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CALORIMETRIC STUDY OF THERMODYNAMICS OF PRODUCTION OF POLYBUTENE-1, POLYPENTENE-1, 4-METHYLPENTENE-1 AND PROPERTIES OF REAGENTS BETWEEN 0 AND 670 K

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Abstract

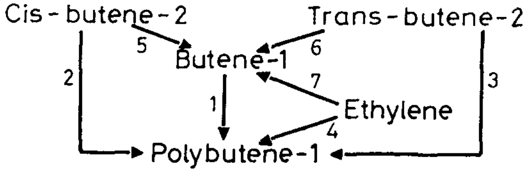
The heat capacities C_p° of polybutene-1, polypentene-1, poly-4-methylpentene-1 and 4-methylpentene-1 were studied calorimetrically from 6 to (500–700) K. Temperatures, enthalpies of melting of various crystalline forms and the parameters of the glass transition were determined. The thermodynamic functions $H^\circ(T)-H^\circ(0)$, $S^\circ(T)$ and $G^\circ(T)-H^\circ(0)$ were calculated between 0 K and (500–700) K. From the calorimetric values obtained and literature data, the thermodynamic characteristics of the following processes were estimated for the corresponding alkenes-1, and *cis*- and *trans*-alkenes-2: the polymerization of alkenes-1, the monomer-isomerization polymerization of *cis*- and *trans*-alkenes-2 to polyalkenes-1 and the isomerization of *cis*- and *trans*-alkenes-2 to alkenes-1 in the same temperature interval at standard pressure.

Keywords: alkenes, isomerization, polymerization, thermodynamic parameters

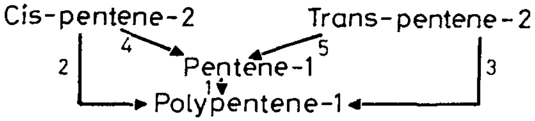
Introduction

From precise calorimetric measurements, the thermodynamic parameters of the reactions leading to the formation of polybutene-1 (scheme A), polypentene-1 (scheme B) and poly-4-methylpentene-1 (scheme C) were obtained.

Scheme A:



Scheme B:



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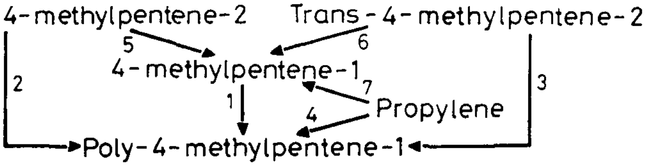
Scheme C:



For all the processes illustrated in schemes A, B and C, the thermodynamic parameters were determined in the temperature range between 0 K and 500–700 K. They are given in Table 1 for $T = 298.15$ K and standard pressure.

Experimental

The enthalpies of reactions (ΔH°) were calculated from the enthalpies of formation of the reagents ΔH_f°. For the monomer compounds, they were taken from [1]; for the polymers, the enthalpies were estimated from the enthalpies of combustion ΔH°_{comb}, which in turn were determined from the energies of combustion ΔU_{comb} measured in an isothermal bomb calorimeter. The energetic equivalent of the calorimeter was obtained from the ΔU_{comb} data on standard benzoic acid. The operational reliability of the calorimeter was checked by the measurement of ΔU_{comb} for standard succinic acid. The difference between our values of ΔU_{comb} from the certificated ones was not more than 0.017%. All measurements and calculations of ΔH° were made at $T = 298.15$ K and $p = 101.325$ kPa. At other temperatures, the enthalpies for the processes were calculated via Kirchhoff's equation; for this purpose, the temperature dependences of heat capacity, temperatures and enthalpies of physical transitions of reagents were used.

