Thermodynamics of the reaction between poly-1,1,2-trichlorobuta-1,3-diene and poly(ethylene imine) to form interpolymer

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Thermodynamic parameters of the interpolymer reaction between poly-1,1,2-trichlorobuta-1,3-diene and poly(ethylene imine) giving a polymer-polymer compound (incorporating the starting components in a molar ratio of 1 : 2) have been determined by calorimetry. The enthalpy (ΔH°_m), entropy (ΔS°_m), and Gibbs function (ΔG°_m) for this reaction are negative over the whole temperature range studied. The enthalpy of the reaction in chloroform at 298.15 K is about two times smaller, due to the difference in the enthalpies of dissolution of the starting polymers and the enthalpy of swelling of the interpolymer in the same solvent. The glass transition temperature of the interpolymer lies between those of the starting polymers and coincides with the value calculated from the Fox equation. The heat capacity of the interpolymer is smaller than additive values calculated from C_p° of the starting polymers. From the experimentally determined C_p° for the polymers, the thermodynamic functions $C_p^\circ(T)$, $H^\circ(T) - H^\circ(0)$, and $S^\circ(T)$ were calculated for the 0—330 K temperature range, and their configurational entropies S_c° were estimated.

Key words: interpolymer; enthalpy, entropy, Gibbs free energy; enthalpy of dissolution and swelling; glass transition temperature; calorimeter.

Interaction of macromolecules to give polymer—polymer compounds (interpolymers) is possible in those cases where chemical or hydrogen bonds arise between them or where they form charge transfer complexes.[1—4] In previous studies,[4—8] thermodynamic parameters of some reactions yielding interpolymers due to intermolecular hydrogen bonds have been studied; and general and specific features of the thermodynamics of interpolymer reactions of this type have been identified and formulated.

However, thermodynamic parameters of the interpolymer reactions in which interpolymers are formed through chemical bonds between macromolecules have not been studied. No data on the thermodynamic properties of the corresponding interpolymers or on the relationship between these properties and the properties of the initial polymers have been published. In the present work, to take the first step in the investigation of the thermodynamics of interpolymers of this type, we studied by calorimetry thermodynamic parameters of the reaction between poly-1,1,2-trichlorobuta-1,3-diene (PTCB) and poly(ethylene imine) (PEI) and thermodynamic properties of the resulting interpolymer PTCB · 2 PEI (IP) and of the starting polymers in the 5—330 K range under a standard pressure. In particular, temperature dependences of heat capacity C_p° were studied, and temperatures and enthalpies of physical transformations of the polymers were measured; the enthalpies of the reaction PTCB + 2 PEI → PTCB · 2 PEI in chloroform, the enthalpies of dissolution of PTCB and PEI, and the enthalpy of swelling of IP in the same solvent at $T = 298.15$ K were measured. The results obtained were used to calculate the thermodynamic functions $C_p^\circ(T)$, $H^\circ(T) - H^\circ(0)$, and $S^\circ(T)$ for the 0—330 K range as well as the standard thermochemical parameters, *i.e.*, enthalpies ($\Delta_f H^\circ_m$), entropies ($\Delta_f S^\circ_m$), and free Gibbs energies ($\Delta_f G^\circ_m$) for the interpolymer reaction carried out without a solvent in the same temperature range.

Experimental

PTCB was prepared from the corresponding monomer by the procedure described in a previous paper.[9] To keep PEI (commercial sample) away from moisture, it was stored in a vacuum desiccator over P_2O_5. The procedure for the preparation of IP was described in a known paper.[10] The initial PTCB and PEI were introduced into the reaction in a stoichiometric molar ratio of 33 : 67%. The reaction was carried out in a 2% solution in chloroform at room temperature for 72 h. The

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Table 1. Main characteristics of the studied polymers

Polymer	$\bar{M}_w$	M*/g mol^{-1}	$\frac{\text{Found}}{\text{Calculated}}$ (%)			
			C	H	N	Cl
Poly-1,1,2-trichlorobuta-1,3-diene (PTCB)	$6 \cdot 10^4$	157.427	31.10 30.51	2.03 1.92	— —	66.76 65.57
Poly(ethylene imine) (PEI)	$1 \cdot 10^4$	43.070	55.75 55.79	11.67 11.70	31.48 32.51	— —
Interpolymer (IP) or PTCB·2PEI	—	243.563	38.87** 39.40	5.07 5.37	11.06 11.49	45.00 43.74

* The weight of the repeating monomeric unit. ** Found from the difference between the precise weight of a sample and the weights of Cl, N, and H that it includes.

resulting black insoluble precipitate was filtered off, washed with chloroform, and dried *in vacuo* to a constant weight. The weight of the IP formed was ~96% of the sum of the weights of PTCB and PEI taken for the reaction. The composition of the IP obtained corresponded to the PTCB and PEI repeating units being present in a molar ratio of 1 : 2. The main characteristics of the polymers studied are listed in Table 1. The viscosity-average molecular weight of PTCB was determined from the viscosities of its solutions in chloroform at 298 K, and that of PEI was found from the viscosity of solutions in anhydrous ethanol at 293 K.

