

## PHYSICAL CHEMISTRY | RESEARCH ARTICLE

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# Thermodynamics of $\alpha$ -angelicalactone polymerization

Konstantin Leonidovich Kaygorodov<sup>1</sup>, Valery Evgenievich Tarabanko<sup>1\*</sup> and Nikolay Tarabanko<sup>1</sup>

**Abstract:** Thermodynamics of sodium butoxide-catalyzed polymerization of  $\alpha$ -angelicalactone (a five-member unsaturated lactone) is studied by calorimetric methods. A polymer with  $M_w = 2,500$  g/mol and the ratio of C–O to C–C inter-monomeric bonds 87–13% is obtained; this polymerization is characterized by the values of  $\Delta H_{\text{pol}}^\circ = -33.41$  kJ/mol,  $\Delta S_{\text{pol}}^\circ = -42.69$  J/(mol·K) and  $\Delta G_{\text{pol}}^\circ = -20.68$  kJ/mol. This and similar polymers and copolymers are biodegradable and can be produced from commercially available green bio-platform feedstock: renewable carbohydrates and levulinic acid.

**Subjects:** Chemistry; Material Science; Materials Science

**Keywords:** angelicalactone; polyester; polymerization; thermodynamics

### 1. Introduction

$\alpha$ -Angelicalactone (5-methyl-2(3H)-furanone,  $\alpha$ AL) (3) is a product of levulinic acid dehydration (2). The latter can be obtained from hexose carbohydrates (1)—a renewable plant resource—as shown in Scheme 1.

### ABOUT THE AUTHORS

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Nikolay Tarabanko, PhD, is a researcher at the ICCT SB RAS. The author specializes in inorganic heterogeneous catalysis (by inclination), and in chemistry of renewable resources (by call of duty). This combination makes him a bit of an odd-man-out in the team, usually serving as the hitman who is called upon to deal with various research complications that require the attention of a flexible and meticulous mind.

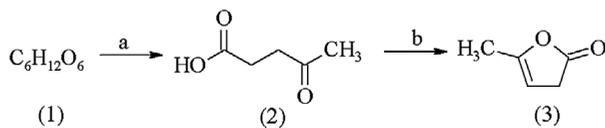
### PUBLIC INTEREST STATEMENT

This work relates to polymers obtained from renewable plant matter. Specifically, the polymer of  $\alpha$ -angelicalactone (a lactone obtained by acid-catalyzed carbohydrate conversion) that can become a biodegradable alternative to commonly used polyester materials; the presence of double bonds in the polymer allows for additional functionalization. In the present study, the thermodynamic parameters of  $\alpha$ -angelicalactone polymerization are experimentally measured; these parameters are necessary to know under which conditions this polymerization may occur. It is shown that in this regard,  $\alpha$ -angelicalactone behaves differently from other five-member lactones like  $\gamma$ -butyrolactone or  $\gamma$ -valerolactone: polymerization of the latter is thermodynamically restricted and only becomes feasible under stern conditions like exceedingly high pressure. On the other hand,  $\alpha$ -angelicalactone polymerizes under mild conditions (80°C), and the obtained data indicate that in theory (with the right catalyst) it could polymerize under normal conditions.



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**Scheme 1. Synthesis of  $\alpha$ -angelicalactone (3). Reaction conditions: (a) HCl (cat.), 370–373 K, 4 h; (b)  $H_3PO_4$  (cat.), 25 Torr, 340–345 K.**



There are two polymerizable groups in a molecule of  $\alpha$ AL: the lactone ring and the C–C double bond. Therefore, there are two possible polymerization pathways: the double bond opening resulting in the polyfuranone chain (4) and the formation of the unsaturated polyester—polyangelicalactone (PAL) (5) via ring opening (Figure 1).

