{-1} (see Ref. 103) and the highly elastic polymer $\Delta_f H^\circ(298.15\text{ K}) = 173.6$ kJ mol^{-1}, calculated from the equation quoted by Lebedev and Kiparisova.[46] The calculated enthalpy of the polymerisation of hex-1-ene, $\Delta_{pol}H^\circ = -82.8$ kJ mol^{-1}, published by Lebedev and Lebedev,[96] is significantly too low.

The thermodynamic functions of hex-1-ene in the range 0–300 K have been published by Lebedev and Lebedev.[96] All these data, together with the results presented in Table 4, have been used to calculate the thermodynamic parameters of the polymerisation of hex-1-ene in bulk in the range 0–300 K (Table 6). Evidently the change in the standard Gibbs free energy $\Delta_{pol}G^\circ(T)$ is negative throughout, while the numerical values are such that one may conclude that the equilibrium is almost fully displaced to the right. Extrapolation based on the $\Delta_{pol}H^\circ(T) = f(T)$ and $T(\Delta_{pol}G^\circ(T) = f(T)$ relations for the liquid monomer → highly elastic polymer process leads to an upper limiting polymerisation temperature of 865 K. The thermodynamic equilibrium concentration of the monomer in the reaction mixture $[M]^\circ_e = 2 \times 10^{-12}$ M was estimated from the equation of the van't Hoff isotherm and the value of $\Delta_{pol}G^\circ$ (300 K).

The reactions leading to the formation of isotactic poly-4-methylpent-1-ene may be represented by the Scheme 3:

Scheme 3



The reactions leading to the polymerisation of 4-methylpent-1-ene and *cis* and *trans*-4-methylpent-2-enes to poly-4-methylpent-1-ene in bulk and the reaction in which propene dimerises to 4-methylpent-1-ene have upper limiting polymerisation temperatures which are respectively 590, 540, 530, and 570 K. The numerical values of T°_{ceil} were found graphically from the intersection of the corresponding temperature variations of the enthalpies and the entropy factors: $\Delta_r H^\circ = f(T)$ and $T\Delta_r S^\circ(T) = f(T)$. The enthalpies and entropies were taken from Table 6. At $T < T^\circ_{ceil}$, the equilibria in processes *1–4* in Scheme 3 are displaced towards the formation of the reaction products ($\Delta_r G^\circ < 0$). The enthalpies and entropies of these processes are

Table 6. The enthalpies (kJ mol^{-1}), entropies (J mol^{-1} K^{-1}), and Gibbs free energies (kJ mol^{-1}) of the polymerisation of olefins in bulk with formation of polyolefins under standard pressure.

