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THERMODYNAMICS OF PROPANAL POLYMERIZATION AND THERMODYNAMIC FUNCTIONS OF POLYPROPANAL FROM 0 K TO 370 K AT STANDARD PRESSURE

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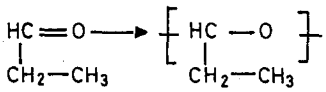
The heat capacity C_p^o of polypropanal was studied in a vacuum adiabatic calorimeter between 11 and 330 K, and in an ADKTTM automatic differential calorimeter from 320 to 370 K. The thermodynamic parameters of melting and glass transition of polypropanal were also determined. From the results, the thermodynamic functions of the polymer were calculated in the range 0 K to 360 K. The enthalpy of depolymerization of polypropanal to the starting monomer was measured in a DAK–1–1 differential automatic microcalorimeter. From the results of this study and literature data on the thermodynamic properties of propanal, the enthalpy, entropy and Gibbs function of bulk polymerization of propanal were estimated from 0 K to 330 K. Ceiling limiting temperatures of transitions of the liquid monomer to crystalline and high-elasticity polymer were determined.

Keywords: polymerization, propanal, thermodynamic parameters

Introduction

Propanal (P) is polymerized according to the scheme:



(P) (PP)

with the formation of polypropanal (PP). The kinetic aspects of the polymerization of this aldehyde and others were discussed in detail earlier [1]. The thermodynamic properties of propanal have been given elsewhere [2]. The thermodynamic properties of polypropanal were first studied in the present work.

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Experimental

Samples: The sample of polypropanal was prepared by the polymerization of propanal. The starting monomer was purified by the procedure described in [3]. The polymerization of propanal was performed in pentane solution, the ratio of the monomer and the solvent being 1:4 by volume. As an initiator, lithium tert-butylate was used in an amount of 0.2% on the monomer mass basis. The process was carried out at T=195 K and at normal pressure, similarly as given earlier [4]. On completion of the polymerization process, 200 ml of acetone cooled down to 195 K and containing 0.5 ml of acetic acid was added. The addition of acetic acid is necessary to isolate the initiator. The polypropanal formed was spontaneously precipitated from the solution as a white substance. It was washed with acetone and toluene, filtered and dried under vacuum. The polypropanal obtained was a white wax-like substance insoluble in common organic solvents. Elementary analysis indicated (mass %): C, 62.12; H, 11.00; theoretical: C, 62.00; H, 10.4. The IR spectrum of the polypropanal (Specord instrument) was fully similar to that described elsewhere [4]. X-ray analysis (DRON 3.0 instrument) indicated that the polymer is partially crystalline at room temperature.

The calorimetric data showed that its degree of crystallinity was 37%.

Equipment: To measure the heat capacities of polypropanal at temperatures ranging from 11 to 330 K, a vacuum adiabatic calorimeter was used, its design and the procedure being given earlier [5]. It was established by calibration testing that the calorimeter and its procedure allow the heat capacity of the substance in the condensed state to be obtained within about 1% near 10 K, 0.5% in the range 30 to 50 K, and 0.2% between 50 and 330 K.

The heat capacity over the range 320 to 370 K was measured in an ADKTTM automatic differential calorimeter operating on the principle of a triple thermal bridge [6, 7]. This calorimeter allows the measurement of heat capacity within an error of 1–4% between 80 and 700 K at a heating rate of from 3.3×10^{-3} to 1.7×10^{-1} deg/s.

A DAK-1-1 automatic differential microcalorimeter was used to measure the enthalpy of polypropanal depolymerization. The design and the procedure of measurement were described elsewhere [8, 9].

Results and discussion

Heat capacity

The mass of the polypropanal sample studied was 1.392×10^{-3} kg. 102 experimental values of C_p° were obtained in 14 series of measurements (Table 1). In the range 11 to 230 K, the experimental results are satisfactorily approximated by the following equation:

$$C_p^\circ = A\theta^{-2} + B\theta^{-1} + C + D\theta + E\theta^2 + F\theta^3 \qquad (1)$$

where $\theta = T/100$, e.g. for the range 100–200 K the coefficients are $A=3.473\cdot10^3$, $B=-1.261\cdot10^3$, $C=1.797\cdot10^3$, $D=1.256\cdot10^4$, $E=4.373\cdot10^3$ and $F=-6.015\cdot10^2$. The relative deviation of the experimental data from the smoothed values of C_p° calculated with the equation is 0.8% between 11 and 45 K, 0.6% from 40 to 70 K, 0.14% for 60–105 K, 0.16% in the range 100–200 K and 0.05% between 180 and 230 K.