The double bond polymerization of  $\alpha$ AL is caused by strong Lewis acids (1,2), ionizing radiation, intensive mechanoactivation (2) or basic catalysts (3). A polyfuranone ( $M_n = 810$ ,  $M_w = 862$ ) (4) obtained from  $\alpha$ AL in the presence of  $BF_3$  was found to be non-degradable by *Saccharomyces cerevisiae*, *Streptomyces chrysomallus* and *Streptomyces lividans* (4). Also, opening of the double bond occurs during copolymerization of  $\alpha$ AL with methyladamantylmethacrylate, maleic anhydride, norbornene or polyhydroxystyrene (5,6). In such copolymerization processes, the fraction of  $\alpha$ AL included in the products did not exceed 30%.

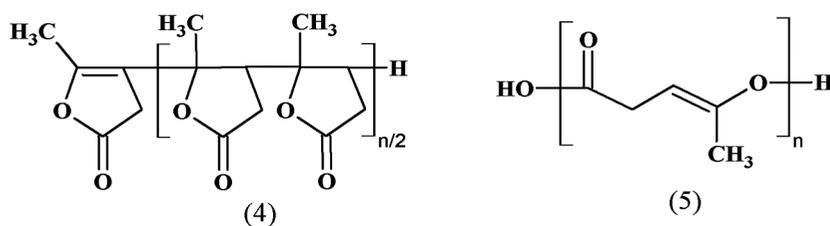
The ring-opening polymerization (ROP) of  $\alpha$ AL is more interesting. The product (5) of this reaction is supposedly biodegradable (7–10). However, five-member lactones (at least, the saturated ones) are not predisposed to polymerization. For example,  $\gamma$ -butyrolactone does not polymerize, and the Gibbs free energy of this process is positive (8). Similarly, there appears to be a lack of experimental reports about  $\gamma$ -valerolactone ( $\gamma$ VL) polymerization, and this lactone can only undergo co-polymerization with other lactones (11)—this suggests that the polymerization Gibbs free energy of pure  $\gamma$ VL is also positive.

Nonetheless, it was recently found that  $\alpha$ AL polymerizes under the action of sodium hydroxide, sodium butoxide (4,12,13) and stannous octoate (14), resulting in products with molecular weight ranging from 1,000 to 30,000 g/mol, and polydispersity index (PDI) = 1,6–2,2.

PALs obtained from  $\alpha$ AL in the presence of 5 wt.% of sodium butoxide (ButONa) at room temperature are slightly yellow resins or solids with  $M = 1,120$ – $1,800$  g/mol and PDI = 1,8.  $^1H$  NMR data showed that 68–80% of the inter-monomeric bonds in the resulting polymers are esteric, and 20–32% of the bonds are formed due to the double bond opening (4). Unlike polyfuranones (4), these PALs are fully degraded by *S. cerevisiae* (over 1–1.5 weeks), *S. chrysomallus* (2–3 weeks) and *S. lividans* (3–4.5 weeks) (4,12).

Solubilized in aprotic solvents,  $\alpha$ AL can be easily polymerized when treated by sodium and aluminium alkoxides at 333–338 K for 40–60 min, which produces polyesters with  $M = 15,000$ – $19,000$  g/mol, and PDI = 1,6–2,2 (12,15).

**Figure 1. Structures of the possible  $\alpha$ -angelicalactone polymers.**



Copolymerization of the unsaturated PAL and styrene (Sty) results in further molecular weight increase, and improvement of the viscoelastic properties (12). Fusion of the PAL and styrene (1–5 mol%) with boron trifluoride as the catalyst forms cross-linked polymers with  $M = 200,000\text{--}500,000$  g/mol. These polymers are mostly or fully degradable after 20 weeks in grey forest soil. The obtained copolymers have the following characteristics: density  $1.15\text{--}1.16 \times 10^3$  kg/m<sup>3</sup>, yield strength 40–60 MPa, ultimate strength 70–80 MPa and ultimate strain of 10–20% (15).

There appears to be a lack of published data on the thermodynamic properties of PAL, and on the thermodynamics of its formation process. The hereinabove described facts about successful syntheses of angelicalactone polymers suggest that the thermodynamics of such polymerization does not follow the pattern of the corresponding parameters for other five-member lactones. Thus, there is incentive towards experimental measurement of the  $\alpha$ AL polymerization thermodynamic parameters. In this work, we present the experimental study of the thermodynamic properties of PAL and  $\alpha$ AL as dependences vs. temperature and phase composition of the reactants. The heat capacity of partially crystalline (67%) PAL was measured by DSC in the temperature interval 7–430 K. Finally, the standard thermodynamic functions for PAL and  $\alpha$ AL formation were obtained from combustion calorimetric data.

