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Thermodynamics of polylactones

B V Lebedev

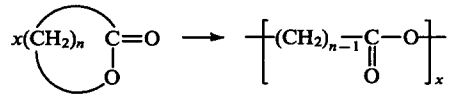
Contents

I.	Introduction	1063
II.	Calorimetric research methods	1065
III.	Heat capacity	1065
IV.	Thermodynamics of fusion	1070
V.	Parameters of vitrification and the vitreous state	1072
VI.	Thermodynamic functions	1073
VII.	Thermochemical characteristics	1073
VIII.	Thermodynamic parameters of the polymerisation reactions of lactones	1076
IX.	The regularities and characteristics of the thermodynamic properties of polylactones and of the parameters of the polymerisation reactions of lactones	1078

Abstract. The thermodynamic properties of polylactones and the thermodynamic parameters of their formation reactions involving the polymerisation of lactones in the range 0 – 400 K are examined on the basis of the results of calorimetric studies. The selected thermodynamic quantities which have been recommended for use are presented. The regularities and characteristics of the thermodynamic properties and parameters of the lactone polymerisation reaction and their dependence on the composition, structure and physical state of the reactants and on temperature at the standard pressure are described. The bibliography includes 99 references.

I. Introduction

Polylactones are obtained by the polymerisation of the corresponding lactones in accordance with the scheme



The interest in the thermodynamic properties of polylactones and the thermodynamic parameters of the reactions involving their synthesis is due to the wide variety of theoretical and applied studies on reactants and reactions [1–5] in connection with the good prospects for the practical employment of polylactones as complex aliphatic polyesters with a chain structure.[6–8] A series of polylactones and their copolymers are being manufactured industrially and are used in practice. As an example, one may point to polyglycolide and its copolymers with lactide, which are used in medicine as biocompatible surgical materials,[7,9] and to polypivalolactone [10,11] and poly-β-butyrolactone,[3,8] which are used as biodegradable materials. The thermodynamic characteristics of polylactones and their formation reactions are needed in the planning and implementation of theoretical and applied developments designed to obtain and process these materials and in the development of industrial technologies for their manufacture and conversion into articles.[12] The thermodynamic parameters of the polymerisation reactions of lactones are used in the search for the optimum physical conditions in their implementation, ensuring the maximum yield of products, for the determination of the temperature ranges of thermodynamic stability of polylactones relative to their depolymerisation to the initial monomers, and also for the determination of the temperature ranges corresponding to the existence of the polymers in particular physical states, which in many respects determine their specific applications.[13,14]

Spontaneous polymerisation of the monomers takes place when the Gibbs free energy $\Delta_{pol}G(T,p)$ decreases.[15] The standard Gibbs free energy $\Delta_{pol}G^\circ(T)$, characterising the state of thermodynamic equilibrium in the reaction, indicates directly the possibility or impossibility in principle, from the thermodynamic standpoint, of the conversion of the lactone into the corresponding polylactone under specific physicochemical conditions.[13,15,16] For $\Delta_{pol}G^\circ(T) < 0$, the process equilibrium is displaced to the right — towards the formation of the polymer, while for $\Delta_{pol}G^\circ(T) > 0$ it is actually displaced to the left and the monomer predominates in the equilibrium reaction mixture. If the positive standard Gibbs free energy is less than 40 kJ mol^{-1}, then change of the physicochemical conditions in carrying out the reaction may lead to a change in the sign of $\Delta_{pol}G(T)$ and to a shift of the equilibrium to the right.[16] For $\Delta_{pol}G^\circ(T) > 40$ kJ mol^{-1}, the spontaneous reaction is thermodynamically prohibited. In this case, the conversion of the monomer into the polymer is possible only with expenditure of energy from outside.

If the positive value of $\Delta_{pol}G^\circ(T)$ is small, then a low equilibrium polymer concentration corresponds to it in the equilibrium reaction mixture. If it is possible to create conditions such that the polymer formed is removed continuously from the equilibrium reaction mixture, then the conversion of the monomer into the polymer can be continued until the complete exhaustion of the monomer. Realistically this is possible, for example, in cases where the polylactone formed is insoluble in the reaction mixture and precipitates.[17] Calculations have shown that the standard Gibbs free energy for δ-valerolactone and ε-caprolactone are

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negative, whilst those for γ-butyrolactone are positive.[13] Accordingly, δ-valerolactone and ε-caprolactone are readily converted into the corresponding polymers under the influence of catalysts; γ-butyrolactone cannot be polymerised under the same physicochemical conditions. However, an increase in pressure from 10^5 to 2×10^9 Pa alters the sign of $\Delta_{pol}G(T)$ and leads to the virtually complete conversion of the monomer into poly-γ-butyrolactone.

The yield of the polymer corresponding to thermodynamic equilibrium and the content of the residual monomer in the polymer at any temperature for which the standard Gibbs free energy is known may be readily calculated from the values of $\Delta_{pol}G^\circ(T)$.[14] $\Delta_{pol}G^\circ(T)$ may be calculated if the enthalpies $\Delta_{pol}H^\circ(T)$ and entropies $\Delta_{pol}S^\circ(T)$ of polymerisation are known. The latter are usually found from the results of calorimetric measurements. The calculation of these quantities from the equilibrium concentrations of the monomer $[M]_e^\circ$ in the reaction mixture as a function of temperature, as averages for a certain temperature range in which $\Delta_{pol}H^\circ(T)$ and $\Delta_{pol}S^\circ(T)$ are independent of temperature or depend little on the latter, is possible in principle.[18] When this method is used, it is necessary to monitor rigorously the onset of the polymerisation-depolymerisation equilibrium in the reaction mixture at a specified temperature and pressure.[18-20] One must bear in mind that the approach to equilibrium is frequently slow, usually owing to the high viscosity of the reaction mixture.

For several of the lactone polymerisation reactions investigated, the quantities $\Delta_{pol}H^\circ$ have been obtained from the enthalpies of combustion Δ_cH° of the monomers and the corresponding polymers or from their enthalpies of formation Δ_fH° at 298.15 K and the standard pressure. For other reactions, $\Delta_{pol}H^\circ$ has been measured directly during polymerisation in calorimeters. We may note that the quantity $\Delta_{pol}H^\circ(T)$ is independently important as the initial parameter for the calculation of the energy balances in the development of industrial technologies for the synthesis of polymers.

The entropies of polymerisation of lactones $\Delta_{pol}S^\circ(T)$ are calculated from the absolute entropies of the reactants, which are evaluated in their turn from the experimental temperature variations of the heat capacities and the temperatures, and enthalpies of the physical transformations of the polymers and monomers using the Third Law of Thermodynamics.[21] For these calculations, it is necessary that the heat capacities of the test substances should be measured from as low temperatures as possible. The absolute entropies of the monomers are calculated in the usual way,[21] whilst their calculation for the polymers is complicated by the fact that in any physical state the entropies of the polymers at $T = 0$ K are not zero,[22,23] since polymers have a zero-point (residual) entropy $S^\circ(0)$.[22-24] This is associated with the fact that polymers, particularly polylactones, are partly crystalline or amorphous and constitute a mixture of macromolecules having different masses.[23,24] Furthermore, when polymers are cooled the conformations of the macromolecules are frozen at the glass transition temperature T_g°. On further cooling, such macromolecules do not pass to the state corresponding to thermodynamic equilibrium owing to the enormous activation energy for the rearrangement of their constituent segments and give rise to the so called conformational contribution S_{conf}° to the zero-point entropy of the polymer.[25-27] There are also other causes of the existence of $S^\circ(0)$.[23]

The problem of the zero-point entropy remained for a long time a serious obstacle to the calculation of the absolute entropies of polymers and hence to the employment of calorimetric methods for the determination of the thermodynamic parameters of polymerisation reactions.[24,28] A consequence of the neglect of the values of $S^\circ(0)$ for polymers was serious errors in the calculations of $\Delta_{pol}G^\circ(T)$, $[M]_e^\circ$, and the polymerisation-depolymerisation equilibrium constants, K_{pol}°.

Lebedev and Rabinovich[29] found a way of estimating the zero-point entropies of polymers in the amorphous state from experimental temperature variations of the heat capacities and the temperatures and enthalpies of the physical transformations of partly crystalline polymers. An approximate method for the determination of the configurational entropies S_{conf}° of amorphous polymers from the increments in their heat capacities on devitrification $\Delta C_p^\circ(T_g^\circ)$ at T_g° and from the ratio $T_g^\circ/T_2^\circ \approx 1.29$, where T_2° is the Kauzmann temperature,[30] has been proposed.[25,26] It was shown that the configurational entropy constitutes the main contribution to the zero-point entropies of polymers and in many cases S_{conf}° is close or even equal to $S^\circ(0)$.[25-27] Thus the problem of the calculation of the absolute entropies of polymers from calorimetric data has been virtually solved. The values of $\Delta_{pol}S(T)$ for more than 150 polymerisation reactions of monomers, including many lactones, have now been found from the absolute entropies of the reactants.

The physical transformations occurring on heating or cooling the test substances are manifested clearly in the temperature variations of the heat capacity, and the temperatures and enthalpies of these transformations may be measured accurately. By employing the heat capacities and the temperatures and enthalpies of the physical transformations, the enthalpies $H^\circ(T) - H^\circ(0)$, the entropies $S^\circ(T)$, and the Gibbs free energies $G^\circ(T) - H^\circ(0)$ may be found. These thermodynamic functions are used in their turn to calculate the enthalpies, entropies, and Gibbs free energies of the polymerisation processes. The thermochemical parameters Δ_fH°, Δ_fG°, Δ_fH°, and K_f°, of the formation of the monomers and polymers are calculated from the standard enthalpies of combustion and $S^\circ(298.15\ K)$. The degrees of crystallinity α of partly crystalline polymers are also estimated from calorimetric data.[31,32]

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

$$\alpha = 100\ \frac{\Delta_{fus}H^\circ(\alpha)}{\Delta_{fus}H^\circ(\alpha = 100\%)}, \quad (2)$$

where $\Delta C_p^\circ(\alpha)$ and $\Delta C_p^\circ(\alpha = 0)$ are respectively the increments in heat capacity on devitrification of the polymers at T_g° for the polymer with a degree of crystallinity α and for the fully amorphous polymer and $\Delta_{fus}H^\circ(\alpha)$ and $\Delta_{fus}H^\circ(\alpha = 100\%)$ are the enthalpies of fusion of the polymer with a degree of crystallinity α and the fully crystalline polymer.

The properties of polymers in the amorphous and crystalline states are estimated with the aid of the thermodynamic properties of the partly crystalline polymers. The method used for such estimations has been described.[29,33] The results permit, apart from the calculation of $S^\circ(0)$ for amorphous polymers, also the calculation of the difference between the zero-point enthalpies of the polymer in the vitreous and crystalline states $H_g^\circ(0) - H_{cr}^\circ(0)$ at $T = 0$ K.[33,34] Using the values of $S^\circ(0)$ and $H_g^\circ(0) - H_{cr}^\circ(0)$ as well as the temperature variations of the heat capacities of the monomers in the amorphous and crystalline states, it is possible to find the thermodynamic parameters of the conversion of the amorphous polymer into the crystalline form: $\Delta H^\circ(a;cr)$, $\Delta S^\circ(a;cr)$, and $\Delta G^\circ(a;cr)$ in the range $0 - T_{fus}^\circ$. The values of $\Delta G^\circ(a;cr)$ represent a kind of estimate of the absolute thermodynamic stability of the amorphous polymer in relation to its crystalline state.[35,36]

Polylactones are convenient objects for the determination of the dependences of the changes in the properties and thermodynamic parameters of the polymerisation reactions on the compositions and structures of the reactants — the monomer repeat units in the polymer macromolecules. In a series of polylactones, the composition changes by a CH_2 group on passing from one polylactone to another. This gives rise to a regular variation of the melting points and glass transition temperatures, heat capacities, thermodynamic functions, thermochemical parameters of formation, thermodynamic parameters of the polymerisation reactions, and other characteristics. If the above variations can be found, it is possible to estimate the properties of hitherto

uninvestigated polymers, as has been done for the alkanes,[35] polyalkenes,[36] and polyalkynylenes.[37]

In the present review, partly crystalline high-molecular-mass polylactones are examined (Table 1). For the polymers the degree of crystallinity of which has been determined, the latter proved to be somewhat greater than 60%. The masses of the monomer repeat units in the macromolecules of the polylactones were taken from Domalsky.[38]

II. Calorimetric research methods

1. Combustion calorimetry

Combustion calorimetry is used in direct measurements of the combustion energies $\Delta_c U$. The enthalpies of combustion $\Delta_c H^\circ$ and formation $\Delta_f H^\circ$ of compounds at 298.15 K and the standard pressure are calculated from the values of $\Delta_c U$. They are in turn necessary for the calculation of the enthalpies of polymerisation $\Delta_{pol} H^\circ$ under the same physical conditions. For this very purpose, Sunner and coworkers,[39] Hall,[40] Andruzzi,[41] and Kiparisova and the author of the present review[36] carried out experiments designed to determine $\Delta_c H^\circ$ and $\Delta_f H^\circ$ for lactones and the corresponding polylactones. The calorimetric apparatus and the methods used to measure $\Delta_c U$ by the above investigators did not differ fundamentally and in general were similar to those described by Skuratov et al.[42] However, Sunner and coworkers[39] used a rotating bomb calorimeter†.

Lebedev and Kiparisova[36] used a calorimeter with an isothermal jacket and a static bomb of the inverted type. In the calculation of the combustion energies $\Delta_c U$ under the conditions in the bomb calorimeter, the usual thermochemical corrections were taken into account.[42] The values of $\Delta_c U$, adjusted to the standard pressure, were then used to calculate $\Delta_c H^\circ$ and $\Delta_f H^\circ$.

The majority of the values of $\Delta_c H^\circ$ were determined with an error of ~0.02%.