For measurement of the C_p° values of the polymer in the range 320 to 370 K, the calorimeter and the substance were heated at a rate of 2.5×10^{-2} deg/s. The sample mass was 6.26×10^{-4} kg. Since the ranges of heat capacity measurements in the adiabatic and dynamic calorimeters overlapped one another, the conditions of C_p° measurement in the dynamic calorimeter were chosen so that the C_p° values measured in it coincided with those obtained in the vacuum adiabatic calorimeter.

In this connection, the accuracy of the values measured over the range 320–370 K is assumed to be close to that attained in the vacuum adiabatic calorimeter. In this case it seems to be within 1%.

A relatively sharp increase in the C_p° values between 230 and 250 K is associated with the devitrification of an amorphous component of the polymer (Fig. 1). The temperature of glass transition for polypropanal was found by the method given in [10] to be $T_g^\circ=240\pm1$ K. The character of the variation in the values of C_p° from 90 to 240 K is noteworthy: a broad blurred hump can be seen. The occurrence of such humps was predicted and in some cases was observed by Sochava and Trapeznikova [11]. This is connected with the change from the hindered rotation of side radicals linked with a chain macromolecule of the polymer to free rotation. In this case it is apparently due to the excitation of the hindered rotation of a C_2H_5 group in polypropanal.

Melting of the polymer crystals starts even at about 280 K, and leads to a relatively rapid increase in the C_p° values in the interval from 280 to 350 K. The anomalous increase in the heat capacity beginning at 360 K is caused by the onset of thermal destruction of the polymer.

Degree of crystallinity and thermodynamic parameters of melting of the polymer.

The degree of crystallinity (α=37%) was calculated from our calorimetric data via the equation [12]

$$\alpha = 1 - \Delta C_p^\circ(\alpha) / \Delta C_p^\circ(\alpha=0)\ 100 \qquad (2)$$

where $\Delta C_p^\circ(\alpha)=20.7$ J/(deg·mol) is the increase in the heat capacity on the devitrification of the amorphous component of the polymer sample (it is found graphically; Fig. 1, curve BE); $\Delta C_p^\circ(\alpha=0)=32.95$ J/(deg·mol) is the increase in the

Table 1 Experimental heat capacities of polypropanal, J/(K·mol)

T/K	C_p^o	T/K	C_p^o	T/K	C_p^o
Series 1		Series 4		145.99	72.21
11.76	2.681	64.53	29.60	149.26	74.25
13.27	3.173	68.03	31.32	152.53	77.80
15.75	4.521	71.68	32.80	155.63	80.57
16.72	4.990	75.35	34.11	158.75	80.20
17.68	5.322	78.98	35.61	162.14	80.94
18.58	5.761	Series 5		Series 8	
19.50	6.553	82.74	37.11	151.74	73.22
20.61	7.072	85.10	37.68	153.54	74.35
22.02	7.820	88.40	38.57	Series 9	
23.42	8.431	91.52	39.39	165.13	82.81
24.92	9.780	94.56	41.36	171.39	79.98
Series 2		97.79	43.04	174.32	86.48
26.60	11.11	Series 6		178.04	87.34
28.41	11.87	100.99	43.80	186.26	90.26
30.39	13.14	104.44	46.33	189.56	92.02
32.53	14.05	108.38	48.96	192.82	92.43
34.79	15.96	112.29	52.34	Series 10	
37.36	17.55	113.38	52.76	181.39	90.03
39.38	19.14	117.04	56.47	184.76	90.86
42.50	20.24	120.70	58.28	190.65	92.83
45.41	21.98	124.38	61.21	196.87	92.02
48.43	23.72	127.69	63.70	198.63	92.23
Series 3		131.43	66.27	202.92	93.15
51.58	26.14	135.48	67.98	Series 11	
54.41	27.27	Series 7		208.28	94.16
57.44	27.82	138.98	70.26	212.79	94.24
61.01	28.76	142.60	71.99	219.82	95.39
225.27	96.58	Series 14		332.1	198.8
230.63	97.36	289.63	126.2	333.9	207.8
235.81	99.96	294.22	128.1	335.7	217.1
240.15	110.0	297.85	130.4	337.5	225.8
244.97	120.1	299.20	130.6	339.5	231.0
249.43	120.5	302.87	132.2	341.5	236.4
253.53	120.0	306.41	132.8	343.4	239.7
Series 12		310.20	133.4	345.4	241.5