## 2. Experimental section

### 2.1. Materials

$\alpha$ -Angelicalactone (Alfa Aesar, 98%) was purified by melt fractional crystallization. The total impurities content was  $0.10 \pm 0.02$  mol%, according to <sup>1</sup>H-NMR data. Spontaneous polymerization of the  $\alpha$ AL during 9 months storage, and during experiments did not occur.

Sodium butoxide was synthesized according to the standard procedure (16).

### 2.2. Polymerization of $\alpha$ -angelicalactone by sodium butoxide

10 g ( $\sim 0.102$  mol) of  $\alpha$ -angelicalactone and 0.30 g ( $\sim 3.06 \times 10^{-3}$  mol) of sodium butoxide were sealed in a nitrogen-filled glass ampule, placed in a thermostat, and left there for 14 h at  $350 \pm 1$  K. After that, the viscous yellow product was washed by decantation with several portions of cold diethyl ether, and then cleared of volatile matter at 80°C at 2 Torr for 1.5 h. There remained 8.2 g of a slightly yellow tacky solid with  $M_w$  2,500 g/mol, PDI 2.3, the fraction of the ester inter-monomeric bonds was 0.87.

### 2.3. Equipment and analysis techniques

The structure of the polymer was elucidated by <sup>1</sup>H-NMR spectroscopy (spectrometer Bruker DPX-200 W, Krasnoyarsk Regional Research Equipment Center of SB RAS) in CDCl<sub>3</sub> solution (12 mg/ml).

The relative molecular weight of the polymer was determined by phase-reversal chromatography relative to polystyrene standards. The column was Nova-Pak CIS (Waters Corporation, USA) packed with octadecyl-functionalized silica; evaporative light scattering detector device was used (model 500, Alltech Corporation, USA); the eluent was an acetonitrile–tetrahydrofuran mixture (MeCN/THF = 58/42), flow rate 1 ml/min.

The internal energy of combustion  $\Delta U_c$  was determined using a static isothermal combustion calorimeter V-08MA, according to the standard technique (17). The initial temperature was  $25.0 \pm 0.2^\circ\text{C}$  and the initial pressure was 2,940 kPa. The samples to be burnt were placed into weighted polyethylene ampules and weighed to the accuracy of 0.01 mg. The ampoule was placed into the bomb crucible in the proximity of the fuse used for ignition; if necessary, an auxiliary cotton fuse was used. The bomb was flushed with dried oxygen for three minutes, then sealed and filled with oxygen to the initial pressure mentioned above. The calorimeter constant was determined by calibration against benzoic acid combustion (the certified combustion energy 26,434.6 J/g). The calorimeter constant was calculated from at least ten combustion runs, resulting in the value of  $W = 15,126.6 \pm 3.8$  J/K.

After combustion, the gas mixture was evacuated from the bomb. The combustion gas products were analysed with the Gazochrom-3101 gas chromatograph. For CO<sub>2</sub>, the data error was 0.4%, and for CO—0.06%. The walls and fittings of the bomb were washed with 200 mL of double-distilled water. Three 50 mL samples of the solution were titrated with 0.1 N NaOH solution. The mean value from the three titrations was used for the calculation of the nitric acid amount resulting from the combustion.

The experimental values of combustion energy were corrected to the standard state ( $T = 298.15$  K and  $P = 101.3$  kPa) according to the Washburn equation (18), recommended for the case of compounds comprising carbon, hydrogen and oxygen. The relative error in the determination of the combustion heat values was 0.022%.

The standard combustion enthalpies  $\Delta H_c^\circ$  of the samples were calculated from the corresponding values of internal energy of combustion  $\Delta U_c$ .