The entropies of reactions (ΔS°) were estimated from absolute values of reagent entropies, which were obtained from the data on the temperature dependence of heat capacity, temperatures and enthalpies of physical transitions for the substances participating in the reactions. The heat capacity from 5 to 330 K was measured in a vacuum adiabatic calorimeter, and between 220 and 670 K in a differential scanning calorimeter operating on the principle of a triple thermal bridge. The measurement error of heat capacities in the vacuum adiabatic calorimeter was about ±0.2%, and in the dynamic one from 0.5 to 2%. The Gibbs functions for the processes (ΔG°) were calculated from the enthalpies and entropies of the reagents for the processes.

Results and discussion

All polymerization processes studied have ceiling temperatures T°_{ceil} since their ΔH° and ΔS° values are negative. The T°_{ceil} data were found from the intersection points of the plots $\Delta H^\circ = f(T)$ and $T\Delta S^\circ = f(T)$. For processes A-1, A-2 and A-3, T°_{ceil} was 520, 500 and 490 K; for B-1, B-2 and B-3, 590, 560 and 550 K; and for C-1, C-2 and C-3, 590, 540 and 530 K, respectively.

The isomerization processes A-5, A-6, B-4, B-5, C-5 and C-6 have no ceiling and lower limiting temperatures, which is characteristic of processes for which $\Delta H^\circ > 0$ and $\Delta S^\circ > 0$. Accordingly, such processes have $\Delta G^\circ > 0$. For the above processes, ΔG° has small positive values: $\Delta G^\circ < 10\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$. This means that, in an equilibrium reaction mixture of isomers, the isomers with a C=C bond in position 1 are present only in small quantity. It follows that, for the transformations of *cis*- and *trans*-isomers-2 to polybutene-1, polypentene-1 and poly-4-methylpentene-1 through isomerization to the corresponding isomers with a C=C bond in position 1, it is necessary to remove butene-1, pentene-1 and 4-methylpentene-1 effectively from the reaction mixture, e.g. by their rapid polymerization.

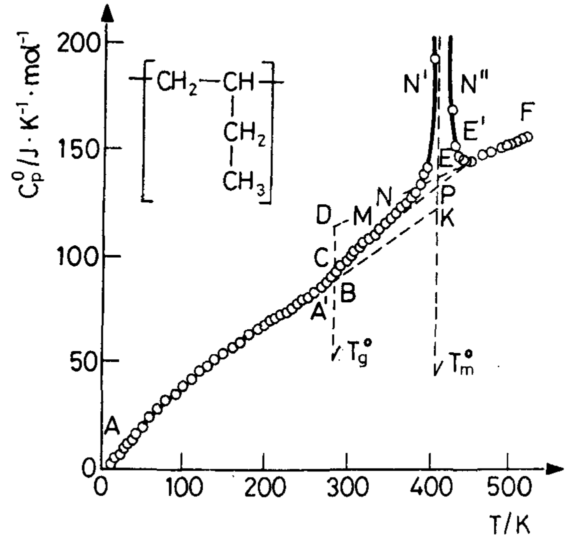


Fig. 1 Heat capacities of isotactic polybutene-1: ABK is for crystalline polymer, DE – high-elastic [2], EF – liquid, AA'B – partially crystalline (crystals of form I, α = 77%, amorphous fraction of the polymer in glassy state), CMNP – partially crystalline with amorphous portion in high-elastic state, NN'N''E' is apparent heat capacity in the melting region

By taking the value ΔG° for the polymerization, it is easy to calculate the thermodynamic equilibrium monomer concentration $[M]^\circ_e$ in the reaction mixture from the equation:

$$[M]^\circ_e = \exp(\Delta G^\circ / RT)$$

Table 1 Enthalpies ΔH°, entropies ΔS° and Gibbs functions ΔG° for the processes at T = 298.15 K and p = 101.325 kPa