T/K	Physical state of reactants[a]	$-\Delta_{pol}H^\circ$	$-\Delta_{pol}S^\circ$	$-\Delta_{pol}G^\circ$
Ethene → polyethylene[b]				
0	cr;cr	86.50	0	86.50
	cr;g	80.95	−5.4	80.95
100	cr;cr	88.59	34.9	85.10
	cr;g	82.92	26.7	80.25
200	gas;cr	108.7	171	74.44
	gas;g	102.7	161	70.42
298.15	gas;cr	108.8	172	57.52
	gas;h.e	101.4	156	54.80
400	gas;cr	108.8	172	40.04
	gas;h.e	99.63	151	39.11
500	gas;l	98.61	148	24.81
600	gas;l	97.02	145	10.20
Propene → polypropylene[b]				
0	cr;cr	76.65	0	76.65
	cr;g	72.44	−1.1	72.44
100	l;cr	82.07	74.8	74.59
	l;g	77.67	69.6	70.72
200	l;cr	87.14	111	64.90
	gas;g	82.55	105	61.61
298.15	gas;cr	106.5	198	47.59
	gas;h.e	100.8	187	45.11
400	gas;cr	106.3	197	27.50
	gas;h.e	98.37	180	26.45
500	gas;l	95.96	175	8.71
But-1-ene → polybut-1-ene[69]				
0	cr;cr	71.8	0	71.8
	cr;g	68.1	6.7	68.1
	gas;cr	78.1	12.8	71.8
	gas;g	68.1	6.1	68.1
100	l;cr	77.8	75.5	70.2
	l;g	74.1	68.9	67.2
200	l;cr	83.1	114	57.2
	l;g	79.5	107	58.0
298.15	gas;cr	108	207	45.8
	gas;h.e	103	196	44.3
400	gas;cr	107	204	25.4
	gas;h.e	99.7	187	24.8
500	gas;l	94.0	182	3.2
600	gas;l	91.0	177	−14.7
***cis*-But-2-ene → polybut-1-ene**[69]				
0	cr;cr	61.6	0	61.6
	cr;g	58.0	−6.7	58.0
100	cr;cr	62.9	20.7	60.8
	cr;g	59.3	14.0	57.9
200	l;cr	74.8	106	53.6
	l;g	71.1	99.0	51.3
298.15	gas;cr	101	201	40.8
	gas;h.e	95.7	190	39.2
400	gas;cr	99.0	196	20.5
	gas;h.e	92.1	179	20.4
500	gas;l	85.7	172	0.3
600	gas;l	82.6	166	−17.2
***trans*-Бутен-2 → полибутен-1**[69]				
0	cr;cr	56.3	0	56.3
	cr;g	52.7	−6.7	52.7
100	cr;cr	57.4	17.0	55.7
	cr;g	53.8	10.3	52.7
200	l;cr	70.9	99.9	50.9
	l;g	67.2	93.2	48.6
298.15	gas;cr	96.4	195	38.3
	gas;h.e	91.5	184	36.8
400	gas;cr	95.7	193	18.6
	gas;h.e	88.7	175	18.6
500	gas;l	83.0	170	−1.9
600	gas;l	80.4	165	−18.6
Isobutene → polyisobutylene[c]				
0	cr;g	37	−5.7	37
50	cr;g	37	2.6	37
100	cr;g	39	20.3	36
150	l;g	47	81.7	34
200	l;h.e	49	97.1	30
250	l;h.e	51	102.5	25
298.15	gas;h.e	72	183.5	17
300	gas;h.e	72	184.1	17
350	gas;h.e	71	180.1	8
380	gas;h.e	70	178.2	2
Pent-1-ene → polypent-1-ene[77]				
0	cr;cr	82	0	82
	cr;g	80	−4	80
100	cr;cr	84	24	81
	cr;g	81	20	80
200	l;cr	95	117	72
	l;g	93	113	70
298.15	l;cr	99	133	60
	l;h.e	95	124	58
300	l;cr	99	133	59
	l;h.e	95	125	58
400	gas;l	117	198	38
500	gas;l	113	190	18
***cis*-Pent-2-ene → polypent-1-ene**[77]				
0	cr;cr	73	0	73
	cr;g	71	−4	71
100	cr;cr	75	20	73
	cr;g	72	16	71
200	l;cr	87	114	64
	l;g	85	111	63
298.15	l;cr	91	129	52
	l;h.e	87	120	51
300	l;cr	90	129	52
	l;h.e	87	121	51
400	gas;l	109	195	31
500	gas;l	105	185	12
***trans*-Pent-2-ene → polypent-1-ene**[77]				
0	cr;cr	69	0	69
	cr;g	67	−4	67
100	cr;cr	70	18	69
	cr;g	68	14	66
200	l;cr	83	111	61
	l;g	81	102	59
298.15	l;cr	87	127	49
	l;h.e	83	118	48
300	l;cr	87	127	49
	l;h.e	83	119	48
400	gas;l	106	194	29
500	gas;l	103	186	10

Table 6 (continued).