DSC analyses were performed on a scanning calorimeter of the triple heat bridge-type assembled in-house according to the published specification (19–23). Temperature and heat flow were calibrated using the standard materials (23). The temperature data error was 0.05 K. The heat capacity determination error within different temperature intervals is: 7–160 K –  $\pm 0.4$ –0.6%, 160–200 K –  $\pm 0.1$ –0.2%, 200–430 K –  $\pm 1.5$ –2.5%. The error of phase transition enthalpy data was  $\pm 0.4$ %. The heat capacity  $C_p^\circ$  of the PAL was measured within the range 7–400 K at the heating rate 0.02 K/s. The sample mass was 5.3759 g. The heat capacity of the PAL sample was 58% of the total heat capacity of the calorimeter in the entire temperature range. The heat capacity data error was 0.9 J/(mole K).

The glass-transition range and the heat capacity increase therein were determined from heat capacity vs. temperature curves. The glass-transition temperature was determined according to the Alford-Dole's procedure (24).

The melting point was determined by graphical evaluation from the  $T_f(v)$  vs.  $1/v^2$  dependences, where  $T_f$ —temperature corresponding to the maximum magnitude of apparent heat capacity in the melting range,  $v$ —heating rate.

The enthalpy of melting  $\Delta H_m^\circ$  was calculated by integration of  $\Delta C_p^\circ$ —the difference between the heat capacity in the melting interval and  $C_p^\circ = f(T)$  extrapolated from the beginning to the end of melting (19). The entropy of melting  $\Delta S_m^\circ$  was determined from the dependency  $\Delta S_m^\circ = \Delta H_m^\circ / T_m$ .

The configurational entropy  $S_{\text{conf}}$  of the polymer was estimated according to the method described by Adam and Gibbs (25). The zero entropy  $S_g(0)$  was found according to Lebedev and Rabinovich (26).

Calculations of  $(H^0(T) - H^0(0))$  and  $S^0(T)$  were done by integration of the functional dependence  $C_p = f(T)$  and  $C_p = f(\ln T)$ , respectively, according to McCullough and Scott (27).

The standard formation enthalpy of PAL at  $T = 298.15$  K was calculated from its combustion enthalpy,  $\Delta H_f^\circ(\text{CO}_2(\text{g}))$  and  $\Delta H_f^\circ(\text{H}_2\text{O}(\text{l}))$  (28). The standard entropy of formation  $\Delta S_f^\circ$  (PAL) was calculated from the absolute entropy of PAL and reference data on carbon (graphite), hydrogen (gas) and oxygen (gas). Standard Gibbs free energy of formation was calculated from  $\Delta H_f^\circ$  and  $\Delta S_f^\circ$ . The enthalpy of polymerization  $\Delta H_{\text{pol}}^\circ$  of  $\alpha\text{AL}$  in bulk at  $T = 298.15$  K was calculated from  $\Delta H_f^\circ(\alpha\text{AL})$  and  $\Delta H_f^\circ(\text{PAL})$ . The Kirchhoff equation was used to calculate  $\Delta H_{\text{pol}}^\circ$  at different temperatures. The polymerization entropy  $\Delta S_{\text{pol}}^\circ$  was found from the absolute entropies of  $\alpha\text{AL}$  and PAL at the corresponding temperatures.  $\Delta G_{\text{pol}}^\circ$  was calculated from the Gibbs–Helmholtz equation.

The limiting temperature of polymerization was estimated by the Dainton method (29).

Ring strain energies for  $\gamma$ -butyrolactone,  $\gamma$ -valerolactone ( $\gamma$ VL) and  $\alpha$ AL were computed by molecular modelling using the program suite GAMESS (30), (version 11 November 2017, R3 for GNU/Linux x86-compatible 32-bit). Evaluations of the strain energies were performed according to Dudev and Lim (31). Geometry optimizations and frequency calculations were performed using the B3LYP density functional method (32,33) in conjunction with the 6-31G(d) basis set (34).