No.	Process			$-\Delta H^\circ$ / kJ·mol^{-1}	$-\Delta S^\circ$ / J·mol^{-1}·K^{-1}	$-\Delta G^\circ$ / kJ·mol^{-1}
A–1	Butene-1(g)	→	polybutene-1(h.e.)	103	196	44.3
	Butene-1(g)	→	polybutene-1(crl)	108	207	45.8
A–2	*cis*-Butene-2(g)	→	polybutene-1(h.e.)	96	190	39.0
A–3	*trans*-Butene-2(g)	→	polybutene-1(h.e.)	92	184	37.0
A–4	Ethylene(g)	→	polybutene-1(h.e.)	207	325	110
A–5	*cis*-Butene-2(g)	→	butene-1(g)	– 6.9	– 6.0	–5.1
A–6	*trans*-Butene-2(g)	→	butene-1(g)	–11	–12	–7.4
A–7	Ethylene(g)	→	butene-1(g)	105	129	66
B–1	Pentene-1(l)	→	polypentene-1(h.e.)	95	124	58
B–2	*cis*-Pentene-2(l)	→	polypentene-1(h.e.)	87	120	51
B–3	*trans*-Pentene-2(l)	→	polypentene-1(h.e.)	83	118	48
B–4	*cis*-Pentene-2(l)	→	pentene-1(l)	– 8.5	– 3.8	– 7.4
B–5	*trans*-Pentene-2(l)	→	pentene-1(l)	–12.1	– 6.0	–10.3
C–1	4-Methylpentene-1(l)	→	poly-4-methylpentene-1(gl)	95	131	56
C–2	*cis*-4-Methylpentene-2(l)	→	poly-4-methylpentene-1(gl)	88	134	48
C–3	*trans*-4-Methylpentene-2(l)	→	poly-4-methylpentene-1(gl)	83	130	45

Table 1 Continued

No.	Process			$-\Delta H^\circ$/ kJ·mol^{-1}	$-\Delta S^\circ$/ J·mol^{-1}·K^{-1}	$-\Delta G^\circ$/ kJ·mol^{-1}
C–4	Propylene(g)	→	poly-4-methylpentene-1(gl)	216	381	102
C–5	*cis*-4-Methylpentene-2(l)	→	4-methylpentene-1(l)	– 7	3	– 8
C–6	*trans*-4-Methylpentene-2(l)	→	4-methylpentene-1(l)	–12	1	–12
C–7	Propylene(g)	→	4-methylpentene-1(l)	121	250	46

In brackets the physical states of the reagents are given: g – gaseous, cr – crystalline, gl – glassy, l – liquid, h.e. – high-elastic; the polymers are isotactic

Table 2 Thermodynamic parameters of glass transition and glassy state of the compounds*, p =101.325 kPa

Compound	T_g° /	$\Delta C_p^\circ(T_g^\circ)$/	S_{conf}° /	S_{gl}° /	$H_{gl}^\circ(0)-H_{cr}^\circ(0)$ /
	K		J·mol^{-1}·K^{-1}		kJ·mol^{-1}
Polybutene-1	249±1	27.5	7.0	6.7	3.71
Polypentene-1	238±1	21.3	3.5	3.8	2.48
Poly-4-methylpentene-1	300±1	61.0	–	0	2.7
4-Methylpentene-1	80.5±0.5	68.0	17.8	14.8	2.5

*T_g° – glass transition temperature, $\Delta C_p^\circ(T_g^\circ)$ – the increase in the heat capacity on the devitrification of amorphous polymer at T_g°, e.g. section BD in Fig. 1. S_{conf}° and S_{gl}° are configurational and zero entropies of glass, $H_{gl}^\circ(0)-H_{cr}^\circ(0)$ is the difference of zero enthalpies of glass and crystal at 0 K.

All the polymers are isotactic, their degree of isotacticity being about 95%, and the crystallinity degree is 65, 60 and 35–40% for polybutene-1, polypentene-1 and poly-4-methylpentene-1, respectively.