Table 1 Continues

T/K	C_p^o	T/K	C_p^o	T/K	C_p^o
253.84	121.4	319.05	135.5	349.4	141.1
256.73	121.5	323.00	137.0	351.4	140.1
260.09	121.3	327.52	138.3	353.4	140.9
264.12	121.6	Series 15		355.4	140.9
268.45	123.0	319.1	132.9	357.3	140.3
Series 13		321.1	134.1	359.2	140.7
273.04	123.0	323.0	136.3	361.1	141.6
282.63	124.7	324.9	145.6	362.9	143.3
285.82	126.0	326.7	158.8	364.7	147.1
287.41	127.0	328.5	172.6	366.4	152.0
292.88	127.9	330.3	185.6	369.6	167.3
				371.1	271.7

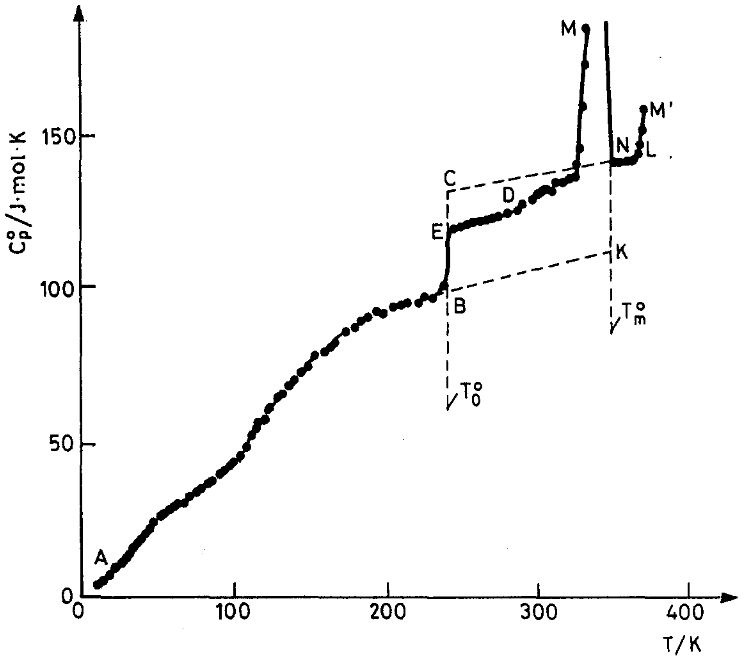


Fig. 1 Heat capacities of polypropanal: ABK is for crystalline polymer, ABED– partially crystalline (α=37%), ABCNL– amorphous (AB– glassy, CN– high-elasticity, NL– liquid); DMN is apparent heat capacity in the range of melting; LM' is apparent heat

heat capacity on the devitrification of completely amorphous polypropanal (it is also obtained graphically; Fig. 1, curve BC).

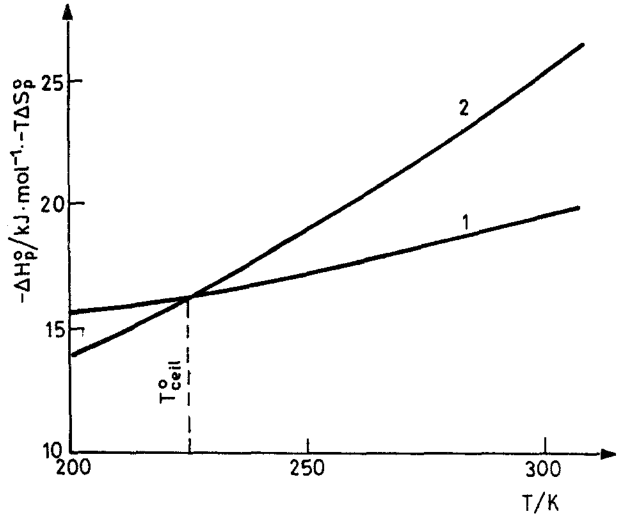


Fig. 2 Temperature dependences: 1,$-\Delta H^o_{pol}=f(T)$; 2, $T\cdot\Delta S^o_{pol}=f(T)$