### 3. Results and discussion

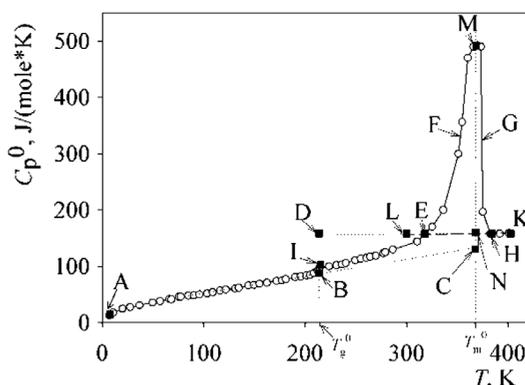
#### 3.1. Heat capacity

Heat capacity of the PAL smoothly increases with temperature (Figure 2), and equals 135.83 J/(mol·K) at 298 K. There are two sharp increases: (a) 210–225 K—devitrification (section BI on Figure 2) and (b) 310–380 K—melting (section EM). The ~ 24 K wide section (EL) corresponds to a metastable state—the supercooled liquid—which occurred when cooling the liquid PAL. Upon further cooling, the sample spontaneously rapidly crystallized with a heating of the calorimeter.

#### 3.2. Phase transition

Parameters of the glassy state and devitrification of the PAL together with the Lebedev's (8) data on poly- $\gamma$ -butyrolactone and poly- $\delta$ -valerolactone are shown in Table 1. From the calorimetric data, the PAL sample crystallinity  $\alpha_c$  is 67%.

**Figure 2. Temperature dependence of the PAL heat capacity. ( $M_r \sim 1300$ . ABC, crystalline; AIE, partly crystalline; AB, vitreous; DEN, high elastic; EMH, apparent melting heat capacity; ENK, liquid; EL, metastable liquid).**



**Table 1. Experimental thermodynamic parameters of the glassy state and devitrification of the PAL, and reference data on poly- $\gamma$ -butyrolactone (PBL) (8) and poly- $\delta$ -valerolactone (PVL) (8)**

	$\Delta T_g^a$ (K)	$T_g^b$ (K)	$H_g^c(0) - H_{cr}^c(0)$ (kJ/mol)	$\Delta C_p^d(T_g^0)$ (J/(mol K))	$S_{conf}^e$ (J/(mol K))	$S^f(0)$ (J/(mol K))
PAL	210–225	214 ± 1	2.5	21.8 ± 5	3.6 ± 1	4.0 ± 1
PBL	–	214	7.9	58	–	19
PVL	–	207	11.7	65	–	30

<sup>a</sup>Glass transition temperature range.

<sup>b</sup>Glass transition temperature.

<sup>c</sup>Difference between the enthalpies of the crystalline and amorphous states at 0 K.

<sup>d</sup>Heat capacity change at the glass transition temperature.

<sup>e</sup>Conformational entropy.

<sup>f</sup>Entropy at 0 K.

**Table 2. Experimental melting parameters of the PAL, and reference data on poly- $\gamma$ -butyrolactone (PBL) (8) and poly- $\delta$ -valerolactone (PVL) (8)**

	$\Delta T_m^a$ (K)	$T_m^b$ (K)	$\Delta H_m^c$ (kJ/mol)	$\Delta S_m^d$ (J/(mole K))	$\Delta C_p(T_m)^e$ (J/(mole K))
PAL <sup>f</sup>	350–380	368 ± 1	6.5 ± 0.1	17.7 ± 0.3	16.7 ± 0.5
PBL <sup>g</sup>	–	338 ± 1	13.2 ± 0.3	39.4 ± 0.6	29
PVL <sup>h</sup>	–	331 ± 2	18.2 ± 0.3	55 ± 1	40

<sup>a</sup>Melting temperature range.

<sup>b</sup>Melting point.

<sup>c</sup>Melting enthalpy.

<sup>d</sup>Entropy of melting.