T/K	Physical state of reactants[a]	$-\Delta_{pol}H^\circ$	$-\Delta_{pol}S^\circ$	$-\Delta_{pol}G^\circ$
3-Methylbut-1-ene → poly-3-methylbut-1-ene[78]				
0	cr;cr	71	0	71
	cr;g	70	0	70
100	cr;cr	73	20	71
	cr;g	72	20	70
200	l;cr	84	112	61
	l;g	83	112	60
298.15	gas;cr	112	211	49
	gas;g	111	211	48
400	gas;cr	112	211	28
	gas;h.e	109	206	27
500	gas;cr	111	210	6
	gas;h.e	107	201	6
600	gas;l	104	198	−14
640	gas;l	104	196	−22
Hex-1-ene → polyhex-1-ene[96]				
0	cr;g	84	−7.3	84
50	cr;g	85	−2.3	85
100	cr;g	86	9.9	84
150	l;g	97	94.3	83
200	l;g	100	111	78
250	l;h.e	101	116	72
298.15	l;h.e	101	118	66
300	l;h.e	101	118	66
4-Methylpent-1-ene → poly-4-methylpent-1-ene[80]				
0	cr;cr	82	0	82
	cr;g	77	−8	77
	g;cr	84	15	84
	g;g	79	7	79
100	cr;cr	83	28	80
	cr;g	78	20	76
	ov.l;cr	87	60	81
	ov.l;g	82	52	77
200	l;cr	94	111	72
	l;g	89	103	69
4-Methylpent-1-ene → poly-4-methylpent-1-ene[80]				
298.15	l;cr	99	131	60
	l;g .	94	122	58
400	gas;cr	126	214	41
	gas;h.e	118	198	39
500	gas;cr	124	209	19
	gas;h.e	114	189	20
600	gas;l	107	175	−2
***cis*-4-Methylpent-2-ene → poly-4-methylpent-1-ene**[80]				
298.15	l;cr	93	134	53
	l;g .	87	126	49
400	gas;cr	121	220	33
	gas;h.e	110	197	31
500	gas;cr	119	215	12
	gas;h.e	113	207	9.5
600	gas;l	103	183	−7
***trans*-4-Methylpent-2-ene → poly-4-methylpent-1-ene**[80]				
298.15	l;cr	88	130	49
	l;g	82	128	44
400	gas;cr	117	216	31
	gas;h.e	106	194	28
500	gas;cr	115	214	8
	gas;h.e	102	186	9
600	gas;l	99	182	−10
Dec-1-ene → polydec-1-ene[84]				
0	crII;crII,crI	97	0	97
	crII;g	89	−26	89
100	crII;crII,crI	98	13	97
	crII;g	90	−13	91
200	crI;crII,crI	108	68	95
	crI;g	100	42	92
298.15	l;crI	123	141	81
	l;h.e	116	118	81
350	l;l	117	121	75
400	l;l	118	123	69
450	l;l	119	125	62

[a] The following designations of the states of the polymers have been adopted: l — liquid, gas — gaseous, ov.l — supercooled liquid.
[b] L Ya Tsvetkova's data. [c] N Smirnova's data.

negative throughout and their numerical values depend on the physical state of the reactants and increase with increasing temperature.

The isomerisation reactions of *cis* and *trans*-4-methylpent-2-enes (processes *5* and *6*) have neither an upper nor a lower limiting temperature, which is characteristic of processes for which $\Delta_rH^\circ > 0$ and $\Delta_rS^\circ < 0$.[11] For this reason, the change in the Gibbs free energy is positive. In processes *5* and *6* under consideration, the free energies Δ_rG° have small positive values: $\Delta_rG^\circ < 10$ kJ mol^{-1}. This means that a small amount of 4-methylpent-1-ene is present in the equilibrium reaction mixture of the isomers. In this case, a shift of the equilibrium is possible provided that 4-methylpent-1-ene is continuously removed from the reaction mixture, for example when it is polymerised to poly-4-methylpent-1-ene, which does in fact occur in the isomeric polymerisation of *cis*- and *trans*-alk-2-enes to polyalk-1-enes.[3]

Owing to the similarity of the heat capacities of 4-methylpent-1-ene and the *cis*- and *trans*-isomers of 4-methylpent-2-enes, the influence of temperature on $\Delta_rH^\circ(T)$ and $\Delta_rS^\circ(T)$ is small. The enthalpies of the processes were calculated from the enthalpies of formation of 4-methylpent-1-ene,[112] *cis*- and *trans*-methylpent-2-enes,[103] propene,[103] and poly-4-methylpent-1-ene.[80] The entropies of the reactants required for the calculation of $\Delta_rS^\circ(T)$ were taken from Lebedev et al.[80] and Stull et al.[103]

As for other olefins, the enthalpy and entropy of the polymerisation of dec-1-ene are negative throughout.[84] It follows from this that the polymerisation process has an upper limiting temperature. Indeed, $\Delta_{pol}G^\circ(T)$ decreases in absolute magnitude with increase in temperature and becomes zero at $T^\circ_{ceil} = 890$ K, while at $T > T^\circ_{ceil}$ it is positive throughout. T°_{ceil} was estimated by Dainton's method.[13] The T°_{ceil} obtained is apparently appreciably higher than the temperature of the onset of the thermal degradation of the polymer.