2. Adiabatic vacuum calorimetry

Adiabatic vacuum calorimetry has been used to measure the temperature variation of the heat capacity C_p° and the temperatures and enthalpies of the physical transformations of polylactones in the range from 13.8 to 320 K. The thermodynamic parameters of fusion T_{fus}°, $\Delta_{fus} H^\circ$, and $\Delta_{fus} S^\circ$, the parameters of vitrification and the vitreous state T_g°, the increase in heat capacity on devitrification of the polymer $\Delta C_p^\circ(T_g^\circ)$, the zero-point $[S^\circ(0)]$ and configurational (S_{conf}°) entropies, the Kauzmann temperature T_2°, and the difference $H_g^\circ(0) - H_{cr}^\circ(0)$ were obtained from the above measurements. Hitherto virtually all the measurements of C_p° for polylactones in the range 13.8–370 K have been carried out on a thermophysical apparatus, the design of which and also the methods of measurement have been published.[13,43] Overall, the analysis of the calibrations and checks of the calorimeter employed and of the experimental method permitted the conclusion that the error in the measurements of C_p° for the polymer was to within 1% in the range 13.8–20 K, 0.5% in the range 30–90 K, and 0.25% in the range 90–370 K; the error in the measurement of the temperature was 0.01 K in conformity with the International Practical Temperature Scale (IPTS-68) and that in the enthalpies of the transformations was 0.25%.

An adiabatic calorimeter of the Gal'chenko–Popov type was used in the measurements of the heat capacity in the range 300–550 K. The design of the calorimeter and the method of measurement have been described.[44,45]

3. Differential scanning calorimetry

Differential scanning calorimetry (DSC) has been used in the study of polylactones mainly to obtain the melting points, the crystallisation temperatures, and the enthalpies of fusion.[46–50] Wunderlich and coworkers[50] used this method to investigate the temperature variation of the heat capacity, the glass transition temperature, the crystallisation temperature, and the melting point of polypivalolactone. The principles underlying the design of the differential scanning calorimeters and of the methods for their employment have been examined in a series of studies[51–55] and on the whole are well known. The results obtained are consistent throughout with the data of the U S National Bureau of Standards[56] to within approximately ±0.1%. The details of the methods of measurement are described by Jin and Wunderlich.[57]

4. Isothermal calorimeter of the Mathews type

An isothermal calorimeter of the Mathews type has been used for the direct measurements of the enthalpies of polymerisation of a series of lactones with formation of the corresponding polylactones. The enthalpy of polymerisation was determined from the mass of carbon tetrachloride vaporised at its normal boiling point (349.66 ± 0.05 K) by the energy evolved on polymerisation of the monomer. The design of the calorimeter and the experimental method have been described.[58] The reliability of the operation of the calorimeter has been confirmed by the exact reproduction of Joshi's precision experiments[59] on the polymerisation of methyl methacrylate and styrene.[60] The values of $\Delta_{pol} H^\circ$ obtained for these monomers did not differ from those quoted by Joshi[59] by more than 0.3%.

III. Heat capacity

Polyglycolide. The polymerisation of glycolide with ring opening leads to the formation of polyglycolide. According to the formula of its smallest repeat unit (Table 1), it can be formally regarded as a polylactone which might have been obtained from a three-membered lactone, the latter apparently not existing owing to the high ring strain energy. The results of calorimetric measurements of the heat capacity of a partly crystalline (α = 67%) polyglycolide with a molecular mass (found from the viscosity) of 3.8×10^4 have been published by Lebedev et al.[61] The heat capacity was determined in adiabatic calorimeters with an error of ~0.3% in the range 13.8–335 K[43] and ~0.7% in the range 335–550 K.[44] In the ranges 13.8–250, 340–450, and 501–550 K, the heat capacity of the polyglycolide increases smoothly with increasing temperature (Fig. 1). The rapid increase in C_p° in the range 250–345 K is associated with the devitrification of the amorphous component of the specimen, while the sharp increase in heat capacity and the break in the $C_p^\circ - T$ plot in the range 440–501 K are caused by the fusion of the crystalline component of the test specimen. Overall, the temperature variation of the heat capacity of polyglycolide is typical of that for partly crystalline polymers:[14] in the range from 60–80 K up to the temperature of the onset of

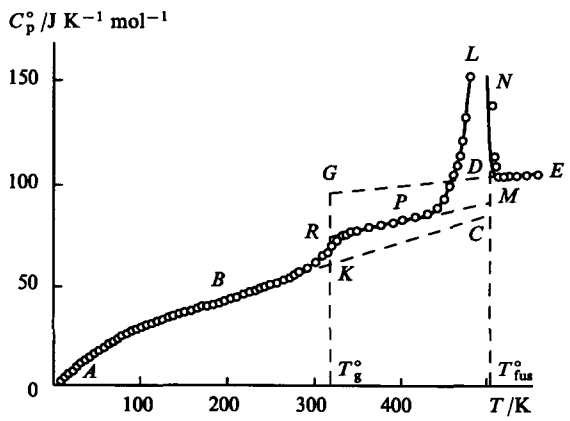


Figure 1. The heat capacity of polyglycolide:[61] *ABRPM* — with 67% crystallinity, *AKC* — crystalline, *AK* — vitreous, *GD* — highly elastic, *DE* — liquid; *PLND* — apparent heat capacity in the melting range.

† All the characteristics of the calorimeter employed by the above workers may be found in the paper of Lebedev and Kiparisova.[36]

Table 1. The polylactones considered in the review.

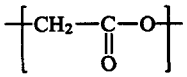
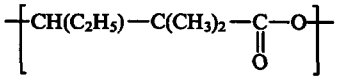
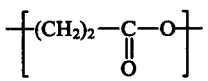
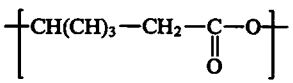
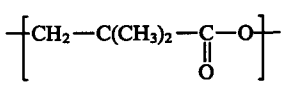
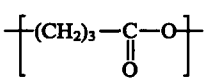
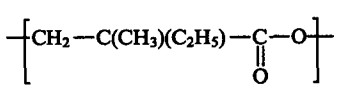
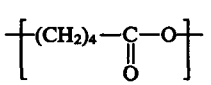
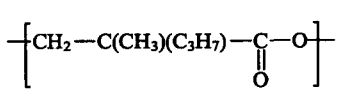
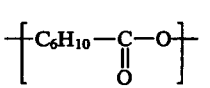
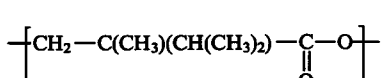
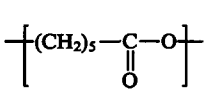
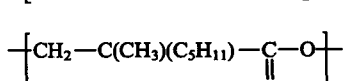
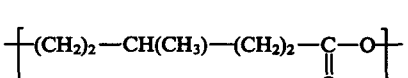
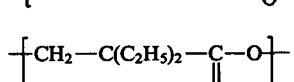
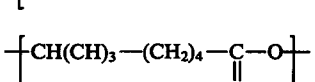
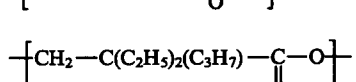
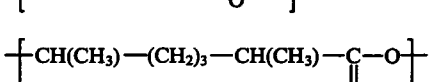
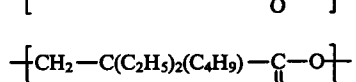
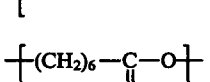
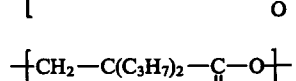
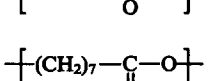
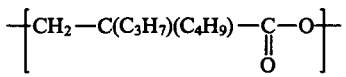
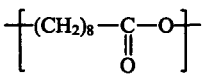
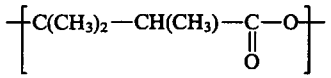
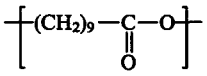
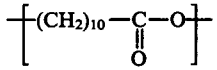
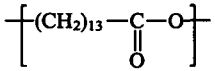
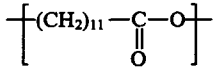
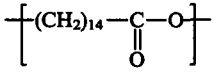
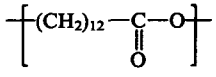
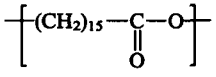
Polylactones	Monomer repeat unit		Polylactones	Monomer repeat unit	
	formula	mass /g mol^{-1} [a]		formula	mass /g mol^{-1} [a]
Polyglycolide		58.038	Poly-β-ethyl-α,α-dimethyl-β-propiolactone		128.171
Poly-β-propiolactone		72.063	Poly-β-methyl-β-propiolactone		86.090
Poly-α,α-dimethyl-β-propiolactone		100.117	Poly-γ-butyrolactone		86.090
Poly-α-ethyl-α-methyl-β-propiolactone		114.144	Poly-δ-valerolactone		100.117
Poly-α-methyl-α-n-propyl-β-propiolactone		128.171	Polyoxacarbonyl-1,4-cyclohexylene		126.155
Poly-α-isopropyl-α-methyl-β-propiolactone		128.171	Poly-ε-caprolactone		114.149
Poly-α-methyl-α-pentyl-β-propiolactone		156.224	Poly-γ-methyl-ε-caprolactone		128.171
Poly-α,α-diethyl-β-propiolactone		128.171	Poly-ε-methyl-ε-caprolactone		128.171
Poly-α-ethyl-α-n-propyl-β-propiolactone		142.197	Poly-α,ε-dimethyl-ε-caprolactone		142.197
Poly-α-ethyl-α-n-butyl-β-propiolactone		156.224	Poly-η-caprylolactone		128.171
Poly-α,α-di-n-propyl-β-propiolactone		156.224	Poly-λ-laurolactone		142.197

Table 1 (continued).

Polylactones	Monomer repeat unit		Polylactones	Monomer repeat unit	
	formula	mass /g mol^{-1} [a]		formula	mass /g mol^{-1} [a]
Poly-α-n-butyl-α-n-propyl-β-propiolactone		170.343	Polynonanolactone		156.224
Poly-α,α-dimethyl-β-methyl-β-propiolactone		114.144	Polydecanolactone		170.343
Polyundecanolactone		184.278	Polytetradecanolactone		226.358
Polydodecanolactone		198.305	Polypentadecanolactone		240.385
Polytridecanolactone		212.331	Polyhexadecanolactone		254.505

[a] Values taken from Domalsky.[38]

the devitrification of the amorphous component of the polymer, the heat capacity is a linear function of temperature; the heat capacity of liquid polyglycolide is also a linear function of temperature, as for many other polymers.[50,62]

Poly-β-propiolactone. The results of calorimetric measurements of the heat capacity of poly-β-propiolactone have been published.[63] The specimen was obtained by the polymerisation of β-propiolactone. The mass-average ($\bar{M}_w$) and number-average ($\bar{M}_n$) molecular masses of the polymer were respectively 3×10^4 and 8.3×10^3, the polydispersity coefficient was $\bar{M}_w/\bar{M}_n = 3.8$, and the degree of crystallinity was $\alpha = 79\%$. The heat capacity of poly-β-propiolactone was measured in an adiabatic vacuum calorimeter[43] in the temperature range 13.8–330 K with an error of ~0.3% and in an adiabatic calorimeter[44] in the range 330–400 K with an error of ~1%. The devitrification of the amorphous component of the specimen began at 240 K (Fig. 2), its completion being masked by the onset of the fusion of the crystalline component; the break in the $C_p^\circ - T$ relation in the melting range is also associated with this factor. In the range 100–210 K, the heat capacity is a linear function of temperature and is described by the following equations subject to an error of ±0.3%:

$$C_p^\circ = 14.7 + \frac{T}{4},$$

where C_p° is the molar heat capacity of the polymer expressed in J mol^{-1} K^{-1}. The heat capacity of the poly-β-propiolactone melt is also a linear function of temperature. The temperature variations of the heat capacity of poly-β-propiolactone in the amorphous and crystalline states have been plotted on the basis of the experimental data by the method proposed in the study of Lebedev and Rabinovich[29] (Fig. 2).

Poly-β-methyl-β-propiolactone (poly-β-butyrolactone) is obtained by the polymerisation of β-butyrolactone with ring opening[64,65] or from (*R*)-3-hydroxybutyric acid under the influence of microorganisms in the course of enzymic reactions.[8,66] Lebedev et al.[67] investigated the temperature variation of the heat capacity of a poly-β-methyl-β-propiolactone specimen obtained from (*R*)-3-hydroxybutyric acid by a biotechnological method.[68] The number-average molecular mass of the polymer was 10^5 and its degree of crystallinity was 66%. The specimen was highly isotactic. The heat capacity was measured in the temperature range 10–490 K: in an adiabatic vacuum calorimeter (AVC)[68] in the temperature range 10–340 K with an error of ~0.2% and in a dynamic calorimeter (DC)[69] in the range 340–490 K with an error of 0.5%–1.5%. The results are presented in Fig. 3.

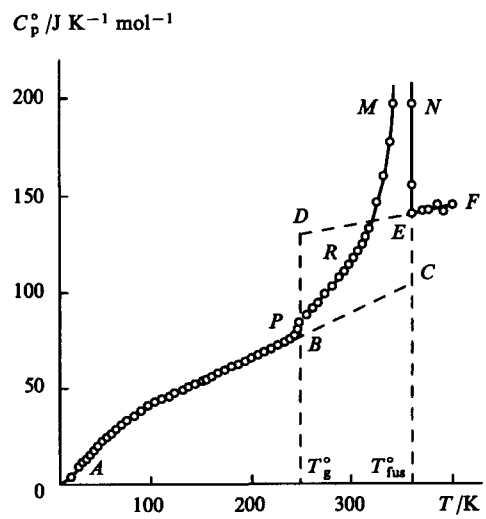


Figure 2. Temperature dependence of the heat capacity of poly-β-propiolactone.[63]
State of the polymer: *ABC* — crystalline; *AB* — vitreous; *DE* — highly elastic; *EF* — liquid; *APR* — partly crystalline, $\alpha = 79\%$; *RMNE* — apparent heat capacity in the melting range.