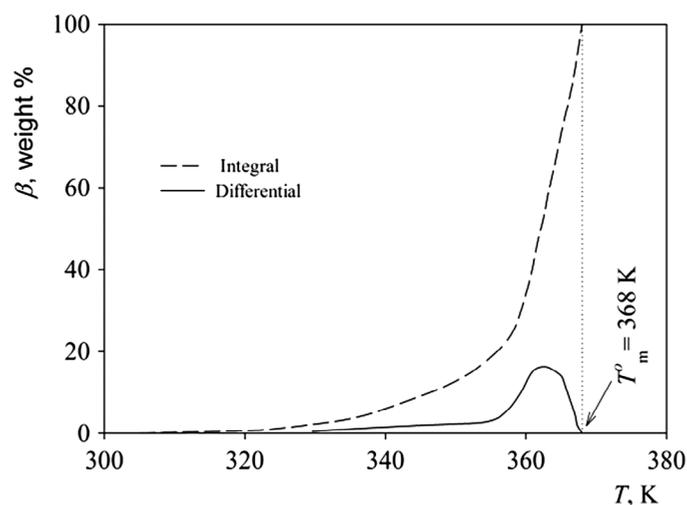
<sup>e</sup>Heat capacity change at the melting point.

<sup>f</sup>Crystallinity 67%.

<sup>g</sup>Crystallinity 100%.

<sup>h</sup>Crystallinity 100%.

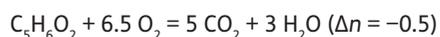
**Figure 3. Temperature dependency of melted/crystalline ratio  $\beta$  during the PAL melting.**



The PAL melting spans a 30 K wide temperature range, and the melting parameters are presented in Table 2 together with the reference data (8). Results of the calorimetric study of the PAL melting process are shown in Figure 3. The PAL is melting over a wide temperature range, and the largest portion of the crystals melt at  $T = 362$  K, which is 6 K lower than  $T_m^0$ . The values obtained for the phase transitions of PAL are lower comparing to literature data on the other polylactones (8).

### 3.3. Combustion heats

The combustion experimental data are given with respect to the following reaction, the same for  $\alpha$ AL and PAL:



These data were recalculated into the thermodynamic functions of  $\alpha$ AL and the PAL. Table 3 shows the combustion and standard formation enthalpies of liquid  $\alpha$ AL, and the PAL in high-elastic state (67% crystallinity) at  $T = 298.15$  K.

**Table 3. Standard enthalpies of combustion ( $-\Delta H_c^\circ$ ) and formation ( $-\Delta H_f^\circ$ ) of  $\alpha$ AL and the PAL ( $T = 298.15$  K,  $p^\circ = 0.1$  MPa)**

Substance (physical state)	$-\Delta H_c^\circ$ (kJ/mol)	$-\Delta H_f^\circ$ (kJ/mol)
PAL (high-elastic)	2,545.31 $\pm$ 0.16	279.73 $\pm$ 0.61
$\alpha$ AL (liquid)	2,578.72 $\pm$ 0.12	246.32 $\pm$ 0.65

### 3.4. Thermodynamic characteristics of the $\alpha$ -angelicalactone polymerization

Table 4 shows the thermodynamic characteristics of the polymerization reaction of  $\alpha$ -angelicalactone.

The results show that the monomer-polymer equilibrium is shifted towards the formation of PAL throughout the studied temperature range. The  $\Delta G_p^\circ$  values increase with rising temperature. The enthalpy and entropy of polymerization are negative. Hence, there exists a ceiling temperature of polymerization. Calculated by the Dainton's method, the ceiling temperature is  $T = 425.5$  K.

The polymerization enthalpy of  $\alpha$ AL into PAL  $\Delta H_p^\circ = -33.41 \pm 1.2$  kJ/mol at 298 K. This value is in between the corresponding data for  $\beta$ -propiolactone ( $\beta$ PL) and  $\delta$ -valerolactone ( $\delta$ VL) polymerization ( $\Delta H_p^\circ = -75$  and  $-10.5$  kJ/mol at 298 K, correspondingly), and is considerably lower than the datum for  $\gamma$ -butyrolactone ( $\gamma$ BL) polymerization ( $\Delta H_p^\circ = +5$  kJ/mol at 298 K). Similar relation is observed for the Gibbs free energies of the lactones polymerization (see (8) and Table 4). The enthalpy obtained is lower than the earlier estimated enthalpy for the  $\alpha$ AL oligomerization to the trimer ( $\Delta H_p = -26$  kJ/mol (14)).