X. Principal regularities and characteristics of the thermodynamic properties of polyolefins and of the parameters of their formation reactions †

1. Thermodynamic functions

Since the C_2-C_6 and C_{10} polyolefins with linear side substituents which have been investigated differ from one another by the number of methylene groups in these substituents, one may expect, for the same physical state of the polymers and under identical temperatures and pressures, a regular change in the thermodynamic properties as a function of the number of carbon atoms n in the repeat units of the polymers, as happens, for example, in the paraffins,[113] polyalkenes,[7] polyaldehydes,[114] and polylactones.[64]

The existence of such relations is due to the regular additive contribution of the methylene groups to the corresponding properties of the above polymers. It was found that this is fully valid also for polyolefins. As an example, Figs 9–11 present the isotherms (298.15 K) of the thermodynamic properties of polyolefins. Evidently, the dependences of the heat capacity C_p°, the enthalpy $H^\circ(T)-H^\circ(0)$, the entropy $S^\circ(T)$, and the Gibbs free energy on n are represented by straight lines described satisfactorily by the equations

$$C_p^\circ(\text{cr}) = -8 + 25.5n, \quad (11)$$

$$C_p^\circ(\text{h.e.}) = 8 + 27.8n, \quad (12)$$

$$[H^\circ(T) - H^\circ(0)](\text{cr}) = -1.1 + 4.0n, \quad (13)$$

$$[H^\circ(T) - H^\circ(0)](\text{h.e}) = -2.42 + 4.68n, \quad (14)$$

$$S^\circ(\text{cr}) = -21.2 + 30.2n, \quad (15)$$

$$S^\circ(\text{h.e}) = -17.8 + 32.2n, \quad (16)$$

$$[G^\circ(T) - H^\circ(0)](\text{cr}) = 6.1 - 5.2n, \quad (17)$$

† Prepared jointly with the senior scientific member of the Institute of Chemistry at the Nizhnii Novgorod State University, Candidate in Chemical Sciences N N Smirnova.

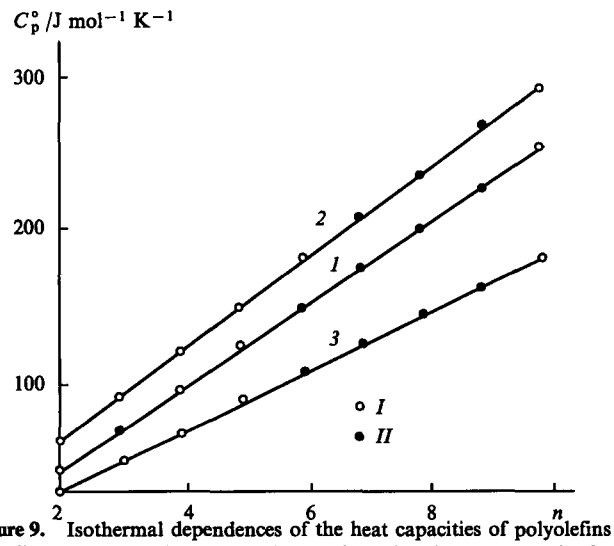


Figure 9. Isothermal dependences of the heat capacities of polyolefins with linear side substituents on the number of carbon atoms n in the monomer repeat unit.
State of the polymer: (*1*) crystalline; (*2*) highly elastic at $T = 298.15$ K; (*3*) crystalline and vitreous at $T = 200$ K; (*I*) experimental values; (*II*) extrapolated data.

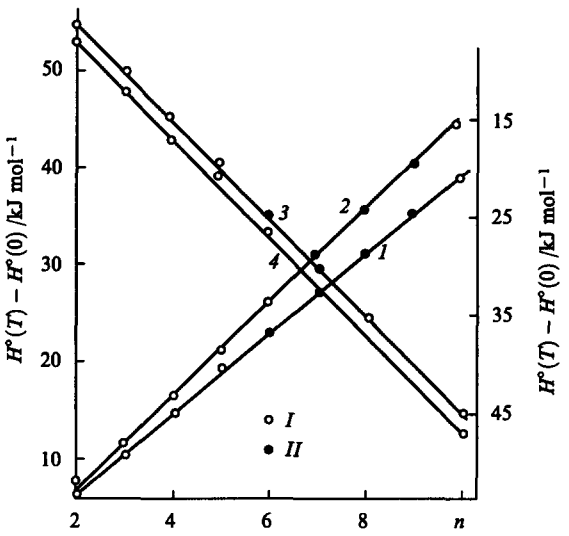


Figure 10. Isothermal dependences of the enthalpies (*1*, *2*) and Gibbs free energies (*3*, *4*) of polyolefins with linear side substituents on the number of carbon atoms n in the monomer repeat unit at 298.15 K.
State of the polymer: (*1*) and (*3*) highly elastic; (*2*) and (*4*) crystalline; (*I*) experimental values; (*II*) extrapolated data.