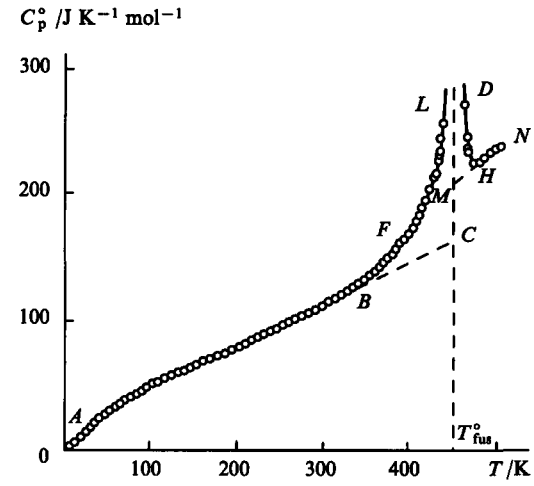


Figure 3. Temperature dependence of the heat capacity of poly-β-methyl-β-propiolactone.[67]
State of the polymer: *ABC* — crystalline; *MHN* — liquid; *ABF* — partly crystalline, $\alpha = 66\%$; *FLDH* — apparent heat capacity in the melting range.

A characteristic feature of the temperature variation of the heat capacity of poly-β-methyl-β-propiolactone obtained is the absence of the devitrification of the amorphous component of the specimen — only the fusion of the crystalline component is manifested. Such relations are usually characteristic of polymers with a degree of crystallinity close to 100% (more than 90%). In the given instance, it was only 66%. For virtually the same degree of crystallinity, the devitrification of polyglycolide (Fig. 1) is manifested very clearly. The reason for this is probably the degree of interaction of the crystalline and amorphous components in partly crystalline polymer specimens — microheterogeneous systems.[70] It appears that the greater the uniformity in the distribution of the microheterogeneous crystalline and amorphous components in the bulk of the specimen, the greater the uniformity in their mutual influence and, in particular, in the reinforcement of the amorphous component of the polymer by crystals, which prevents the excitation of segmental motions in the polymer molecules on devitrification.[71,72]

Poly-α,α-dimethyl-β-propiolactone (polypivalolactone). The heat capacity of poly-α,α-dimethyl-β-propiolactone has been determined by Wunderlich and coworkers[50] in a DSC-7 differential scanning calorimeter in the range 140–550 K at a rate of heating of the calorimeter with the test substance of 1.7×10^{-1} K s^{-1}. A specimen with a molecular mass of 2.5×10^5 was investigated; the degree of crystallinity of the initial specimen was 51%. The devitrification of the amorphous component of the polymer in the range 260–280 K (section *BC*) and two transitions were manifested on the temperature variation of the heat capacity (Fig. 4, curve *1*): the first transition in the form of a diffuse hump (*DGN*) and the second in the form of the typical temperature variation of the apparent heat capacity of the polymer in the melting range (*NRSU*).

The first transition begins at 380 K, the maximum apparent heat capacity (point *G*) corresponds to 421.5 K, and the end of the transformation is masked by the onset of the fusion process. The nature of the transition is not altogether clear. However, one may postulate that it is due to the transformation of one crystalline modification of poly-α,α-dimethyl-β-propiolactone into another.

Poly-α,α-dimethyl-β-propiolactone is known to be capable of forming three crystalline modifications — α, β, and γ.[73,74] The crystals melt in the range 497–530 K. The maximum apparent heat capacity corresponds to 511 K. The temperature variation of

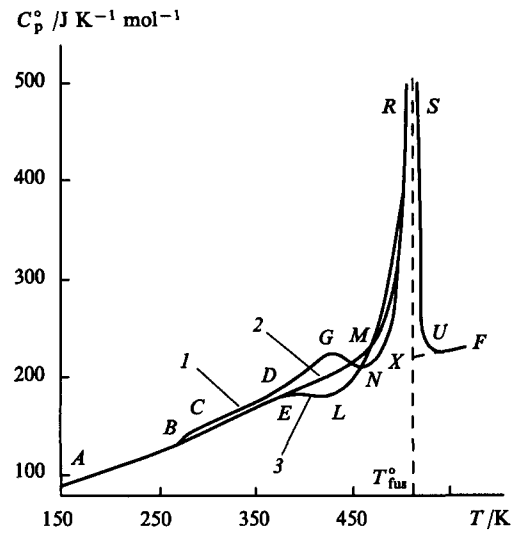


Figure 4. Temperature dependence of the heat capacity of poly-α,α-dimethyl-β-propiolactone.[50]
(*1*) Initial specimen; (*2*) specimen obtained by natural cooling of the melt in air; (*3*) specimen obtained by cooling the melt with liquid nitrogen (cooling rate 5.3 K s^{-1}); for the significance of the letter designations, see text.

C_p° of the polymer melt cooled naturally from 540 K in air is described by curve *2* in Fig. 4. It was found that the degree of crystallinity in the specimen obtained in this way is 68%. Only fusion, which begins at 502 K and ends at 530 K, is manifested on the curves describing the $C_p^\circ = f(T)$ relation; the maximum in the apparent heat capacity corresponds to 513 K.

The third series of measurements was carried out for a specimen of poly-α,α-dimethyl-β-propiolactone obtained by rapid cooling of the polymer melt with liquid nitrogen (rate of cooling ~5.3 K s^{-1}). Vitrification was again manifested on the $C_p^\circ = f(T)$ relation (Fig. 4, curve *3*) together with an exothermic transformation (*ELN* section) and fusion. Even on such rapid cooling, the polymer was obtained in a highly crystalline form, its degree of crystallinity being close to that of the initial specimen. Repeated measurements of C_p° in the range 150–260 K and averaging of the latter yielded the following equation which makes it possible to determine the heat capacity of the polymer with an error of ~0.3%:

$$C_p^\circ = \exp[-48.06197 + 27.29137 \ln T - \\ -4.791726(\ln T)^2 + 0.28686(\ln T)^3], \quad (3)$$

where C_p° is expressed in J mol^{-1} K^{-1}.

For the liquid polymer, the following equation was obtained also as a result of several experimental measurements:

$$C_p^\circ = 112.4 + 0.221T,$$

which reproduces satisfactorily (with an error of ±0.13%) the heat capacities in the range 510–550 K.

Using the results of experimental determinations of the heat capacity and the vibration frequency of the atoms and atomic groups in poly-α,α-dimethyl-β-propiolactone, Wunderlich and coworkers[50] calculated the heat capacity of the polymer in the range 0.1–1000 K. The isochoric heat capacity, C_v, as well as the contributions to this quantity by skeletal and atomic vibrations calculated per monomer repeat unit in the polylactone macromolecules were estimated for the same range.

Poly-γ-butyrolactone. The results of the study of the temperature variation of the heat capacity of poly-γ-butyrolactone in an adiabatic vacuum calorimeter[43] at temperatures in the range 13.8–340 K have been published by Evstropov et al.[75] The error of the measurements was 0.3%. The test specimen was obtained by the bulk polymerisation of γ-butyrolactone under a pressure of 2×10^6 kPa, because at the usual pressure the monomer does not polymerise. The number-average molecular mass of the polymer was $\overline{M}_n = 3 \times 10^3$ and its degree of crystallinity was $\alpha = 67\%$. The amorphous component of the specimen devitrified in the range 200–235 K and the crystalline component melted in the range 245–335 K. In the course of slow stepwise cooling of poly-γ-butyrolactone melt, Evstropov et al.[75] were able to measure the C_p° of the polymer in the supercooled liquid (highly elastic) state up to a temperature 12 K below its melting point. Overall, the plot of the temperature variation of the heat capacity of poly-γ-butyrolactone has a form similar to that of the plot of the same relation for poly-β-propiolactone (Fig. 2).

Poly-δ-valerolactone. Evstropov et al.[76] Published the results of a study of the temperature variation of the heat capacity of poly-δ-valerolactone in an adiabatic vacuum calorimeter[43] in the range 13.8–340 K. The error of the measurements of C_p° was ~0.3%. The test specimen was obtained by the polymerisation of δ-valerolactone. The viscosity-average and number-average molecular masses of poly-δ-valerolactone were respectively 3.6×10^3 and 1.4×10^3, the polydispersity coefficient was ~2.5, and the degree of crystallinity of the specimen was 70%. The $C_p^\circ - T$ plot was similar to that presented in Fig. 2 for poly-β-propiolactone. The amorphous component of the polymer devitrified in the range 190–215 K and fusion, accompanied by a break in the $C_p^\circ = f(T)$ function, occurred in the range 250–330 K. On slow stepwise cooling of the polymer melt, it was possible to measure its heat capacity in the supercooled liquid state — from the melting point corresponding to thermodynamic equilibrium down to a temperature 10 K below it.

Poly-ε-caprolactone. The results of calorimetric studies of the heat capacity of poly-ε-caprolactone have been published by Lebedev and coworkers.[77,78] The measurements in an adiabatic vacuum calorimeter[43] in the range 13.8–340 K were carried out with an error of ~0.3%,[77] while those in a differential scanning calorimeter in the range 77–360 K were subject to an error of ~1.5%.[78]

Since all the subsequent calculations and conclusions are based on the treatment of the results of Lebedev et al.[77], we shall note the most important characteristics of the polymer which they investigated. The poly-ε-caprolactone specimen was obtained by the polymerisation of ε-caprolactone ($\overline{M}_w = 2.9 \times 10^4$, $\alpha = 63\%$). The temperature variation of the heat capacity of the polymer had no singularities: it increased smoothly with increase in temperature, a more rapid rise in C_p° being observed, as for other polylactones, in the devitrification range for the amorphous part of the specimen (200–245 K); the sharp rise in C_p° and the break in the $C_p^\circ - T$ plot in the range 298–336 K are due to the fusion of the crystalline component of the polymer. The differences between the heat capacities quoted in the above two studies[77,78] do not exceed 1.5% in the range 90–130 K, 0.5% in the range 130–200 K, and 1% in the range 200–250 K.

Polyundecanolactone. The temperature variation of the heat capacity of polyundecanolactone in the temperature range 0–370 K has been published by Evstropov.[79] The measurements of C_p° were carried out in an adiabatic vacuum calorimeter[43] in the range 14–366 K subject to an error of ~0.3%. The test specimen was obtained by the polymerisation of undecanolactone. The viscosity-average and number-average molecular masses of the polymer were 3.4×10^4 and 1.0×10^4 respectively. The degree of crystallinity of the specimen was 73%. The $C_p^\circ - T$ plot was similar to that presented in Fig. 2 for poly-β-propiolactone. The amorphous component of the specimen devitrified in the range 190–270 K and fusion, accompanied by a break in the $C_p^\circ - f(T)$ relation, occurred in the range 270–365 K. On slow stepwise cooling of the polyundecanolactone melt, it was possible to measure its heat capacity in the supercooled liquid (highly elastic) state in the temperature range from T_{fus}° to 350 K, which is 15 K below the melting point of polyundecanolactone.

Polytridecanolactone. The results of the study of the temperature variation of the heat capacity of polytridecanolactone in the range 0–370 K have been published by Lebedev et al.[80] The polymer specimen investigated was obtained by the polymerisation of tridecanolactone. The intrinsic viscosity of polytridecanolactone, measured in chloroform at 298 K, was 0.82 dl g^{-1} and its degree of crystallinity was 75%. The heat capacity was determined in an adiabatic vacuum calorimeter[43] in the range 14–370 K. The error of the values of C_p° obtained was ~0.3%. The devitrification of the amorphous component began at 200 K and its end was masked by the incipient fusion of the crystalline component in the range 280–365 K. The polytridecanolactone melt hardly supercooled. Overall, the $C_p^\circ - T$ plot is similar to that presented in Fig. 2 for poly-β-propiolactone.

Polypentadecanolactone.[81] The heat capacity of polypentadecanolactone was determined in an adiabatic vacuum calorimeter[43] in the range 13.8–372 K with an error of ~0.3%. The test specimen was obtained by the polymerisation of pentadecanolactone. The intrinsic viscosity of a solution of the polymer in chloroform at 298 K was 0.93 dl g^{-1} and the degree of crystallinity of the polymer was 77%. The $C_p^\circ - T$ plot for polypentadecanolactone is similar to the plot presented in Fig. 3 for poly-β-methyl-β-propiolactone. The amorphous component devitrified in the range 200–270 K. In the range 140–200 K, the heat capacity of polypentadecanolactone is described by the equation

$$C_p^\circ = 51.34 + 1.0659T,$$

The deviation of the experimental C_p° points from those calculated by the equation is throughout within the limits of 0.2%. The heat capacity of the fused specimen, like that of other polylactones, is a linear function of temperature. In contrast to some of the preceding polylactones, polypentadecanolactone does not supercool in the liquid state.

IV. Thermodynamics of fusion

The fusion of all partly crystalline polylactones takes place over a wide temperature range. The $C_p^\circ - T$ plots in the melting range have left-hand branches, which ascend comparatively rapidly with increase in temperature, and rapidly descending right-hand branches (Figs. 1–4). Fig. 5 presents typical integral and differential fusion curves for polylactones in relation to poly-ε-caprolactone as an example.[77] They reflect the distribution of the crystals with respect to the melting points. Evidently poly-ε-caprolactone melts in the range 210–337 K, approximately 70% of the mass of the crystals melting over a comparatively narrow temperature range (328–337 K), and most of them melt at 336 K.

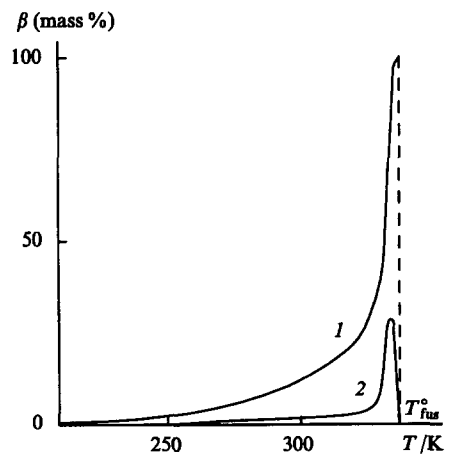


Figure 5. Temperature dependence of the fraction of the melt in the crystalline component of a poly-ε-caprolactone specimen (α = 75%).[77] Integral (*1*) and differential (*2*) curves.