The enthalpy of melting of polypropanal was estimated by the known method of continuous energy input described in detail earlier [10]; $\Delta H^o_m(\alpha=37\%)=$ 1.85 kJ/mol. The recalculation of this enthalpy for polypropanal of 100% crystallinity via the expression

$$\Delta H^o_m=100\ \Delta H^o_m(\alpha=37\%)/\alpha \qquad (3)$$

gives rise to the value $\Delta H^o_m(\alpha=100\%)=4.99\pm$ 0.05 kJ/mol. The temperature at which the last polymer crystals with the most perfect organization exist (the temperature of the melting range end) was considered as the temperature of melting, $T^o_m=347\pm1$ K. From the values of ΔH^o_m and T^o_m, the entropy of melting $\Delta S^o_m=5.4\pm0.1$ J/(deg·mol) was calculated.

Thermodynamic functions

For calculation of the thermodynamic functions for polypropanal (Table 2) the relation $C^o_p=f\ (T)$ was extrapolated from 11 to 0 K with the Debye function for the heat capacity:

$$C^o_p=nD(\theta_D/T) \qquad (4)$$

Table 2 Thermodynamic functions of polypropanal (per repeating unit M=58.08); p=101.325 kPa

T/K	C_p^o, $JK^{-1}\cdot mol^{-1}$	$H^\circ(T)-H^\circ(0)$, $kJ\cdot mol^{-1}$	$S^\circ(T)$, $JK^{-1}\cdot mol^{-1}$	$-[G^\circ(T)-H^\circ(0)]$, $kJ\cdot mol^{-1}$
		Crystalline state		
5	0.193	0.0002	0.0457	0.00003
10	1.482	0.0038	0.4899	0.0001
15	4.076	0.0175	1.565	0.0006
20	6.679	0.0442	3.085	0.0174
25	9.677	0.0845	4.870	0.0972
30	12.87	0.1409	6.915	0.0666
40	19.01	0.3013	11.49	0.1585
50	25.05	0.5206	16.36	0.2976
60	28.59	0.7914	21.29	0.4861
70	31.97	1.092	25.92	0.7223
80	35.92	1.432	30.46	1.004
100	43.74	2.224	39.26	1.702
120	58.23	3.235	48.43	2.577
140	70.52	4.530	58.39	3.645
160	79.84	6.036	68.43	4.913
180	88.43	7.720	78.34	6.381
200	92.95	9.546	87.96	8.045
220	95.44	11.43	96.92	9.895
240	98.05	13.37	105.4	11.92
260	100.9	15.36	113.3	14.11
280	103.0	17.40	120.9	16.45
298.15	105.0	19.29	127.4	18.70
330	108.8	22.70	138.3	22.94
347	110.7	24.61	143.9	25.39
		Liquid		
347	140.3	29.59	158.3	25.39
350.0	140.4	29.96	159.3	25.80
360.0	140.6	31.36	163.3	27.42
		Glassy		
10	1.482	0.0038	3.18	0.028
20	6.679	0.0442	5.77	0.071
30	12.87	0.1409	9.61	0.147
40	19.01	0.3002	14.15	0.266

Table 2 Continued

T/K	C_p° JK^{-1}·mol^{-1}	$H^\circ(T)$–$H^\circ(O)$/ kJ· mol^{-1}	$S^\circ(T)$/ JK^{-1}·mol^{-1}	–$G^\circ(T)$–$H^\circ(O)$/ kJ· mol–1
150	75.31	5.259	66.08	4.653
200	92.95	9.546	90.61	8.577
240	98.04	13.37	108.0	12.56
		High-elasticity state		
240	130.9	13.37	108.0	12.56
300	136.2	21.43	137.9	19.96
340	139.7	26.94	155.2	25.83
347	140.3	29.59	158.3	25.40

where D denotes the Debye function for the heat capacity, and n=2 and θ_D=94.4 K are specially chosen parameters. With these parameters, this equation describes the experimental values of the heat capacity for the polymer in the range 11 to 20 K to a precision of about 1%.