$$[G^\circ(T) - H^\circ(0)](\text{h.e}) = 3.5 - 5.1n. \quad (18)$$

The equations were obtained using experimental C_p° data and data calculated from the temperature variations of the heat capacities, the temperatures and enthalpies of the physical transformations, and the enthalpies, entropies, and Gibbs free energies of the polyolefins investigated. The corresponding experimental values of C_p° agree, subject to an error to within 2.5%, with the heat capacities calculated by Eqns (11) and (12); the enthalpies calculated by Eqns (13) and (14) and the entropies calculated by Eqns (15) and (16) agree with experimental values to within 2% and 3% respectively. This makes it possible in its turn to estimate the numerical values for a series of hitherto uninvestigated polyolefins in the same physical states and for the same physical conditions. The results of these estimates by Eqns (11)–(18) are presented in Table 7 for the closest analogues of the polyolefins investigated. We suggest that the errors of these estimates for C_p°, $H^\circ(T)-H^\circ(0)$, S°, and $G^\circ(T)-H^\circ(0)$ are within the limits of 3%.

Table 7. Thermodynamic functions of a series of higher polyolefins calculated by Eqns (11)–(18) for $T = 298.15$ K and $p = 101.325$ kPa.

Substance	Physical state	$C_p^\circ(T)$	$S^\circ(T)$	$H^\circ(T)-H^\circ(0)$	$-[G^\circ(T)-H^\circ(0)]$
		/J mol^{-1} K^{-1}		/kJ mol^{-1}	
Polyhept-1-ene	cr	171	190	26.9	29.7
	h.e	203	208	30.3	31.7
Polyoct-1-ene	cr	196	220	30.9	34.7
	h.e	230	240	35.0	36.6
Polynon-1-ene	cr	222	251	34.9	39.9
	h.e	258	272	39.7	41.4
Polyundec-1-ene	cr	273	311	42.9	49.8
	h.e	314	336	49.1	51.1
Polydodec-1-ene	cr	298	341	46.9	54.8
	h.e	342	369	53.7	56.3

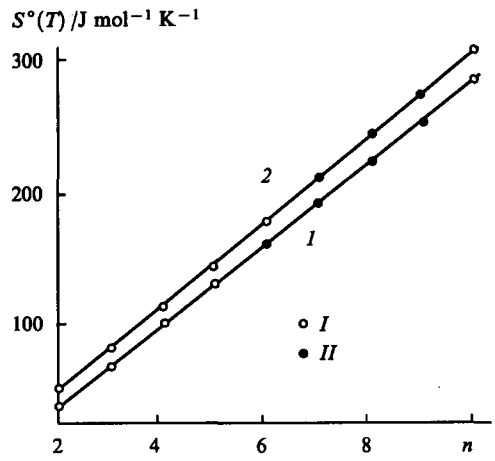


Figure 11. Isothermal dependences of the entropies of polyolefins with linear side substituents on the number of carbon atoms n in the monomer repeat unit.
State of the polymer: (*I*) crystalline; (*2*) highly elastic at $T = 298.15$ K; (*I*) experimental values; (*II*) extrapolated data.

2. Thermochemical parameters of the formation reactions

The enthalpies of combustion $\Delta_c H°$ and formation $\Delta_f H°$ and the entropies of formation $\Delta_f S°$ of the C_2-C_6 polyolefins investigated as well as their thermodynamic functions are described satisfactorily by the relations between the thermochemical parameters and the number of carbon atoms in the monomer repeat unit in the macromolecule. At $T = 298.15$ K and the standard pressure, we have

$$\Delta_c H°(\text{cr}) = -4.3 - 648.95\,n, \quad (19)$$

$$\Delta_c H°(\text{h.e}) = -7.97 - 649.5\,n, \quad (20)$$

$$\Delta_f H°(\text{cr}) = 4.4 - 30.4\,n, \quad (21)$$

$$\Delta_f H°(\text{h.e}) = 8.35 - 29.9\,n. \quad (22)$$

The deviations of the experimental enthalpies of combustion from the corresponding straight lines [Eqns (19) and (20)] are within the limits of 2.3% and the deviations of the enthalpies of formation [Eqns (21) and (22)] are within the limits of 5%.

Under the same physical conditions, the entropies of formation of the polyolefins considered are described by the following equations

$$\Delta_f S°(\text{cr}) = -6.1 - 108\,n, \quad (23)$$

$$\Delta_f S°(\text{h.e.}) = -3.8 - 105.4\,n. \quad (24)$$

Table 8. The enthalpies of combustion and thermochemical parameters of the formation of a series of higher polyolefins calculated by Eqns (19)–(24) for $T = 298.15$ K and $p = 101.325$ kPa.