As a typical temperature dependence of the heat capacity for the studied polymers, Fig. 1 shows the relation $C_p^\circ = f(T)$ for polybutene-1. Tables 2 and 3 give the thermodynamic parameters of the physical transitions of the substances.

Table 3 Thermodynamic parameters of melting of the compounds*, p = 101.325 kPa

Compound	T_m° / K	ΔH_m° / kJ·mol^{-1}	ΔS_m° / J·mol^{-1}·K^{-1}	$\Delta C_p^\circ(T_m^\circ)$ / J·mol^{-1}·K^{-1}
Polybutene-1, form III	374	10.68	26.8	–
Polybutene-1, form II	393	3.68	9.36	–
Polybutene-1, form I	406.8	7.11	17.5	–
Polypentene-1	388	5.58	14.4	16.1
Poly-4-methylpentene-1	508	9.93	19.5	11.5
4-Methylpentene-1	118.90±0.05	4.93±0.17	41.5±1.4	45.6±0.5

* T_m°, ΔH_m°, ΔS_m° – temperature, enthalpy and entropy of melting, respectively; $\Delta C_p^\circ(T_p^\circ)$ – a jump of heat capacity at T_m°, e.g. KE in Fig. 1.

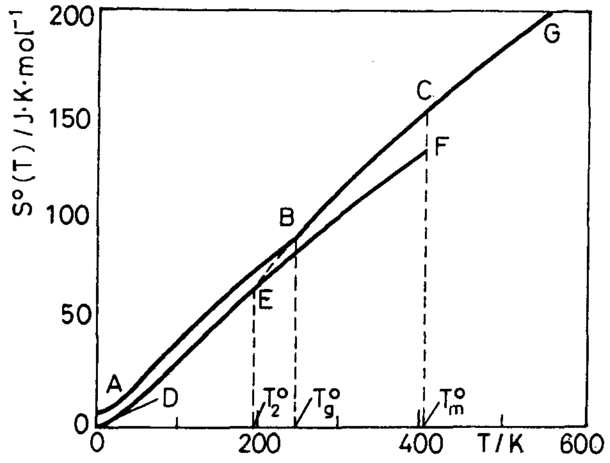


Fig. 2 Entropy diagram of polybutene-1: DF is entropy of crystal, AB – of glass, BC – of high-elastic state, CG – of liquid

From the experimental data, the thermodynamic functions $H^\circ(T)-H^\circ(0)$, $S^\circ(T)$ and $G^\circ(T)-H^\circ(0)$ were calculated from 0 K to (500–670) K. Entropy diagrams were constructed for the polymers and 4-methylpentene-1. The entropy diagram for polybutene-1 (Fig. 2) is given as an example.

The details of the experiments and calculations were reported earlier [3].

References

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Zusammenfassung — Kalorimetrisch wurden im Temperaturintervall von 6 bis (500–700) K die Wärmekapazitäten C_p^o von Polybuten-1, Polypenten-1, Poly-4-methylpenten-1 und 4-Methylpenten-1 untersucht. Dabei wurde die Schmelztemperatur, die Schmelzenthalpie verschiedener kristalliner Formen und die Parameter für die Glasumwandlung bestimmt. Für die Temperatur von 0 bis (500-700) K wurden die thermodynamischen Funktionen $H^o(T)$-$H^o(0)$, $S^o(T)$ und $G^o(T)$–$H^o(0)$ errechnet. Anhand der erhaltenen kalorimetrischen Werte und der Literaturangaben wurden die thermodynamischen Charakteristika der nachstehenden Prozesse für die entsprechenden Alken-1 sowie *cis*- und *trans*-Alken-2 Verbindungen geschätzt: Polymerisierung von Alken-1, Monomerisomerisations-Polymerisierung von *cis*- und *trans*-Alken-2 zu Polyalken-1 und die Isomerisation von *cis*- und *trans*-Alken-2 zu Alken-1 im selben Temperaturintervall unter Standarddruck.