The difference between the Gibbs energies of polymerization reactions of two five-member lactones— $\gamma$ BL and  $\alpha$ AL—can be explained by the difference of their respective ring strain values. The strain energy of  $\alpha$ -angelicalactone is greater than that of  $\gamma$ -butyrolactone (Table 5). Another saturated five-member lactone,  $\gamma$ -valerolactone, exhibits the strain energy similar to that of  $\gamma$ BL; and as was described in Introduction,  $\gamma$ VL is not prone to polymerization just like  $\gamma$ BL. Therefore, we can conclude that the presence of the double bond in the  $\alpha$ AL ring causes the strain in the five-member lactone structure that makes this compound sufficiently endergonic to thermodynamically enable the ring-opening polymerization.

**Table 4 Thermodynamic parameters of lactones polymerization ( $p = 101.325$  kPa)**

Lactone $\rightarrow$ poly lactone	T (K)	Physical state <sup>a</sup> (L/PolyL)	$-\Delta H_{pol}^\circ$ (kJ/mol)	$-\Delta S_{pol}^\circ$ (J/(mole K))	$-\Delta G_{pol}^\circ$ (kJ/mol)
$\alpha$ AL $\rightarrow$ PAL	100	cr/cr	19.37	23.00	17.07
$\alpha$ AL $\rightarrow$ PAL	220	cr/cr	29.93	32.54	22.77
$\alpha$ AL $\rightarrow$ PAL	298.15	l/he	33.41	42.69	20.68
$\alpha$ AL $\rightarrow$ PAL	400	l/l	50.44	104.13	8.78
$\gamma$ BL $\rightarrow$ PBL <sup>b</sup>	298.15	l/he	-5	30	-14
$\beta$ PL $\rightarrow$ PPL <sup>b</sup>	298.15	l/he	75	54	59
$\delta$ VL $\rightarrow$ PVL <sup>b</sup>	298.15	l/he	10.5	15	6

<sup>a</sup>cr—crystalline, gl—glassy, l—liquid, he—high-elastic.

<sup>b</sup>Lebedev (8).

**Table 5. Strain energies (in kJ/mol) for  $\delta$ VL,  $\gamma$ VL,  $\alpha$ AL and  $\gamma$ BL**

Source	$\delta$ VL	$\gamma$ VL	$\alpha$ AL	$\gamma$ BL
Our calculation	-	30.6	38.9	33.0
Chen et al. (14)	41.4	30.8	39.5	32.6
Brown et al. (35)	39.7	30.5	-	32.2

#### 4. Conclusions

Most five-member lactones are inactive in ring-opening polymerization, but  $\alpha$ -angelicalactone can undergo such reaction. Explanation of this unusual behaviour is required, therefore we studied thermodynamic properties of  $\alpha$ -angelicalactone and a polyangelicalactone. The polyangelicalactone ( $M_w = 2,500$  g/mol) with the fractions of the C–O and C–C inter-monomeric bonds being 87 and 13%, respectively was studied by calorimetric methods. Thermodynamic functions of the PAL formation were determined. Heat capacity and thermodynamic parameters of phase transitions of the polymer were calculated.

Finally, the standard thermodynamic functions of the polymerization process were determined:  $\Delta H_{\text{pol}}^{\circ} = -33.41$  kJ/mole,  $\Delta S_{\text{pol}}^{\circ} = -42.69$  J/(mole·K) and  $\Delta G_{\text{pol}}^{\circ} = -20.68$  kJ/mole. Based on these, the ceiling temperature of  $\alpha$ AL polymerization  $T_c = 425$  K is estimated. The obtained standard thermodynamic functions of the  $\alpha$ -angelicalactone polymerization are in a good agreement with the data on other lactones. The obtained results indicate that the double bond in the structure of  $\alpha$ AL strains the ring and makes it active in the ring-opening polymerization.

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#### Competing interests

The authors declare no competing interest.

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#### Erratum

This article was originally published with errors. This version has been corrected. Please see Erratum (<https://doi.org/10.1080/23312009.2018.1457128>).

#### Cover image

Source: Authors.

#### References

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