Table 3 Experimental values of enthalpy of polypropanal (α=37%) depolymerization and enthalpy of mixing of propanal with acetic acid at T=298.15 K and p=101.325 kPa

P/g	–Q_1/J	$-\Delta H_1^\circ$ / Jg^{-1}	(PP), g	Q_2/J	ΔH_2° / Jg^{-1}
0.0631	3.02	47.8	0.0448	10.5	234
0.047	2.20	46.8	0.0440	10.1	230
0.046	2.18	47.5	0.0442	10.3	234
		$-\Delta H_1^\circ$=47.4			ΔH_2°=232.7

Q_1 is the quantity of energy released on depolymerization of the above amount of the polymer;

ΔH_1° is the specific enthalpy of polypropanal depolymerization in acetic acid;

Q_2 is the quantity of energy absorbed on mixing of the monomer with acetic acid;

ΔH_2° is the specific enthalpy of mixing of the monomer with acetic acid.

In calculation of the functions, it was assumed that at T<11 K the equation reproduces the C_p° values of polypropanal with the same accuracy. The calculation of $H^\circ(T)$–$H^\circ(0)$ and $S^\circ(T)$ were made by numerical integration of the relations C_p°=$f(T)$ and C_p°=$f(\ln T)$ on a computer. In evaluations of C_p° for completely crystalline polypropanal, it was taken into account that below T_g° the heat capacities of amorphous, partially crystalline and crystalline polymers were the same within the errors of C_p^o measurement. The linear extrapolation of $C_p^o=f(T)$ from T_g^o to T_m^o (Fig. 1, curve BK) was believed to reproduce correctly the temperature dependence of C_p^o for polypropanal of 100% crystallinity. Curve ABCN presents, in turn, the relation $C_p^o=f(T)$ for the amorphous polymer. This was explained in detail elsewhere [11].

Zero parameters of the polymer

From the results obtained (Table 2), the difference in the enthalpies of glassy and crystalline polymers at T=0 K was estimated to be $H_{gl}^o(0)$-$H_{cr}^o(0)$= 1.62 kJ/mol, and the entropy of glassy polypropanal was $S_{gl}^o(0)$=2.69 J/(deg·mol) at the same temperature. The calculations were made with the equations [13]

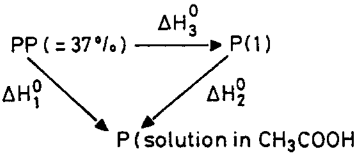
$$H_{gl}^o(0)-H_{cr}^o(0)=\int_0^{T_m}[C_p^o(\text{cr})-C_p^o(\text{a})]\mathrm{d}T+\Delta H_m^o \tag{5}$$

$$\mathrm{d}S_{gl}^o(0)=\int_0^{T_m}[C_p^o(\text{cr})-C_p^o(\text{a})]\,\mathrm{d}\ln T+\Delta S_m^o \tag{6}$$

where C_p^o(cr) and C_p^o(a) are the temperature dependences of the polypropanal heat capacity in the crystalline (cr) and amorphous (a) states; ΔH_m^o is the molar enthalpy of melting for the polymer of 100% crystallinity.

Thermodynamic parameters of propanal polymerization

Table 4 lists the thermodynamic parameters of propanal polymerization obtained from our calorimetric values and the data on the thermodynamic properties of the monomer given earlier [2]. The enthalpy of bulk polymerization of propanal was calculated from calorimetrically measured values of the transitions at T=298.15 K and p=101.325 kPa (Table 3) according to the following scheme:



ΔH_1^o=13.5±0.1 kJ/mol is the enthalpy of depolymerization of PP (α=37%) with the formation of 6% monomer solution in acetic acid; ΔH_2^o=–2.8 ±0.1 kJ/mol is the enthalpy of dissolution of the monomer in acetic acid with formation of the solution of the above concentration; ΔH_3^o=16.3 kJ/mol is the enthalpy of depolymerization of 37% crystallinity polymer with the formation of the pure monomer in the liquid state; this was calculated from the values of ΔH°_1 and ΔH°_2 by using $\Delta H^\circ_3=\Delta H^\circ_1-\Delta H^\circ_2$. Since the enthalpy of polypropanal depolymerization is equal in absolute value, but opposite in sign, to that of propanal polymerization, the enthalpy of monomer polymerization with the formation of polypropanal (α=37%) is ΔH°_{pol} (α=37%)=−16.3± 0.2 kJ/mol. By using the molar enthalpy of melting of the polymer, the enthalpies of bulk polymerization of propanal to form polymers in high elasticity (h.e.) and crystalline (cr) states were estimated:

P(l) PP(h.e.); ΔH°_{pol}(l; h.e.)=−14.4±0.2 kJ/mol

and

P(l) PP(cr); ΔH°_{pol}(l; cr)=−19.4±0.2 kJ/mol.