The nonisothermal nature of fusion is known to be caused by the polycrystallinity of polymers — the presence of a set of different metastable and crystalline formations with ultramicroscopic and microscopic dimensions and with different chemical potentials. For ultramicroscopic dimensions of the crystals, the Gibbs free energy of the surface constitutes a significant proportion of the total Gibbs free energy *G*. Below the melting point corresponding to thermodynamic equilibrium, $G(\text{cr}) < G(\text{l})$ and at this temperature $\Delta G = 0$. This condition is attained at different temperatures for small crystals of different size: the smaller the crystal, the lower its melting point. This is in fact the reason for the nonisothermal nature of fusion.[14] The fact that the crystallisation of the polymer does not entail the formation of microscopically ideal crystals of one definite type, the chemical potential of which depends only on the temperature and pressure, can also be accounted for by mainly kinetic causes.

Table 2 presents the thermodynamic parameters of the fusion of polylactones found from the results of calorimetric measurements. The greatest number of data have been obtained by adiabatic vacuum calorimetry. The melting points, corresponding to thermodynamic equilibrium, of defect-free ideal polymer crystals are presented for polylactones investigated by this method. For their calorimetric determination, measurements were made of the melting points T_F°, corresponding to thermodynamic equilibrium, for fractions *F* of the polymer melt. It was found that, for the polylactones investigated, the $T_F^\circ - F^{-1}$ plots are straight lines described satisfactorily by the equation

$$T_F^\circ = T_0^\circ - F^{-1}(T_0^\circ - T_1^\circ), \qquad (4)$$

where T_1° and T_0° are the melting points, corresponding to thermodynamic equilibrium, of the crystals of the polymer specimen employed and a hypothetical defect-free crystal of the same polymer respectively. The above equation is used mainly for low-molecular-mass substances.[83] For example, the following results have been obtained for poly-ε-caprolactone:[77]

F^{-1}	4.456	2.610	1.305	1.071
T_F°/K	314.584	325.586	334.408	335.420.

T_1° = 336 K was obtained from the $T_F^\circ - F^{-1}$ plot for $F^{-1} = 1$ and T_1° = 342 K was found by extrapolation for $F^{-1} = 0$.

The enthalpies of fusion of the test specimens of the polymers were measured by the method involving the continuous injection of energy[82] and were calculated by the equation

$$\Delta_{fus}H^\circ(\alpha) = \left\{\Delta H_i^\circ - \int_{T_i^\circ}^{T_{fus}^\circ} C_p^\circ(\text{s})\,dT - \int_{T_{fus}^\circ}^{T_f^\circ} C_p^\circ(\text{l})\,dT - \int_{T_i^\circ}^{T_f^\circ} C_{cal}\,dT\right\}\frac{M}{m}, \qquad (5)$$

where ΔH_i° is the amount of energy consumed in the heating of the calorimeter with the test substance from the initial experimental temperature T_i° to the final temperature T_f°, $C_p^\circ(\text{s})$ and $C_p^\circ(\text{l})$ are the temperature variations of the heat capacities of a polymer specimen (placed in the calorimeter) with a mass *m* in the solid (s) and liquid (l) states, C_{cal} is the heat capacity of the empty calorimeter, and *M* is the molecular mass of the specimen.

The average value of $\Delta_{fus}H^\circ(\alpha)$ was calculated from the results of 3–4 experiments and was then used to calculate the molar enthalpy of fusion of the crystalline polymer $\Delta_{fus}H^\circ(\alpha = 100\%)$ from the formula

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

where α is the degree of crystallinity.

In the study of the fusion process by differential scanning and dynamic calorimetry, the temperatures corresponding to the maximum apparent heat capacity in the melting range or the

Table 2. Thermodynamic parametera of the fusion of polylactones.

Polylactone	T°_{fus} /K	$\Delta_{fus}H^\circ(\alpha = 100\%)$ /kJ mol^{-1}	$\Delta_{fus}S^\circ(\alpha = 100\%)$ /J mol^{-1} K^{-1}	$\Delta C^\circ_p(\alpha = 100\%)$ /J mol^{-1} K^{-1}	Method of determination	Ref.
Polyglycolide	501 ± 1	11.8 ± 0.5	24 ± 1	20	DSC	61
Poly-β-propiolactone	366 ± 1	10.2 ± 0.5	29.9 ± 1.4	35	AVC	63
Poly-α,α-dimethyl-β-propiolactone	513	14.9	29.0	44	DSC	47, 50
Poly-β-methyl-β-propiolactone	454	12.6	27.7	45	DC	8,67
Poly-α,α-diethyl-β-propiolactone	531	21.0	40.0	–	DSC	49
Poly-γ-butyrolactone	338 ± 1	13.2 ± 0.3	39.4 ± 0.6	29	AVC	75
Poly-δ-valerolactone	331 ± 2	18.2 ± 0.3	55 ± 1	40	AVC	76
Poly-ε-caprolactone	342 ± 1	19.0 ± 0.3	55.5 ± 1.1	38	AVC	77, 78
Poly-η-caprylolactone	354	24.4	70	–	Interpolation	82
Poly-λ-laurolactone	358	28.2	79	–	"	82
Polynonanolactone	361	31.9	88.5	–	"	82
Polydecanolactone	363	35.6	98	–	"	82
Polyundecanolactone	365 ± 1	38.2 ± 0.8	105.2	64	AVC	79
Polydodecanolactone	366	43	118	–	Interpolation	82
Polytridecanolactone	368 ± 1	46 ± 1.5	125 ± 4	63	AVC	80
Polytetradecanolactone	369	51	137	–	Interpolation	82
Polypentadecanolactone	371 ± 1	56 ± 2	151 ± 6	87	AVC	81

maximum temperature of the melting range were adopted as T°_{fus}.[69] This is in fact the usual explanation of the discrepancies between the melting points quoted in different publications for the same polylactone. Unfortunately the temperatures T°_{fus} obtained by differential scanning calorimetry at specific rates of heating of the calorimeter with the test substance have not been adjusted to the zero heating rate. The enthalpies of fusion $\Delta_{fus}H^\circ(\alpha)$ were also determined in several experiments. The method has been described, for example, by Lebedev et al.[84] The average value of $\Delta_{fus}H^\circ(\alpha)$ obtained was then recalculated as $\Delta_{fus}H^\circ(\alpha = 100\%)$ by Eqn (6).

The entropies of fusion $\Delta_{fus}S^\circ(\alpha = 100\%)$ for all the polylactones (Table 2) were found from the enthalpies $\Delta_{fus}H^\circ(\alpha = 100\%)$ and the melting points T°_{fus} by the equation

$$\Delta_{fus}S^\circ(\alpha = 100\%) = \frac{\Delta_{fus}H^\circ(\alpha = 100\%)}{T^\circ_{fus}}. \quad (7)$$

The heat capacity change $\Delta C^\circ_p(\alpha = 100\%)$ on passing from the crystalline to the liquid polymer at the melting point was found graphically. For example, $\Delta C^\circ_p(\alpha = 100\%)$ for polyglycolide is represented by section *CD* in Fig. 1.

In conclusion we may note that the results of measurements of the melting point and enthalpy of fusion of poly-β-propiolactone by differential scanning calorimetry have been published by Crescenzi et al.:[46] $T^\circ_{fus} = 357$ K and $\Delta_{fus}H^\circ(\alpha = 100\%) = 9.6$ kJ mol^{-1}. The enthalpy of fusion agrees satisfactorily with the value published by Lebedev et al.[61] (Table 2), while the melting point is significantly lower, which is natural since Lebedev et al.[61] calculated the melting point for an ideal defect-free poly-β-propiolactone crystal. Kort and Glet[85] gave the melting point and the specific enthalpy of fusion for poly-α-methyl-α-n-propyl-β-propiolactone as 370 K and 8 J g^{-1}, but there are no data on the degree of crystallinity of the test specimen. For this reason, it is impossible to calculate $\Delta_{fus}H^\circ(\alpha = 100\%)$ for this polymer.

Kort and Glet[85] found that the melting point of poly-γ-butyrolactone is 334–335 K. This also differs slightly from the temperature quoted in Table 2. The reason for the difference is the same as in the case of poly-β-propiolactone. Tadokoro et al.[86] determined $T^\circ_{fus} = 326$ K for poly-δ-valerolactone, which is 5 K lower than the corresponding temperature in Table 2. The values $\Delta_{fus}H^\circ(\alpha = 100\%) = 19 \pm 2$ kJ mol^{-1} and $T^\circ_{fus} = 336$ K have been obtained[78] for poly-ε-caprolactone in adiabatic vacuum calorimetry. The same quantities found by differential scanning calorimetry[46] proved to be $\Delta_{fus}H^\circ(\alpha = 100\%) = 15.9$ kJ mol^{-1} and $T^\circ_{fus} = 336$ K. The enthalpies of fusion found from the results of Lebedev et al.[77] and Beraty[78] agree, while the value measured by Crescenzi et al.[46] is apparently too low.

We may note that, according to our observations,[14] the decrease in the melting points of polymers ($\Delta T^\circ_{fus} = T^\circ_0 - T^\circ_1$ is usually between 4 and 10 K, which is much larger than for the corresponding monomers with approximately the same content of impurities in the usual sense. In the case of polymers, the end groups of the macromolecules and crystal defects are also regarded as impurities.

In conclusion,we shall give a list of the melting points of di- and tri-alkyl-substituted poly-β-propiolactones published by Cornibert et al.[87] and Thielaut et al.[88]

Polylactone	T°_{fus} /K
Poly-β-propiolactone	357
Polyα,α-dimethyl-β-propiolactone	513
Poly-α-ethyl-α-methyl-β-propiolactone	398
Poly-α-methyl-α-n-propyl-β-propiolactone	370
Poly-α-isopropyl-α-methyl-β-propiolactone	298
Poly-α-methyl-α-pentyl-β-propiolactone	327
Poly-α,α-diethyl-β-propiolactone	531
Poly-α-ethyl-α-n-propyl-β-propiolactone	478
Poly-α-n-butyl-α-thyl-β-propiolactone	453
Poly-α,α-di-n-propyl-β-propiolactone	530
Poly-α-n-butyl-α-n-propyl-β-propiolactone	500
Poly-α,α-di-n-butyl-β-propiolactone	518
Poly-α,α-dimethyl-β-methyl-β-propiolactone	458
Poly-β-ethyl-α,α-dimethyl-β-propiolactone	423

V. Parameters of vitrification and the vitreous state

Table 3 presents the parameters of the vitrification and the vitreous state of polylactones obtained from the results of calorimetric measurements by adiabatic vacuum and differential scanning calorimetry; the glass transition temperatures of a series of polylactones have been found by the torsional pendulum (TP) method.[91] The temperature of the onset of the devitrification of polylactones in partly crystalline states is distinctly manifested on the temperature variations of C_p° (see, for example, Figs 1 and 2). However, the end of the devitrification process is in most cases masked by the incipient partial fusion of polylactones and it is therefore difficult to determine the temperature at which devitrification comes to an end. Nevertheless, one may conclude that polylactones are devitrified in the range from 20 K (for example, in the case of poly-α,α-dimethyl-β-propiolactone[50]) to 60 K (for polyundecanolactone[79]). The glass transition temperature T_g° is usually close to the average temperature of the vitrification range, but can be determined more accurately from the point of inflection in the $C_p^\circ - T$ and $S^\circ(T) - T$ plots.[92]

We may note that, since vitrification is a relaxation process,[14] it follows that in the vitrification temperature range the relaxation time of the conformational motions of the segments is of the same order of magnitude as the duration of the experiment (the time required to supply energy to the system). The results of the determination of T_g° therefore depend on the rate at which measurements are made and on the method of the preliminary heat treatment of the polymers (for example, quenching and annealing). The glass transition temperature of poly-β-propiolactone has been found as 245 ± 2 K by the torsional pendulum method,[90] which is slightly below the value obtained by the AVC method (Table 3). For a rapidly cooled specimen of poly-α,α-dimethyl-β-propiolactone, $T_g^\circ = 259.8$ K,[50] while for a specimen with a degree of crystallinity of 79% it amounts to 267.8 K. The following values of T_g° have been found for poly-ε-caprolactone by different investigators using the torsional pendulum method: 202 K,[89] 209 K,[92] and 218 K.[93] The lowest value of T_g° corresponds to the fully amorphous polymer specimen and the highest to the specimen with the highest degree of crystallinity.

Thus an increase in the degree of crystallinity leads to an increase in T_g°. This can apparently be explained by the effect of the reinforcement of the amorphous component of the polymer by crystals, which hinder the excitation of the motion of the segments of the macromolecules on devitrification.[71] As a result of this, the devitrification of partially crystalline polymers occurs at higher temperatures, in contrast to amorphous polymers in which there is no reinforcement effect.

The increase in heat capacity on devitrification of the fully amorphous polymer at the glass transition temperature has been found graphically (Table 3). For example, $C_p^\circ(T_g^\circ)$ for poly-β-propiolactone is represented by section *DB* in Fig. 2. The justification of the validity of the extrapolation of the heat capacity, presented, for example, in Fig. 2, has been described in detail.[29] The difference between the enthalpies of the polymer in the vitreous and crystalline states and the zero-point (residual) entropies of the polymers in the vitreous state at 0 K have been calculated by the equations[24,29,34]

$$H_g^\circ - H_{cr}^\circ(0) = \int_0^{T_{fus}^\circ} [C_p^\circ(cr) - C_p^\circ(a)]dT + \Delta_{fus}H^\circ(\alpha = 100\%), \quad (8)$$

$$S_g^\circ(0) = \int_0^{T_{fus}^\circ} [C_p^\circ(cr) - C_p^\circ(a)]d\ln T + \Delta_{fus}S^\circ(\alpha = 100\%), \quad (9)$$

where $C_p^\circ(a)$ and $C_p^\circ(cr)$ are respectively the temperature functions of the heat capacity of the polymer in the vitreous or highly elastic amorphous ($\alpha = 0$) and crystalline ($\alpha = 100\%$) states (see sections *ABDE* and *ABC* respectively in Fig. 2); $\Delta_{fus}H^\circ(\alpha = 100\%)$ and $\Delta_{fus}S^\circ(\alpha = 100\%)$ are the enthalpy and entropy of fusion of the crystalline polymer.