Substance	Physical state	$-\Delta_c H°$ /kJ mol^{-1}	$-\Delta_f H°$ /kJ mol^{-1}	$\Delta_f G°$ /kJ mol^{-1}	$-\Delta_f S°$ /J mol^{-1} K^{-1}
Polyhept-1-ene	cr	4547	208.4	18.8	762
	h.e	4554	201.0	20.2	742
Polyoct-1-ene	cr	5196	238.8	20.6	870
	h.e	5204	230.9	21.6	847
Polynon-1-ene	cr	5845	269.2	22.4	978
	h.e	5853	260.8	23.0	952
Polyundec-1-ene	cr	7143	330.0	26.0	1194
	h.e	7152	320.6	26.2	1163
Polydodec-1-ene	cr	7792	360.4	27.8	1302
	h.e	7802	350.5	27.9	1269

The deviations of the experimental values of $\Delta_f S°$ from the calculated entropies are within the limits of 2%.

The relations discovered also made it possible to estimate the corresponding thermodynamic characteristics for the hitherto uninvestigated polyolefins and to calculate $\Delta_f G°$ from the values of $\Delta_f H°$ and $\Delta_f S°$ for these substances (Table 8).

3. Thermodynamic parameters of fusion

Polymorphism is characteristic of higher polyolefins.[72, 90] Starting with polydecene,[86] two types of crystals appear on crystallisation: those formed by the main chains of the macromolecules and by the side substituents respectively. The thermodynamic parameters of the fusion of various crystalline modifications of the same polyolefin differ markedly. For example, the crystalline form III of polybut-1-ene melts at 374 K, while form I melts at 407 K; the enthalpies and entropies of the fusion of these forms are respectively 2.67 and 7.11 kJ mol^{-1} and 7.14 and 17.5 J mol^{-1} K^{-1}. The melting points of the polydec-1-ene crystals formed by the main chains and side substituents (276 and 301 K) differ by 25 K, whereas their enthalpies and entropies of fusion differ only slightly. For the majority of polyolefins, having several crystalline modifications the thermodynamic parameters of the fusion of one or two have been investigated. For example, poly-4-methylpent-1-ene is known to be capable of forming five different crystalline modifications.[80]

The thermodynamic characteristics of only one of them have been investigated hitherto (Table 2).[80] Owing to the insufficient amount of experimental data, the search for quantitative regularities in the thermodynamic characteristics of the fusion of polyolefins is so far difficult. One may only note that, among the polyolefins investigated, polydecene has the lowest melting point (276 K). Crystals of form II, formed from the main chain, melt at this temperature. The highest melting point is that of poly-4-methylpent-1-ene (508 K). Polybut-1-ene (crystalline form III) has the lowest enthalpy of fusion (2.67 kJ mol^{-1}), whilst poly-4-methylpent-1-ene has the highest enthalpy of fusion (10.24 kJ mol^{-1}). The entropies of fusion of polyolefins are in the range from 7 to 20 J mol^{-1} K^{-1}.

4. Parameters of the vitrification process and of the vitreous state

The glass transition temperatures of polyolefins with linear side chains decrease from 249 K for polybut-1-ene to 208 K for polydec-1-ene. for polyolefins with branched side substituents, $T_g°$ is greater than for polyolefins with unbranched substituents. For example, the glass transition temperatures of poly-3-methylbut-1-ene and poly-4-methylpent-1-ene are respectively 327 and 300 K. $T_g°$ for poly-3-methylbut-1-ene is higher by 100 K than for its structural isomer polypent-1-ene, while $T_g°$ for poly-4-methylpent-1-ene is higher than that for polyhex-1-ene. This interesting fact requires additional analysis.

The increase in heat capacity on devitrification $\Delta C_p°(T_g°)$ is in the range from 21 to 34 J mol^{-1} K^{-1} for all the polyolefins investigated and corresponds, cn according to Wunderlich,[83] to between 2.5 and 3 'beads' — kinetically independent atomic groups — in the monomer repeat unit of the polymer. However, $\Delta C_p°(T_g°) = 60$ J mol^{-1} K^{-1} for polydec-1-ene, which corresponds to virtually five 'beads'. Clearly this is due to the appearance of additional independently vibrating atomic groups in connection with the increase in the length of the side substituent.