Both values were calculated at T=298.15 K and p=101.325 kPa.

For other temperatures, the enthalpies of polymerization were calculated from Kirchhoff's expression by using literature data [2] and the values listed in Table 2.

Table 4 Thermodynamic parameters of bulk polymerization of propanal per mole of the monomer at p=101.325 kPa

T/K	Physical state of monomer and polymer [σ]	$-\Delta H^\circ_{pol}$/ kJ· mol^{-1}	$-\Delta S^\circ_{pol}$/ JK^{-1}·mol^{-1}	$-\Delta G^\circ_{pol}$/ kJ· mol^{-1}
0	cr; cr	4.38	0	4.38
	cr; gl	1.26	−2.69	1.26
50	cr; cr	4.43	0.16	4.42
	cr; gl	1.32	−2.49	1.19
100	cr; cr	4.76	8.24	3.94
	cr; gl	1.65	5.59	1.09
150	cr; cr	5.52	12.36	2.43
	cr; gl	2.41	9.70	0.96
200	l; cr	15.34	69.2	1.50
	l; gl	12.23	66.6	−1.08
250	l; cr	17.19	77.6	−2.18
	l; h.e.	13.75	73.5	−4.62
298.15	l; cr	19.4	85.5	−6.09
	l; h.e.	14.4	75.8	−8.2
330	l; cr	20.83	90.0	−8.85
	l; h.e.	14.86	77.2	−10.6

[σ] cr – crystalline; gl – glassy; l – liquid; h.e. – high-elasticity

The entropy of polymerization $\Delta S^{\circ}_{\mathrm{pol}}$ was determined from the absolute magnitudes of the entropies for the monomer and the polymer. The Gibbs function of the process $\Delta G^{\circ}_{\mathrm{pol}}$ was calculated from the enthalpy and entropy values for the process at the corresponding temperature.

It is seen that the enthalpy and the entropy of the process in the temperature range studied are negative. It follows that there is a ceiling limiting temperature of the process. Its evaluation from the intercept of the plots $\Delta H^{\circ}_{\mathrm{pol}}=f(T)$ and $T\cdot\Delta S^{\circ}_{\mathrm{pol}}=f(T)$ gives the values $T^{\circ}=225$ K for the process P(1) →PP(cr) and $T^{\circ}=$ 190 K for the process P(1) →PP(h.e.). An example of graphical determination of $T^{\circ}_{\mathrm{ceil}}$ for the process P(1) →PP(cr) is shown in Fig. 2. The process of spontaneous polymerization of propanal into polypropanal is thermodynamically resolved only at temperatures which are lower than those indicated; at above these temperatures, the depolymerization process occurs. This is confirmed by our examination: on storage at room temperature, the polymer is subject to decomposition into the corresponding monomer. In the course of heating of the polymer during the heat capacity measurement, an active process of its depolymerization starts at 360 K (Fig. 1).

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Zusammenfassung — In einem adiabatischen Vakuum-Kalorimeter wurde zwischen 11 und 330 K und in einem automatischen ADKTTM DSC-Kalorimeter zwischen 320 und 370 K die Wärmekapazität C_p von Polypropanal untersucht. Es wurden auch die thermodynamischen Parameter für Schmelzen und Glasumwandlung von Polypropanal bestimmt. Ausgehend von diesen Ergebnissen wurden für den Temperaturbereich 0 K bis 360 K die thermodynamischen Funktionen des Polymers berechnet. In einem DAK-1-1 automatischen Differential-Mikrokalorimeter wurde die Enthalpie der Depolymerisierung zum Ausgangsmonomer gemessen. Anhand dieser Ergebnisse und Angaben in der Literatur über die thermodynamischen Eigenschaften von Polypropanal wurde die Enthalpie-, die Entropie- und die Gibbsche Funktion der Massepolimerisation von Propanal für den Bereich 0 K bis 330 K geschätzt. Weiterhin wurden die Maximumtemperaturen der Umwandlung des flüssigen Monomers in ein kristallines und hochelastisches Polymer ermittelt.