The enthalpies, entropies, and Gibbs free energies of polyglycolide, poly-β-propiolactone, and poly-ε-caprolactone in the amorphous and crystalline states have been calculated for the range $0 - T_{fus}^\circ$.[13,14,77] It was postulated that the difference between the Gibbs free energies is an absolute measure of the metastability of the polymer in the amorphous state in relation to its crystalline state. As an example, Fig. 6 presents typical temperature dependences of the above quantities in the range $0 - T_{fus}^\circ$ for poly-ε-caprolactone.[77] Evidently the absolute enthalpy and entropy increase with increasing temperature, while the Gibbs free energy diminishes and becomes zero at T_{fus}°.

Table 3. Parameters of the vitrification and of the vitreous state of polylactones.

Polylactone	T_g°/K	$\Delta C_p^\circ(T_g^\circ)$ /J K^{-1} mol^{-1}	$H_g^\circ(0) - H_{cr}^\circ(0)$ /kJ mol^{-1}	$S_g^\circ(0)$ /J K^{-1} mol^{-1}	Method	Ref.
Polyglycolide	318	16	5.9	10	AVC	61
Poly-β-propiolactone	249	53	4.9	10	AVC	63
Poly-α,α-dimethyl-β-propiolactone	260	39	–	16	DSC	50
Poly-γ-butyrolactone	214	58	7.9	19	AVC	75
Poly-δ-valerolactone	207	65	11.7	30	AVC	76
Poly-ε-caprolactone	209	60	12.5	31	AVC	77, 78
Poly-γ-methyl-ε-caprolactone	220	–	–	–	TP	89
Poly-ε-methyl-ε-caprolactone	233	–	–	–	TP	89
Poly-α,ε-dimethyl-ε-caprolactone	240	–	–	–	TP	89
Poly-η-caprolactone	228	–	–	–	TP	90
Poly-λ-laurolactone	235	–	–	–	TP	90
Polyundecanolactone	227	111	27	66	AVC	86
Polydodecanolactone	248	–	–	–	TP	80
Polytridecanolactone	229	146	31	75	AVC	89
Polypentadecanolactone	251	167	41	100	AVC	81

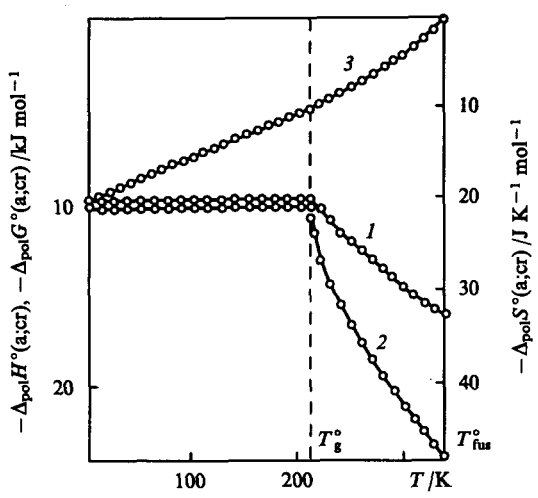


Figure 6. The enthalpies (*1*), entropies (*2*), and Gibbs free energies (*3*) of amorphous and crystalline poly-ε-caprolactone in the range from 0 K to the melting point.[77]

VI. Thermodynamic functions

The thermodynamic functions of polylactones were calculated for the range from 10–14 to 350–550 K (largely with an error of 0.2%–0.3%) from the results of the study of their heat capacities in adiabatic vacuum calorimeters: the enthalpy $H°(T)-H°(0)$, the entropy $S°(T)$, and the Gibbs free energy $G°(T)-H°(0)$; the smoothed heat capacities $C_p°(T)$ were found (Table 4). For the range 0–14 K, the $C_p°$ were obtained by extrapolating the experimental data in terms of the Debye heat capacity formula

$$C_p°(T) = nD\left(\frac{\theta_D}{T}\right), \quad (10)$$

where D is the symbol of the Debye heat capacity and n and θ_D are special parameters chosen so that Eqn (10) describes the values of $C_p°$ in the range from 14 to 20–25 K with an error not exceeding 0.5%–1.0%. It was assumed that at $T < 14$ K it reproduces $C_p°$ with approximately the same error. For example, $n = 3$ and $\theta_D = 93.1$ in Eqn (10) for poly-ε-caprolactone.[77] For the same parameters, the equation describes the experimental $C_p°$ for the polymer in the range 14–20 K with an error within the limits of 1%.

The thermodynamic functions were calculated from the equations

$$H°(T)-H°(0) = \Sigma\int C_p°(T)dT + \Delta_{fus}H°(\alpha = 100\%), \quad (11)$$

$$S°(T) = S_g°(0) + \Sigma\int C_p°(T)d\ln T + \Delta_{fus}S°(\alpha = 100\%), \quad (12)$$

$$G°(T)-H°(0) = [H°(T)-H°(0)]-TS°(T), \quad (13)$$

where $C_p°(T)$ is the temperature dependence of the heat capacity of polylactones in the given physical state: vitreous, crystalline, highly elastic, and liquid. The values of $C_p°(T)$ were determined from the experimental measurements of the heat capacity of partly crystalline polylactones. The corresponding method has already been published.[29] In the calculation of the absolute entropies of the polymers, account was taken of the zero-point entropies $S_g°(0)$ (Table 3).

The heat capacities and thermodynamic functions of polylactones with any degree of crystallinity α can be readily calculated from the numerical values of such functions for the polylactones in the crystalline and amorphous states. This calculation is correct because all the properties listed can be regarded as additive functions of the degree of crystallinity at the specified temperature and pressure. Having designated the property by X, we obtain

$$X(\alpha) = X(\alpha = 1) + [X(\alpha = 0)-X(\alpha = 1)](1-\alpha), \quad (14)$$

where α is expressed as a fraction.

VII. Thermochemical characteristics

Table 5 presents the enthalpies of combustion ($\Delta_cH°$) and formation ($\Delta_fH°$), the entropies $\Delta_fS°$ and the Gibbs free energies $\Delta_fG°$ of formation of polylactones in the crystalline and amorphous states at 298.15 K and standard pressure, as well as the logarithms of the thermodynamic equilibrium constants of the formation reactions of these compounds from the simple substances in their standard states. For all the compounds listed in Table 5, except poly-β-propiolactone and poly-ε-caprolactone, the combustion energies $\Delta_cU°(\alpha)$ were measured. The values of $\Delta_cU°(\alpha)$, adjusted to the standard pressure $[\Delta_cU°(\alpha)]$, were used to calculate the enthalpies of combustion at the standard pressure $\Delta_cH°(\alpha)$. The enthalpies of combustion of the polymers in the crystalline and amorphous (vitreous or highly elastic) states were calculated by the equations

$$\Delta_cH°(\text{cr}) = \Delta_cH°(\alpha) + (1-\alpha)\Delta_{fus}H°(298.15\,\text{K}), \quad (15)$$

$$\Delta_cH°(\text{a}) = \Delta_cH°(\alpha)-\alpha\Delta_{fus}H°(298.15\,\text{K}), \quad (16)$$

where $\Delta_cH°(\alpha)$ is the enthalpy of combustion of the polymer with a degree of crystallinity α and $\Delta_{fus}H°(298.15\,\text{K})$ is the molar enthalpy of fusion of the fully crystalline polymer at 298.15 K. The latter quantity is hypothetical and it was calculated,using the molar enthalpy of fusion of the crystalline polymer at $T_{fus}°$ and the temperature variations of the heat capacities for the polymer in the crystalline and amorphous states, by the Kirchhoff equation[15]

$$\Delta_{fus}H°(298.15\,\text{K}) = \quad (17)$$

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

This equation may be employed because the calculations relate to a constant (standard) pressure.

The quantities $\Delta_cH°(\text{cr})$ and $\Delta_cH°(\text{a})$ for poly-β-propiolactone and poly-ε-caprolactone were calculated from their enthalpies of formation, which were in their turn evaluated from the enthalpies of the polymerisation of the corresponding monomers to the crystalline and amorphous polymers and the enthalpies of formation of the monomers.

The enthalpies and entropies of formation of the polylactones were calculated from $\Delta_cH°(\text{cr})$, $\Delta_cH°(\text{a})$, the enthalpies of formation of liquid water and gaseous carbon dioxide, the absolute entropies of the polymers in crystalline and amorphous states (Table 4), and the entropies of carbon in the form of graphite and gaseous hydrogen and oxygen at $T = 298.15$ K and $p = 101.325$ kPa. The Gibbs free energies of formation of the polymers were found from the formula

$$\Delta_fG° = \Delta_fH°-298.15\Delta_fS°. \quad (18)$$

The logarithms of the thermodynamic equilibrium constants of the formation reactions of the polylactones from the simple substances were calculated from the $\Delta_fG°$:

$$\lg K_f° = \frac{-\Delta G_f°}{2.303R\ 298.15}. \quad (19)$$

Any thermochemical parameter of a polylactone with any degree of crystallinity may be determined by Eqn (14) using the thermochemical characteristics (Table 5). The additivity of the properties of partly crystalline polymers is a consequence of the fact that they are heterogeneous (microheterogeneous) systems.

We may note in conclusion that Hall[40] measured in three experiments the energy of combustion of partly crystalline poly-α,α-dimethyl-β-propiolactone (polypivalolactone) and calculated

Table 4. Thermodynamic functions of polylactones.

T/K	$C_p^\circ(T)$	$H^\circ(T)-H^\circ(0)$	$S^\circ(T)$	$G^\circ(T)-H^\circ(0)$
Polyglycolide [61, 82]				
Crystalline state				
5	0.100	0.00010	0.024	0.000017
10	0.7735	0.00195	0.253	0.00058
15	2.184	0.00921	0.824	0.00315
20	3.973	0.02450	1.691	0.00932
25	5.960	0.04933	2.791	0.02044
50	16.04	0.3324	10.23	0.1790
100	30.47	1.529	26.43	1.094
200	48.22	5.495	53.05	5.110
298.15	65.15	11.06	75.45	11.43
400	82.60	18.59	97.00	20.22
501	99.85	27.80	117.5	31.06
Liquid state				
501	120.0	39.10	140.1	31.06
550	121.8	45.02	151.3	38.20
Vitreous state				
10	0.7735	0.00195	9	0.0875
15	2.184	0.00921	10	0.134
25	5.960	0.04933	12	0.238
50	16.04	0.3324	19	0.595
100	30.47	1.529	35	1.92
200	48.22	5.495	62	6.80
298.15	65.15	11.06	84	14.0
318	68.55	22.36	88	15.6
Highly elastic state				
350	114.2	16.03	99	18.7
400	116.0	21.78	115	24.0
501	120.0	33.74	140	36.5
Poly-β-propiolactone [63]				
Crystalline state				
10	1.39	0.00352	0.473	0.00121
20	5.65	0.0375	2.66	0.0157
30	11.20	0.1212	5.98	0.0581
40	16.56	0.2608	9.96	0.1374
50	21.22	0.4507	14.17	0.2580
100	40.13	2.018	35.15	1.497
150	52.84	4.345	53.85	3.732
200	65.29	7.300	70.77	7.853
250	77.15	10.88	86.67	10.79
298.15	89.74	14.91	101.4	15.32
366	106.6	21.57	121.5	22.88
Liquid state				
366	142.0	31.77	149.3	22.88
400	154.0	36.75	162.3	28.18
Vitreous state				
10	1.39	0.00352	10.5	0.102
20	5.65	0.0375	12.7	0.217
30	11.20	0.1212	16.0	0.358
50	21.22	0.4507	24.2	0.758
100	40.13	2.018	45.2	2.497
150	52.84	4.345	63.9	5.234
200	65.29	7.300	80.8	8.854
245	76.50	10.49	95.1	12.81
Highly elastic state				
298.15	134.8	17.51	111.0	15.58
366	142.0	26.90	149.3	27.74
Poly-β-methyl-β-propiolactone [67]				
Crystalline state				
5	0.2294	0.0003	0.0787	0.0001
10	1.720	0.00447	0.6010	0.0015
15	4.487	0.0198	1.805	0.0727
20	7.937	0.0507	3.560	0.0205
25	11.45	0.0995	5.720	0.0436
50	26.24	0.5783	18.41	0.3420
100	47.23	2.447	43.50	1.901
Crystalline state				
200	77.83	11.67	86.23	8.460
298.15	110.8	17.67	123.1	18.73
400	146.9	31.12	160.9	33.23
454	166.0	39.57	180.7	42.47
Liquid state				
454	210.9	52.18	208.4	42.47
500	234.2	62.37	229.8	52.53
Poly-γ-butyrolactone [75, 82]				
Crystalline state				
5	0.19	0.00024	0.062	0.00007
10	1.47	0.00376	0.501	0.00125
15	4.38	0.0181	1.63	0.00629
20	7.87	0.0487	3.37	0.0186
25	11.57	0.0973	5.52	0.0407
30	15.30	0.1645	7.96	0.0743
50	28.41	0.6062	18.95	0.3416
100	51.76	2.660	46.50	1.990
150	68.48	5.679	70.75	4.934
200	84.70	9.505	92.64	9.024
250	101.3	14.15	113.3	14.18
298.15	117.9	19.63	133.4	20.34
337.5	130.3	24.29	147.8	25.61
Liquid state				
337.5	159.3	37.56	187.1	25.61
345	161.0	38.75	190.7	27.03
Vitreous state				
5	0.19	0.00024	18.7	0.094
10	1.47	0.00376	19.1	0.187
15	4.38	0.0181	20.4	0.288
20	7.87	0.0487	21.7	0.385
30	15.30	0.1645	26.8	0.638
50	29.41	0.6062	37.8	1.281
100	51.76	2.660	65.4	3.871
150	68.48	5.679	89.6	7.753
214	89.30	10.76	117.6	14.38
Highly elastic state				
250	150.8	16.13	140.6	19.00
298.15	155.5	23.50	167.6	26.47
337.5	159.3	29.70	187.1	33.45
Poly-δ-valerolactone [76]				
Crystalline state				
5	0.19	0.00024	0.060	0.00006
10	1.51	0.00386	0.503	0.00117
15	4.38	0.0182	1.622	0.00613
20	8.00	0.0489	3.368	0.01846
25	12.05	0.0989	5.578	0.04060
30	16.33	0.1698	8.154	0.07479
50	32.16	0.6598	20.32	0.3564
100	61.11	3.062	52.47	2.186
150	80.91	6.629	81.13	5.541
200	99.64	11.14	107.0	10.25
250	118.3	16.59	131.2	16.21
298.15	136.3	22.72	153.6	23.08
331	148.6	27.40	168.5	28.37
Liquid state				
331	188.9	45.60	223.5	28.37
350	192.2	49.22	234.1	32.72
Vitreous state				
5	0.19	0.00024	29.8	0.149
10	1.51	0.00386	30.3	0.299
15	4.38	0.0182	31.4	0.453
20	8.00	0.0489	33.2	0.615
30	16.33	0.1698	38.0	0.970
50	32.16	0.6598	50.1	1.845