In the vitreous state at $T = 0$ K, the entropies of the polymers $S_g°(0)$ are small for the majority of higher polyolefins, varying from 0 for poly-3-methylbut-1-ene to 8 for poly-4-methylpent-1-ene. The fact that $S_g°(0)$ is zero for poly-3-methylbut-1-ene is associated with the characteristic features of its structure in the crystalline and vitreous states, the same as for poly-4-methylpent-1-ene, which have been examined in detail.[80] The main reason is that in the crystalline polymer the packing density of the fragments of the macromolecules is smaller than in the vitreous

polymer. In particular, this leads to a decrease in T_g° as well as the density of such polymers with increase in the degree of crystallinity. Conversely, these parameters increase as the polymer passes from the partly crystalline to the amorphous glassy state.

The value $S_g^\circ(0) = 26$ J mol^{-1} K^{-1}, usual for amorphous polymers, has been observed for polydec-1-ene. For understandable reasons, the polymers in the vitreous state have an excess enthalpy compared with the crystalline state. In polyolefins, this excess $H_g^\circ(T) - H_{cr}^\circ(0)$ varies from 2 J mol^{-1} for poly-3-methybut-1-ene to 8.4 J mol^{-1} for polydec-1-ene.

5. Thermodynamic characteristics of polymerisation reactions

In the temperature range investigated, the formation reactions of the higher polyolefins by the polymerisation of the corresponding monomers in bulk under standard pressure are thermodynamically allowed. The standard Gibbs free energy $\Delta_{pol}G^\circ$ is negative throughout. At 298.15 K and the standard pressure, $\Delta_{pol}G^\circ$ is in the range from 80 kJ mol^{-1} for the polymerisation reaction of but-1-ene to 116 kJ mol^{-1} for the polymerisation of dec-1-ene (the monomers and the polymers are in the liquid and highly elastic states respectively). Clearly the monomer $\rightleftarrows$ polymer reaction equilibrium is almost fully displaced towards the formation of the polymer. The enthalpies $\Delta_{pol}H^\circ$ and entropies $\Delta_{pol}S^\circ$ are also negative, so that all the processes considered have the corresponding upper limiting polymerisation temperatures. It is noteworthy that they are all comparatively high and are in the range from 390 K for polyisobutylene to 890 K for polydec-1-ene.

Figure 12 presents the dependences of the enthalpies, entropies, and Gibbs free energies for the polymerisation of olefins in bulk with formation of the corresponding higher polyolefins at 298.15 K and 101.325 kPa on the number of carbon atoms n in the molecules of the initial olefins and the corresponding monomer repeat units in the polymer macromolecules produced (the monomers and polymers were in the liquid and highly elastic states respectively). Evidently, the enthalpies (heats) of the polymerisation reactions increase smoothly from ethene ($n = 2$) to dec-1-ene ($n = 10$), curve *1* tending to a constant value of $\Delta_{pol}H^\circ$ with increase in n.

Lebedev and Rabinovich [118] showed that the enthalpy of the polymerisation of a monomer via a C=C bond may be represented by the following sum:

$$\Delta_{pol}H^\circ(T) = \Delta E_{at} + \Delta E_{conj} + \Delta E_{s.s.} + \Delta E_{mol} + \Delta[H^\circ(T) - H^\circ(0)], \quad (25)$$

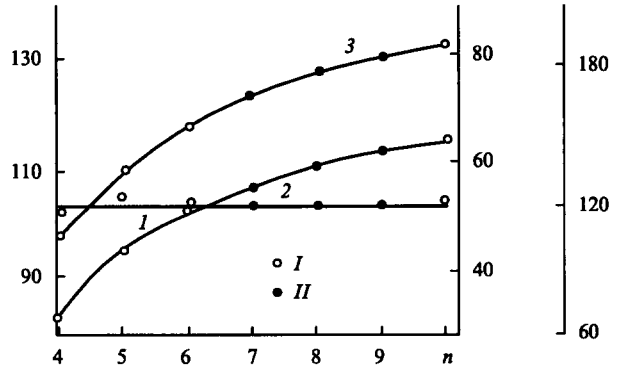


Figure 12. The enthalpies (*1*), entropies (*2*),and Gibbs free energies (*3*) of the polymerisation of olefins in bulk at $T = 298.15$ K and the standard pressure.
Monomers and polymers in the liquid and highly elastic states respectively; (*I*) experimental values; (*II*) extrapolated data.