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-δ-valerolactone [76]				
Vitreous state				
100	61.11	3.062	82.3	5.168
150	80.91	6.629	110.9	10.00
207	102.3	11.85	140.3	17.19
Highly elastic state				
250	174.8	19.20	172.5	23.93
298.15	183.2	27.82	204.0	33.0
331	188.9	33.93	223.5	40.02
Poly-ε-caprolactone [77]				
Crystalline state				
10	2.42	0.0060	0.79	0.0019
20	10.72	0.0690	4.82	0.0274
30	20.66	0.2246	10.99	0.1052
40	30.17	0.4811	18.31	0.2512
50	37.95	0.8216	25.87	0.4721
100	71.14	3.611	63.20	2.709
150	94.19	7.750	96.45	6.718
200	116.9	13.03	126.7	12.31
250	139.7	19.44	155.2	19.36
298.15	161.6	26.70	181.7	27.47
342	181.5	34.22	205.2	35.96
Liquid state				
342	219.3	53.22	260.8	35.96
350	221.6	54.98	265.9	38.09
Vitreous state				
10	2.42	0.0060	31.8	0.312
20	10.72	0.0690	35.8	0.647
30	20.66	0.2246	42.0	1.04
40	30.17	0.4811	49.3	1.49
50	37.95	0.8216	56.9	2.02
100	71.14	3.611	94.2	5.81
150	94.19	7.750	127.5	11.38
200	116.9	13.03	157.7	18.51
209	121.0	14.10	162.9	19.95
Highly elastic state				
250	192.5	21.74	196.3	27.34
298.15	206.5	31.35	231.4	37.64
342	219.3	40.68	260.8	48.45
Polyundecanolactone [79, 82]				250
Crystalline state				
5	0.42	0.00053	0.138	0.00016
10	3.38	0.0083	1.11	0.0027
15	8.51	0.0374	3.39	0.135
20	14.81	0.0950	6.66	0.0382
25	22.33	0.1876	10.76	0.0814
30	29.93	0.3179	15.49	0.1468
40	45.56	0.6953	26.24	0.3543
50	60.18	1.225	38.00	0.6749
100	117.8	5.803	99.18	4.115
150	158.9	12.74	154.9	10.49
200	199.7	21.70	206.2	19.53
250	240.2	32.70	255.1	31.07
298.15	279.7	45.22	300.8	44.46
365	333.8	65.72	362.6	66.64
Liquid state				
365	387.5	103.9	467.3	66.64
400	401.5	117.7	503.4	83.66
Vitreous state				
10	3.38	0.0083	67	0.66
20	14.81	0.0950	73	1.37
30	29.93	0.3179	81	2.11
50	60.18	1.225	104	3.98
100	117.8	5.803	165	10.7
150	158.9	12.74	221	20.4
Vitreous state				
200	199.7	21.70	272	32.7
227	221.6	27.39	299	40.5
Highly elastic state				
250	341.4	35.14	331	47.6
298.15	360.7	52.04	393	65.1
365	387.5	77.05	467	93.4
Polytridecanolactone [80]				
Crystalline state				
5	0.37	0.00032	0.074	0.00005
10	3.30	0.0082	1.05	0.0023
15	9.62	0.0402	3.55	0.0131
20	17.36	0.1073	7.36	0.0399
25	25.98	0.2156	12.16	0.0884
30	35.26	0.3679	17.68	0.1625
40	53.21	0.8098	30.27	0.4010
50	70.45	1.430	44.05	0.7725
100	137.2	6.781	115.6	4.779
150	185.6	14.87	180.5	12.21
200	234.1	25.36	240.6	22.76
250	282.6	38.28	298.0	36.22
298.15	329.3	53.01	351.8	51.88
368	397.1	78.38	428.0	79.11
Liquid state				
368	459.7	124.4	553.0	79.11
Vitreous state				
5	0.37	0.00032	75	0.37
10	3.30	0.0082	76	0.75
15	9.62	0.0302	78	1.13
20	17.36	0.1073	81	1.52
25	25.98	0.2156	86	1.94
30	35.26	0.3679	92	2.38
50	70.45	1.430	118	4.48
100	137.2	6.781	190	12.2
150	185.6	14.87	255	23.3
200	234.1	25.36	315	37.6
229	262.4	32.56	348	47.1
Highly elastic state				
416.0	41.21	384	54.8	
298.15	433.9	61.67	459	75.2
368	459.7	92.87	553	111
Polypentadecanolactone [81]				
Crystalline state				
5	0.46	0.00057	0.148	0.00017
10	3.47	0.0091	1.21	0.0030
15	10.07	0.0429	3.86	0.0150
20	18.48	0.1136	7.86	0.0437
25	28.29	0.2298	13.01	0.0954
30	38.89	0.3979	19.11	0.1753
40	59.66	0.8925	33.19	0.4352
50	79.33	1.587	48.62	0.8434
100	157.2	7.690	130.1	5.320
150	210.8	16.94	204.4	13.72
200	264.5	28.81	272.3	25.65
250	317.8	43.37	337.1	40.96
298.15	369.2	59.91	397.4	58.57
370	446.2	89.36	485.6	90.50
Liquid state				
370	533.1	145.4	637	90.50
Vitreous state				
5	0.46	0.00057	100	0.50
10	3.47	0.0091	101	1.00
15	10.07	0.0429	104	1.52
20	18.48	0.1136	108	2.05

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	$C_p^\circ(T)$	$H^\circ(T)-H^\circ(0)$	$S^\circ(T)$	$G^\circ(T)-H^\circ(0)$
Polypentadecanolactone[81]									
Vitreous state					*Highly elastic state*				
30	38.89	0.3979	119	3.17	251	486.9	43.68	438	66.3
50	79.33	1.587	149	5.86	298.15	504.9	67.07	524	89.2
100	157.2	7.690	230	15.3	370	533.1	104.5	637	131.4
150	210.8	16.94	304	28.7					
200	264.5	28.81	372	45.6					
250	317.8	43.37	437	65.9					

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

Table 5. The enthalpies of combustion and thermochemical parameters of the formation of polylactones at $T = 298.15$ K and $p = 101.325$ kPa per mole of the repeat unit in the polymers.

Polymer	Physical state[a]	$-\Delta_cH^\circ$ /kJ mol^{-1}	$-\Delta_fH^\circ$ /kJ mol^{-1}	$-\Delta_fS^\circ$ /J mol^{-1} K^{-1}	$-\Delta_fG^\circ$ /kJ mol^{-1}	lgK_f°	Ref.
Polyglycolide	cr	705.7±0.8	367.2±0.8	271.6±0.5	286.2±1.0	50.33	
	g	717.5±0.8	355.6±1.3	263.1±1.5	277.1±1.7	48.73	36, 61
Poly-β-propio-	cr	1340.2±4.0	412±4.0	382.0±1.0	298.0±4.0	52.20	
lactone	h.e	1347.2±4.0	405±4.0	372.4±1.3	294.0±4.2	51.50	36, 63
Poly-β-methyl-	cr	2003.2±0.8	428.3±0.8	496.3±1	280.3±1.1	49.16	
β-propiolactone	g	2010.6±0.8	421.0±0.8	482.3±1	277.2±1.1	48.62	36, 67
Poly-γ-butyro-	cr	2002.4±0.9	429.0±1.2	486.2±0.5	284.0±1.4	49.81	
lactone	h.e	2014.3±0.9	417.1±1.2	452.0±1.2	282.2±1.6	49.50	36, 75
Poly-ε-capro-	cr	3313.9±2.4	476.3±2.4	710.4±1.3	264.5±2.8	46.39	
lactone	h.e	3328.4±2.2	461.8±2.4	660.7±1.5	264.8±2.6	46.45	36, 76
Polyundecano-	cr	6539.4±3.3	648.0±3.3	1117±3	315.0±3.9	55.25	
lactone	h.e	6573.3±3.3	613.8±3.3	1024±4	308.5±4.4	54.11	36,79
Polytridecano-	cr	7857.1±4.0	689.0±4.0	1494±4	243.7±5.2	42.75	
lactone	h.e	7897.2±5.0	649.1±5.0	1387±6	235.7±7.8	41.34	36, 89
Polypentadecano-	cr	9157.0±6.7	747.3±6.7	1721±3	234.2±3.9	41.08	36, 81
lactone	h.e	9206.1±7.7	698.2±7.7	1590±4	224.1±8.9	39.31	

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

from the results its enthalpy of combustion as $\Delta_cH^\circ(\alpha) = -2631.7$ kJ mol^{-1}. The degree of crystallinity was unknown.

Andruzzi[41] measured the combustion energies of five specimens of polyoxacarbonyl-1,4-cyclohexylene with different molecular masses — from 2.1×10^3 to 1×10^6. All the specimens investigated were partly crystalline. The number of combustion experiments was 15. Calculation of the enthalpy of combustion showed that $\Delta_cH^\circ(\alpha)$ at $T = 298.15$ K varies from -3686.9 ± 7.6 to -3700.3 ± 9.0 kJ mol^{-1}. The authors believe that the reason for the differences is different degrees of crystallinity of the test specimens and also the different contents of the *cis*- and *trans*-units in the polymer. The results of the determination of $\Delta_cH^\circ(\alpha)$ obtained by Hall[40] and Andruzzi[41] can be regarded only as estimates.

VIII. Thermodynamic parameters of the polymerisation reactions of lactones

The enthalpies of the polymerisation of β-propiolactone,[39] δ-valerolactone,[76] and ε- caprolactone[77] were measured directly in calorimeters;[58,94] those of glycolide,[61,95] α,α-dimethyl-β-propiolactone,[40] γ-butyrolactone,[75] 2-oxabicyclo[2.2.2]octan-3-one,[41] undecanolactone,[79] tridecanolactone,[80] and pentadecanolactone[81] were calculated from the experimental enthalpies of combustion of the monomers and polymers. In all cases, the polylactones were partly crystalline, so that the enthalpies of polymerisation were obtained from experimental data for the processes liquid monomer → partly crystalline polymer, i.e. $\Delta_{pol}H^\circ$(l;p.cr). The values obtained were used to calculate the enthalpies of polymerisation for the processes liquid monomer → crystalline or amorphous (vitreous or highly elastic) polymer. The calculations were performed using the equations[13]

$$\Delta_{pol}H^\circ(1;cr) = \Delta_{pol}H^\circ(1;p.cr) + \int_T^{T_{fus}^\circ}[C_p^\circ(p.cr)-C_p^\circ(cr)]dT - (1-\alpha)\Delta_{fus}H^\circ(T), \quad (20)$$

$$\Delta_{pol}H^\circ(1;a) = \Delta_{pol}H^\circ(1;p.cr) + \int_T^{T_{fus}^\circ}[C_p^\circ(p.cr)-C_p^\circ(a)]dT - \alpha\Delta_{fus}H^\circ(T), \quad (21)$$

where T is the temperature at which the enthalpy of polymerisation was determined experimentally and the calculation was performed; in those cases where the enthalpies of polymerisation were determined from the enthalpies of combustion the temperature was $T = 298.15$ K, whereas in the direct measurements in the calorimeter $T \approx 350$ K. The enthalpy of fusion of the polylactone $\Delta_{fus}H^\circ(T)$ at the temperature of the determination of the enthalpy of polymerisation was calculated by Eqn (17).

For other temperatures, the $\Delta_{pol}H^\circ$ were calculated from the Kirchhoff formula (Table 6):

Table 6. The enthalpies (kJ mol^{-1}), entropies (J mol^{-1} K^{-1}), and Gibbs free energies (kJ mol^{-1}), of the polymerisation of lactones in bulk with formation of polylactones (p = 101.325 kPa).