where ΔE_{at} is the difference between the average energies of the atomic C=C bond being ruptured and the two atomic C–C bonds being formed, ΔE_{conj} is the difference between the conjugation energies of the atomic bonds in the monomer and the polymer, $\Delta E_{s.s.}$ is the difference between the energies of the steric strain in the polymer and the monomer, ΔE_{mol} the difference between the energies of the intermolecular interaction in the monomer and the polymer at 0 K, and $\Delta[H^\circ(T) - H^\circ(0)]$ the difference between the energies associated with the heating of the polymer and the monomer. It is known that $\Delta E_{at} = 88$ kJ mol^{-1}, $\Delta E_{conj} = 9$ kJ mol^{-1} (the hyperconjugation energy in the monomer), $\Delta E_{s.s.} < 4$ kJ mol^{-1} for the polymerisation reactions of monosubstituted vinyl monomers, and $\Delta E_{mol} = 34$ kJ mol^{-1} for the monomers having the same structure. It is found that the change of $\Delta_{pol}H^\circ$ is caused solely by the contribution of $\Delta[H^\circ(T) - H^\circ(0)]$. In fact, the experimental values of $\Delta[H^\circ(T) - H^\circ(0)]$ increase with increase in n and agree, within the limits of the error of the calculations and the assumptions made, with the values obtained by converse calculation from Eqn (25). For example, the experimental and calculated values of $\Delta[H^\circ(T) - H^\circ(0)]$ are 34 and 32 kJ mol^{-1} respectively for the polymerisation of but-1-ene; for polypent-1-ene, the respective values are 40 and 41 kJ mol^{-1}. In both cases, the monomer and the polymer are in the gaseous and highly elastic states respectively at 298.15 K; under these conditions, Eqn (25) yields the best results.

The entropy of polymerisation $\Delta_{pol}S^\circ$ (the monomer and polymer are in the liquid and highly elastic states respectively) at 298.15 K is approximately constant. The decrease in the entropy of the reaction is caused mainly by the formation of chains and corresponds to the rule established by Dainton and Ivin.[13] According to this rule, the polymerisation of liquid monomers via the C=C bond to amorphous polymers leads to a decrease in entropy by 105–125 J mol^{-1} K^{-1} (usually by 125 J mol^{-1} K^{-1}). In the polymerisation of the above olefins, the entropy diminishes by 120 J mol^{-1} K^{-1}.

The Gibbs free energy of polymerisation, like the enthalpy of polymerisation, also gradually increases with increase in n and the form of the dependence of $\Delta_{pol}G^\circ$ on n (Fig. 12, curve *3*) resembles the corresponding dependence of $\Delta_{pol}H^\circ$ on n (curve *1*). This is of course associated with the fact that $\Delta_{pol}H^\circ$ varies with increase in n, while the entropy factor $T\Delta_{pol}S^\circ$ ($T = 298.15$ K) is constant and independent of n. It therefore follows from the equation

$$\Delta_{pol}G^\circ = \Delta_{pol}H^\circ - 298.15\,\Delta_{pol}S^\circ$$

that the forms of the curves representing the $\Delta_{pol}H^\circ$ and $\Delta_{pol}G^\circ$ isotherms as a function of n should be identical.

The existence of smooth dependences of the enthalpies, entropies, and Gibbs free energies of the polymerisation of olefins on n made it possible to estimate the thermodynamic characteristics of the polymerisation reactions of olefins (at 298.15 K and 101.325 kPa) for which experimental determinations have not yet been made. The results of the estimates are as follows (kJ mol^{-1}):

	Hept-1-ene	Oct-1-ene	Non-1-ene
$-\Delta_{pol}H^\circ$	107	111	114
$-\Delta_{pol}G^\circ$	72	76	79

In all cases, the monomer and polymer were in the liquid and highly elastic states and the entropy of polymerisation was 120 J mol^{-1} K^{-1}.

In conclusion we may note that, in the analysis and generalisation of the thermodynamic characteristics of polyolefins and the parameters of the polymerisation reactions of the corresponding olefins published in the literature, the most reliable values were selected (Tables 2–6). These parameters are recommended for practical use. The quantitative dependences of the thermodynamic properties and parameters of the reactions on the composition and structure of the monomer repeat units in the macromolecules of the polyolefins, on the physical state of the

reactants, and on temperature at the standard pressure have been discovered. They have been used to estimate the numerical values for the corresponding polyolefins in the series polyethylene to polydecene which have not yet been investigated experimentally.

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