T/K	Physical states of monomer and polymer [a]	$-\Delta_{pol}H°$	$-\Delta_{pol}S°$	$-\Delta_{pol}G°$
Glycolide → polyglycolide [61]				
0	crII;cr	16.7	0	16.7
	crII;g	5.1	−8.4	5.1
200	crII;cr	16.9	2.7	16.4
	crII;g	5.3	−5.8	6.5
298.15	crII;cr	17.0	3.2	16.1
	crII;g	5.4	−5.3	6.9
350	crI;cr	17.7	5.2	15.8
	crI;h.e	4.5	−8.0	7.3
500	l;cr	27.8	32.5	11.5
	l;h.e	10.3	9.0	5.8
550	l;l	15.7	8.8	10.9
β-*Propiolactone → poly-β-propiolactone* [63]				
0	cr;cr	68	0	68
	cr;g	63	−10	63
100	cr;cr	69	17	67
	cr;g	64	7	63
200	cr;cr	70	24	65
	cr;g	65	14	62
298.15	l;cr	82	74	60
	l;h.e	75	54	59
400	l;l	74	51	54
α,α-*Dimethyl-β-propiolactone →* → *poly-α,α-dimethyl-β-propiolacton* [40,96]				
298.15	l;p.cr	84	74	62
γ-*Butyrolactone → poly-γ-butyrolactone* [75]				
0	cr;cr	−6.5	0	−6.5
	cr;g	−14	−19	−14
100	cr;cr	−6	9	−7
	cr;g	−14	−10	−13
200	cr;cr	−5	13	−7.5
	cr;g	−13	−6	−12
298.15	l;cr	7	65	−13
	l;h.e	−5	30	−14
350	l;l	−6	29	−16
400	gas;l	28	118	−19
δ-*Valerolactone → poly-δ-valerolactone* [76]				
0	crIV;cr	12.5	0	12.5
	crIV;g	1	−30	1
100	crIV;cr	13	−6	13.5
	crIV;g	1.5	−24	4
200	crII;cr	14.5	17	11
	crII;g	3	−13	5.5
	l;cr	27.5	65	8
298.15	l;h.e	10.5	15	6
350	l;l	10	13	5.5
2-*Oxabicyclo*[2.2.2]*octan-3-one →* → *poly-2-oxabicyclo*[2.2.2]*octan-3-one* [41]				
298.15	cr;cr	21		
	l;cr	35	76	12
ε-*Caprolactone → poly-ε-caprolactone* [77]				
0	cr;cr	17	0	17
	cr;g	7	−31	7
100	cr;cr	17	1	17
	cr;g	7	−30	10
200	cr;cr	16	−1	16
	cr;g	7	−32	13
ε-*Caprolactone → poly-ε-caprolactone* [77]				
298.15	l;cr	31	54	15
	l;h.e	17	4	16
350	l;l	13.7	8	11
ξ-*Oenantholactone → poly-ξ-oenantholactone* [96]				
400	l;l	16	1	16
η-*Caprylolactone → poly-η-caprylolactone* [96]				
298.15	l;cr	37	60	19
	l;h.e	19	−2	20
400	l;l	16	1	16
λ-*Laurolactone → poly-λ-laurolactone* [96]				
298.15	l;cr	43	61	25
	l;h.e	21	−7	23
400	l;l	19	−5	21
Nonanolactone → polynonanolactone [96]				
400	l;l	22	−12	27
Decanolactone → polydecanolactone [96]				
400	l;l	24	−18	31
Undecanolactone → polyundecanolactone [13]				
0	crII;cr	43	0	43
	crII;g	16	−67	16
100	crII;cr	42	2	42
	crII;g	16	−64	22
200	crII;cr	42	−5	43
	crII;g	15	−71	29
298.15	l;cr	62	69	41
	l;h.e	28	−24	35
400	l;l	27	−25	37
Dodecanolactone → polydodecanolactone [96]				
400	l;l	17	−25	27
Tridecanolactone → polytridecanolactone [80]				
0	crII;cr	22	0	22
	crII;g	−9	−74	−9
100	crII;cr	22	−1	22
	crII;g	−9	−75	−2
200	crII;cr	20	−9	22
	crII;g	−10	−83	7
298.15	crI;cr	38	50	23
	crI;h.e	−2	−57	15
400	l;l	6	−26	17
Tetradecanolactone → polytetradecanolactone [96]				
400	l;l	2	−26	12
Pentadecanolactone → polypentadecanolactone [81]				
0	crI;cr	31	49	31
	crII;cr	14	0	14
	crII;g	−35	−100	−35
100	crI;cr	31	54	26
	crII;cr	−37	−109	−15
	crII;g	36	−99	−30
200	crI;cr	31	55	20
	crII;cr	12	−10	14
	crII;g	−37	−109	−15
298.15	crI;cr	39	86	13
	crI;h.e	−10	−41	2
400	l;l	−2	−23	8
Hexadecanolactone → polyhexadecanolactone [96]				
400	l;l	0	−21	8

[a] The following designations of the states of the reactants have been adopted: cr — crystalline, g — vitreous (glassy), h.e. — highly elastic, l — liquid, gas — gaseous, crI, crII, crIV — different crystalline modifications, p.cr — partly crystalline.

$$\Delta_{pol}H^\circ(T) = \quad (22)$$
$$= \Delta_{pol}H^\circ(298.15 \text{ or } 350\,K) + \Delta[H^\circ(T) - H^\circ(0)],$$

where $\Delta[H^\circ(T) - H^\circ(0)]$ is the difference between the enthalpies of heating the monomer and the polymer, which may be calculated from the data in Table 4.

We may note the characteristic features of the experimental determinations of the enthalpies of the polymerisation of β-propiolactone, α,α-dimethyl-β-propiolactone, and 2-oxabicyclo[2.2.2]octan-3-one. The enthalpy of the bulk polymerisation of β-propiolactone was measured by Sunner and coworkers[39] in a Calvet calorimeter[94] in seven experiments at $T = 298.15$ K. $\Delta_{pol}H^\circ(\alpha) = -80 \pm 3.8$ kJ mol^{-1} was found. The degree of crystallinity was not determined, but it was possible to measure the enthalpy of fusion of the crystalline component of the polymer as $\Delta_{fus}H^\circ(\alpha) = 7.5$ kJ mol^{-1}. Using the value of $\Delta_{fus}H^\circ$ ($\alpha = 100\%$) (Table 2), Evstropov et al.[63] estimated the degree of crystallinity as 75%. This made it possible in its turn to calculate the enthalpy of the polymerisation of β-propiolactone to crystalline and amorphous poly-β-propiolactone[63] (Table 6).

The enthalpy of the polymerisation of α,α-dimethyl-β-propiolactone to poly-α,α-dimethyl-β-propiolactone at $T = 298.15$ K was found by Hall:[40] $\Delta_{pol}H^\circ$(l;p.cr) = −84 kJ mol^{-1}. It was calculated using the results of the determinations of the enthalpies of combustion of the monomer and the polymer. In order to determine Δ_cH° for the monomer, four experiments were performed, while in the case of the polymer three experiments were carried out. The purity of the monomer specimen was 99%; the polymer was not characterised and it is only known that it was partly crystalline. From this it follows that the value of $\Delta_{pol}H^\circ$ obtained must be regarded only as an estimate.

Andruzzi[41] gives $\Delta_{pol}H^\circ$(cr;cr) = -20.9 ± 2.3 kJ mol^{-1} for the polymerisation of 2-oxabicyclo[2.2.2]octan-3-one to poly-2-oxabicyclo-1,4-cyclohexylene at $T = 298.15$ K. It was obtained from the enthalpies of combustion of the monomer and the polymer. The enthalpy of combustion of the monomer was measured in five experiments and that of the polymer in fifteen experiments. A polymer with $\bar{M}_n$ from 2.1×10^3 to 1×10^6 was used. Analysis of the products of the combustion of the monomer and the polymer showed that the CO_2 content was 99.50 mass% − 99.72 mass% relative to the theoretical amount. For the monomer in the crystalline state, $\Delta_cH^\circ = -3717.5 \pm 1.3$ kJ mol^{-1} while for the polymer $\Delta_cH^\circ(\alpha) = -3686.9 \pm 7.6$ to -3700 ± 9.8 kJ mol^{-1} The reasons for the differences between the enthalpies of combustion of the polymer are probably different degrees of crystallinity and also different contents of the *cis*- and *trans*-units in the macromolecules. Andruzzi[41] attempted to measure $\Delta_{pol}H^\circ$ directly in the calorimeter, but did not succeed because of the unduly low rate of the polymerisation process. Furthermore, he estimated Δ_cH°(l;cr) as -76 ± 10 kJ mol^{-1}. Clearly the value of $\Delta_{pol}H^\circ$ quoted must be regarded as an approximate estimate.

The entropies of the polymerisation reactions of the lactones (Table 6) were calculated from the entropies of the reactants (Table 4):

$$\Delta_{pol}S^\circ(T) = S^\circ(M) - S^\circ(P), \quad (23)$$

where $S^\circ(M)$ and $S^\circ(P)$ are the absolute entropies of the monomer and the polymer respectively at a temperature T.

The Gibbs free energies of the processes were calculated from a $\Delta_{pol}H^\circ(T)$ and $\Delta_{pol}S^\circ(T)$ by the formula

$$\Delta_{pol}G^\circ(T) = \Delta_{pol}H^\circ(T) - T\Delta_{pol}S^\circ(T). \quad (24)$$

The equilibrium concentration of the monomer $[M]_e^\circ$ in the reaction mixture at thermodynamic equilibrium may be determined from the standard Gibbs free energy:

$$[M]_e^\circ = \exp\frac{\Delta G_{pol}^\circ(T)}{RT}, \quad (25)$$

while the equilibrium concentration of the polymer in the same mixture may be found from the formula

$$[P]_e^\circ = 1 - \exp\frac{\Delta_{pol}G^\circ(T)}{RT}. \quad (26)$$

Table 7 presents the limiting polymerisation temperatures of lactones, mainly for the liquid monomer → liquid polymer processes. They were estimated graphically from the point of intersection of the $\Delta_{pol}H^\circ = f(T)$ and $T\Delta_{pol}S^\circ = f(T)$ relations[14,18] or by Dainton's method.[18]

Table 7. The upper limiting polymerisation temperatures of lactones in bulk under standard pressure.

Lactone	T_{ceil}° /K	Method of determination[a]	Ref.
Glycolide	1800	D	61
β-Propiolactone	1450	D	63
α,α-Dimethyl-β-propiolactone	1135	D	This work
δ-Valerolactone	760	G	76
ε-Caprolactone	900	G	77

[a] The following designations have been adopted: D — Dainton's method, G — graphical method.

IX. The regularities and characteristics of the thermodynamic properties of polylactones and of the parameters of the polymerisation reactions of lactones

1. Thermodynamic parameters of fusion

Figure 7 presents the dependences of the melting points and the enthalpies and entropies of fusion of polylactones on the composition of the monomer repeat units, each of which has one methylene group more than the preceding one.[96] Evidently T_{fus}°

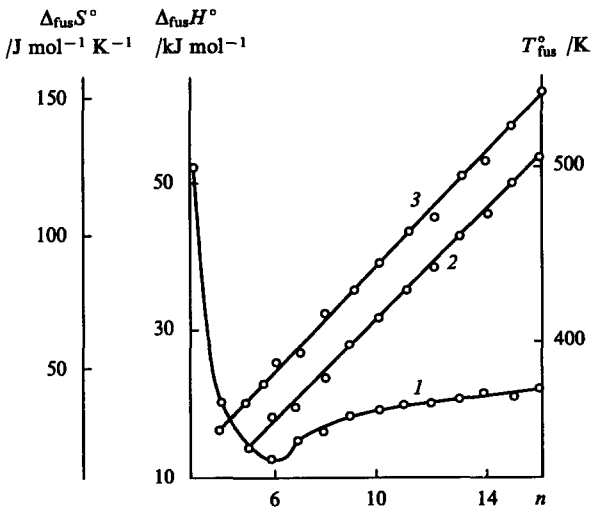


Figure 7. Dependence of the thermodynamic parameters of fusion of polylactones on the number of atoms and atomic groups in the monomer repeat unit of the polymer.[96]
(*1*) Melting point; (*2*) enthalpy of fusion; (*3*) entropy of fusion.

initially decreases rapidly from 501 K for polyglycolide to 331 K for poly-δ-valerolactone and then slowly increases to 371 K for polypentadecanolactone. On further increase in the number of CH_2 groups in the monomer repeat unit in polylactone, T_{fus}° would apparently increase, tending in the limit to T_{fus}° for polyethylene (405 K).[97]

Thielaut et al.[88] investigated the influence of the composition and structure of the alkyl substituents on the melting points of di- and tri-alkyl-substituted poly-β-propiolactones. Qualitative examination of the results showed that polymers having a more symmetrical structure also have higher melting points; polyesters with the same substituents at the α-carbon atom have the highest T_{fus}°. The dependences of $\Delta_{fus}H^{\circ}$ and $\Delta_{fus}S^{\circ}$ on n are linear and are described by the following equation subject to an error of several percent:

$$\Delta_{fus}H^{\circ} = -5.5 + 3.74n, \quad (27)$$

$$\Delta_{fus}S^{\circ} = -9.0 + 9.75n. \quad (28)$$

The existence of these simple relations made it possible to estimate the corresponding parameters of fusion for polylactones which have not yet been investigated (Table 2).

Comparison of the melting points of polylactones and the corresponding lactones showed[13] that T_{fus}° for the polymers is higher than for the monomers. The maximum difference between the T_{fus}° is 126 ° for poly-β-propiolactone and β-propiolactone. With increase in the ring size in lactones, ΔT_{fus}° gradually decreases to 62 ° for polypentadecanolactone and pentadecanolactone. The enthalpies of fusion of polylactones are also higher than for the lactones, usually by a factor of 1.2–1.5, while in the case of the polymers obtained from macrocyclic monomers ($n > 10$) the increase is severalfold. It is of interest that the entropies of fusion of (4–6)-membered lactones are equal to or somewhat greater than the $\Delta_{fus}S^{\circ}$ for the corresponding polylactones; $\Delta_{fus}S^{\circ}$ for (7–16)-membered monomers is smaller than for the corresponding polymers — several times smaller for lactones with $n > 12$.

2. Parameters of vitrification and of the vitreous state

The dependence of T_g° for polylactones on the number of atomic groups in the monomer repeat unit[82] has a form similar to the dependence of T_{fus}° presented in Fig. 7. In the series from four-membered to seven-membered polylactones, T_g° decreases from 318 to 209 K and then increases comparatively slowly to 251 K for polypentadecanolactone. The influence of substitution by methyl groups on T_g° for poly-ε-caprolactone has been discovered.[93] $T_g^{\circ} = 213$ K for poly-ε-caprolactone, 233 K for poly-ε-methyl-ε-caprolactone, and 220 K for poly-γ-methyl-ε-caprolactone and poly-α,ε-dimethyl-ε-caprolactone. Koleske and Lundberg[90] compared the glass transition temperatures of polylactones obtained by the polymerisation of (4–16)-membered lactones. It was found that the difference between the glass transition temperatures of the corresponding polymers and monomers is $\Delta T_g^{\circ} = 70 \pm 3$ K. β-Propiolactone and poly-β-propiolactone and also ε-caprolactone and poly-ε-caprolactone, for which the corresponding differences are 103 and 33 K, are exceptions in the above series.

The $\Delta C_p^{\circ}(T_g^{\circ})$ data obtained for polylactones conform to the familiar Wunderlich rule[98] that the heat capacity increases on devitrification of amorphous polymers by 11.5 ± 1.7 J K^{-1} per mole of beads: for polylactones, the increment is 12.5 ± 2.5 J K^{-1} per mole of beads. The values of $H_g^{\circ}(T) - H_{cr}^{\circ}(0)$ and $S_g^{\circ}(0)$ (Table 3) increase linearly with increase in n, the deviations from the corresponding straight line not exceeding 10%. The accuracy of the calculation of the above quantities is the same.

3. Thermodynamic functions

The dependences of C_p°, $H^{\circ}(T) - H^{\circ}(0)$, $S^{\circ}(T)$, and $G^{\circ}(T) - H^{\circ}(0)$ on n for polylactones at a specified temperature and the standard pressure are straight lines, provided that all the polylactones are in the same physical state.[13,82] For example, at $T = 298.15$ K and $p = 101.325$ kPa, the thermodynamic functions for crystalline polylactones are described (subject to an error within the limits of 1%) by the linear equations

$$C_p^{\circ} = -2.2 + 23.42n, \quad (29)$$

$$H^{\circ}(T) - H^{\circ}(0) = 0.46 + 3.732n, \quad (30)$$

$$S^{\circ}(T) = 7.85 + 24.46n, \quad (31)$$

$$-[G^{\circ}(T) - H^{\circ}(0)] = 1.87 + 3.559n. \quad (32)$$

The dependences of the heat capacities of polylactones on n at different temperatures are presented in Fig. 8. The linear relations between the thermodynamic functions and n are undoubtedly associated with the additivity of the corresponding contributions of the methylene groups to particular properties of polylactones. The existence of these relations makes it possible to estimate reliably the thermodynamic functions of polylactones in the series from four-membered to 20-membered polylactones which have not yet been studied experimentally (Table 4).

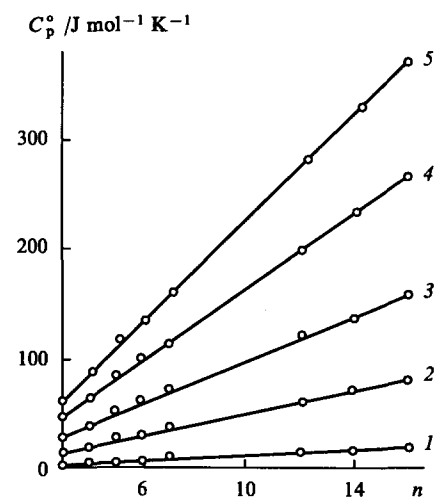


Figure 8. Heat capacity isotherms for polylactones as a function of the number of atoms and atomic groups in the monomer repeat unit of the polymer.[82]
T/K: (*1*) 20; (*2*) 50; (*3*) 100; (*4*) 200; (*5*) 300.

4. Thermochemical characteristics

Using the data in Table 5, Kiparisova and Lebedev[99] fitted by the method of least squares the linear dependences of the thermochemical characteristics of polylactones on the number of carbon atoms ($n' = 3, 4, 6, 11, 13$, and 15) in the monomer repeat units of the macromolecules for $T = 298.15$ K and the standard pressure.

The following relations were found for the enthalpies of combustion and formation of polylactones in the crystalline and vitreous or highly elastic states per mole of the repeat units:

$$\Delta_{\check{c}}H^{\circ}(cr) = -598.2 + 650.0n', \quad (33)$$

$$\Delta_{\check{c}}H^{\circ}(g) = -591.8 + 652.8n', \quad (34)$$

$$\Delta_f H^{\circ}(cr) = -316.8 - 29.0n', \quad (35)$$

$$\Delta_f H^{\circ}(g) = -318.4 - 25.7n'. \quad (36)$$

The deviations of the experimental values of $\Delta_c H^{\circ}(cr)$ and $\Delta_c H^{\circ}(g)$ from the corresponding straight lines [Eqns (33) and (34)] do not exceed 0.2%, while the deviations of the $\Delta_f H^{\circ}(cr)$ and $\Delta_f H^{\circ}(g)$ do not exceed 2%.

The following relations were established for the entropies of formation:

$$\Delta_f S^{\circ}(cr) = -4.7 - 111.6n', \quad (37)$$

$$\Delta_f S°(g) = -5.7 - 103.0n'. \quad (38)$$

The deviations of the experimental points from the calculated $\Delta_f S°$(cr) and $\Delta_f S°$(g) are within the limits of 10%.

The equations found for the Gibbs free energies are as follows:

$$\Delta_f G°(cr) = -315.9 + 4.3n', \quad (39)$$

$$\Delta_f G°(g) = -316.6 + 5.0n'. \quad (40)$$

The deviations of the experimental data from the calculated values of $\Delta_f G°$(cr) and $\Delta_f G°$(g) are within the limits of 15%. It has been suggested[99] that the above equations will prove useful for the estimation of the corresponding thermochemical characteristics of the hitherto uninvestigated polylactones of the series considered. The chemical characteristics found for such polylactones by Eqns (33)–(40) will apparently be subject to approximately the same error as the values found experimentally.

In conclusion, we may note that poly-β-methyl-β-propiolactone and poly-γ-butyrolactone are structural isomers (according to the data of Holmers,[8] poly-β-methyl-β-propiolactone is an isotactic polymer). Their thermochemical characteristics are fairly close (Table 5) and their enthalpies of combustion and formation in the crystalline state are simply identical. In this connection, the obvious conclusion arises that the $\Delta_c H°$ and $\Delta_f H°$ can also be estimated for other methylsubstituted crystalline polylactones — structural isomers of the polymers investigated.

5. Thermodynamic parameters of polymerisation

Figure 9 presents the Gibbs free energies of polymerisation of lactones in the range from 0 to 400 K at p = 101.325 kPa.[13,96] Evidently the values of $\Delta_{pol}G°$ for each lactone vary within a fully defined range as a function of temperature (the sections enclosed between curves *1* and *2*). This range depends on the compositions, structures, and physical states of the reactants. $\Delta_{pol}G° < 0$ for four- and (6–13)-membered lactones, while $\Delta_{pol}G°$ for (14–18)-membered lactones assumes both positive and negative values; for the five-membered lactone, $\Delta_{pol}G° > 0$. With increase in ring size, the limits of the variation of $\Delta_{pol}G°$ increase from −54 – −68 kJ mol^{-1} for β-propiolactone (n = 4) to −31 – −29 kJ mol^{-1} for pentadecanolactone (n = 16). All the lactones can be arranged in a series in terms of the values of $\Delta_{pol}G°$ for liquid monomer → liquid polymer processes: β-propiolactones > undecanolactone > decanolactone > dodecactone > nonadecanolactone > nonanolactone > η-caprylolactone > tridecanolactone > ε-caprolactone > φ-oenantholactone > pentadecanolactone > δ-valerolactone > lactones with

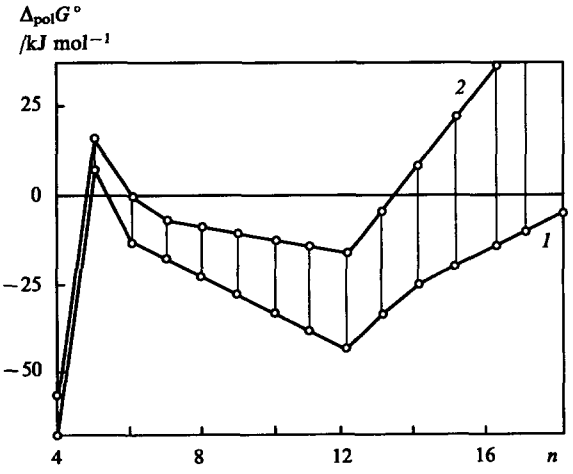


Figure 9. The Gibbs free energies of polymerisation of lactones in the range 0–400 K.[13,96]
Process: (*1*) M(cr) → P(cr) at 200 K; (*2*) M(cr) → P(g) at 0 K.

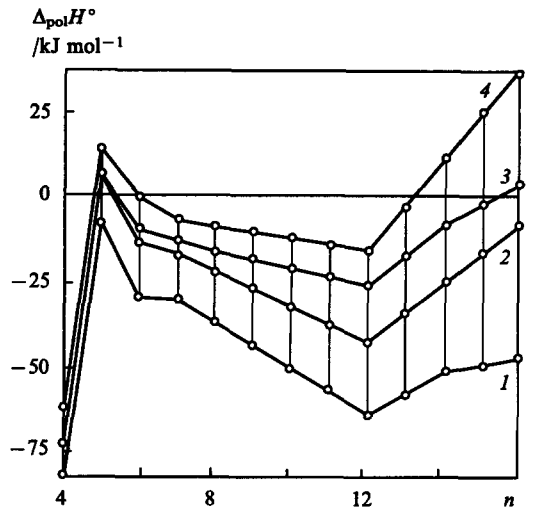


Figure 10. The enthalpies of polymerisation of lactones in the range 0–400 K.[13,96]
Process: (*1*) M(l) → P(cr) at 300 K; (*2*) M(cr) → P(cr) at 0 K; (*3*) M(l) → P(l) at 370 K; (*4*) M(cr) → P(g) at 0 K.

n > 20 > γ-butyrolactone. The sequence thus obtained represents the thermodynamic series for the polymerisabilities of the lactones.

For the same lactone, the $\Delta_{pol}H°$ for the polymerisation reactions with reactants in different physical states can be arranged in the following sequence: M(l) → P(cr) > > M(cr) → P(cr) > M(l) → P(l) > M(cr) → P(g), where M is the monomer and P the polymer.The consecutive arrangement of curves *1*–*4* corresponds to this series in Fig. 10. The $\Delta_{pol}H°$(l;l) increase in the direction from the four-membered to the five-membered lactone, after which they diminish towards the 12-membered lactone, and then again increase. This type of variation of $\Delta_{pol}H°$ on passing from the four-membered to the 16-membered lactone is caused by the variation of the ring strain energy E. The ring strain energy is evolved on polymerisation of lactones with ring opening, making the main contribution to $\Delta_{pol}H°$(l;l). For example $\Delta_{pol}H°$(l;l) = −6 kJ mol^{-1} for tridecanolactone, while E = 8 kJ mol^{-1}.

As the temperature varies from 0 to 400 K, the entropies of polymerisation of lactones assume both positive and negative values (Fig. 11). As was to be expected, $\Delta_{pol}S°$ has minimum

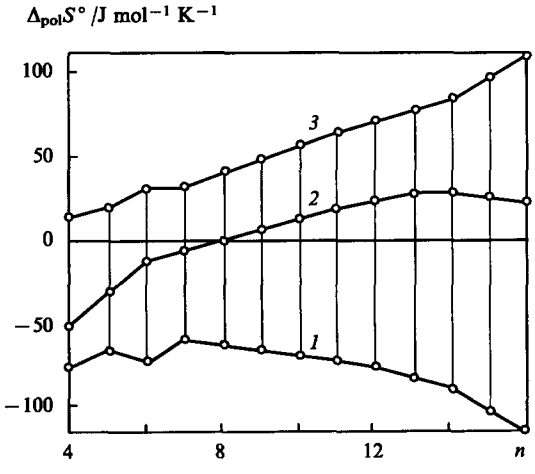


Figure 11. The entropies of polymerisation of lactones in the range 0–400 K.[13,96]
Process: (*1*) M(l) → P(cr) at 330 K; (*2*) M(l) → P(l) at 370 K; (*3*) M(cr) → P(g) at 200 K.

values for the M(l) → P(cr) processes and maximum values for the M(cr) → P(g) processes. For the M(l) → P(cr) process, the entropy of polymerisation varies from −76 for the four-membered ring to −116 J mol^{-1} K^{-1} for the 16-membered ring, while for the process M(cr) → P(g) the variation is from 14 to 108 J mol^{-1} K^{-1} respectively. The increase in $\Delta_{pol}S°$ for the process M(cr) → P(g) is due to the contribution from the zero-point entropy of the polymer $S°_g(0)$, which increases with n. The gradual expansion of the range of variation of $\Delta_{pol}S°$ on passing from the four-membered to the 16-membered ring is associated with the influence of the entropies of the phase transitions of the reactants. The variation of $\Delta_{pol}S°$ for the processes M(l) → P(l) is interesting (Fig. 11, curve *2*). With increase in n, the quantity $\Delta_{pol}S°$(l;l) initially increases from 53 J mol^{-1} K^{-1} for β-propiolactone to 26 J mol^{-1} K^{-1} for tridecanolactone and then decreases. If curve *2* is imagined to be prolonged into the range of values $n > 16$, then $\Delta_{pol}S°$(l;l) = 0 at $n \approx 22-25$. This means that rings of this size and larger ones as well as the corresponding repeat units in the polyester macromolecules are entropically indistinguishable. Since rings of this size are of course unstrained, it follows naturally that $\Delta_{pol}G° = 0$ for such structures.

None of the lactones examined in this review has a lower limiting polymerisation temperature. A series of processes have an upper limiting temperature $T°_{ceil}$. The numerical values of $T°_{ceil}$ are determined by the ratio of a $\Delta_{pol}H°$ and $\Delta_{pol}S°$ at $T°_{ceil}$. Thus $T°_{ceil}$ = 1450 K for β-propiolactone, which is due to the high value of $\Delta_{pol}H°$(l;l) = −74 kJ mol^{-1} and the relatively low value of $\Delta_{pol}S°$ = −51 J mol^{-1} K^{-1}. On passing to δ-valerolactone, $\Delta_{pol}H°$ diminishes sharply and there is only a slight decrease in $\Delta_{pol}S°$. Both these factors lead to $T°_{ceil}$ = 760 K for δ-valerolactone. Lactones in which the number of ring members is between 9 and 16 have neither a lower nor an upper limiting temperature because $\Delta_{pol}H°$(l;l) < 0, and $\Delta_{pol}S° > 0$ for these substances.

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