The temperature dependences of heat capacity and the temperatures and enthalpies of physical transformations were studied using a TAU-1 thermal setup, which is an adiabatic vacuum calorimeter. The design of the calorimeter and the procedures for measurements were described previously.[11] The calibration and check of the setup showed that the error of the measurements of the heat capacities of substances at temperatures close to that of liquid helium is ±2%; when the temperature increases to 40 K, the error decreases to 0.5%, and in the 40—340 K range,[12] it does not exceed 0.2%. The enthalpy of the reaction and the enthalpies of dissolution and swelling of IP were studied using a DAK-1-1A differential automatic microcalorimeter,[13] operating under isothermal conditions in the 300—470 K range. The lowest measurable power was 10^{-6} W and the maximum power was 0.3 W. The sensitivity of the measuring scheme was 0.17 V/W. The error of individual calorimetric measurements was 4%, and the error of the average result, expressed as a confidence region of 95%, does not exceed 2%.

The heat capacity of IP was measured in the 4.5—336 K temperature range, that of PTCB was determined in the 4.4—333.5 K temperature range, and that of PEI was measured at 13.8—339 K.[14] The weights of the polymer samples placed in the calorimeter were $0.5495 \cdot 10^{-3}$, $0.3850 \cdot 10^{-3}$, and $9.9762 \cdot 10^{-3}$ kg, respectively. For IP, 173 experimental C_p° values were obtained in 18 series corresponding to successive measurements of heat capacity; in the case of PTCB, 150 values were obtained in 17 series of experiments, and in the case of PEI, 132 values were found in 10 series. Heat capacity of the polymer samples was 35 to 60% of the overall heat capacity of the calorimetric ampule with the substance. The C_p° points obtained experimentally were averaged using a computer. The root-mean-square deviation of the C_p° values from the corresponding averaging curves $C_p^\circ = f(T)$ did not exceed 0.4% in the 5—90 K temperature range or 0.2—0.3%; in the 90—330 K range. All the experimental C_p° points and averaging curves are shown in Fig. 1.

To measure enthalpies, the polymers under study were placed into sealed thin-wall glass ampules, which were then broken in a solvent (chloroform) in a calorimetric tube[15] (Fig. 2). The yield of the interpolymer was ~100% in all runs.

Results and Discussion

In the temperature range studied, IP, PTCB, and PEI exist only in the glassy and highly elastic states. Glass transition is clearly manifested on the $C_p^\circ = f(T)$ curves (see Fig. 1) as the *LN*, *GJ*, and *BD* sections on the curves. A virtually linear $C_p^\circ = f(T)$ plot typical of chain polymers is observed in the 70—200 K temperature range for PEI, in the 100—250 K range for PTCB,

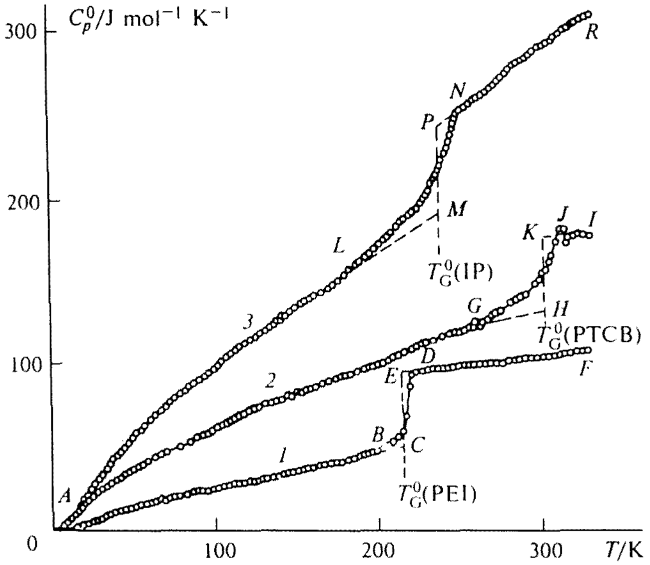

Fig. 1. Temperature dependences of the heat capacity of PEI (*1*) in the glassy state (*AC*), in the highly elastic state (*EF*), and in the range of glass transition (*BD*); that for PTCB (*2*): in the glassy state (*AH*), in the highly elastic state (*KI*), and in the range of glass transition (*GJ*); that for the interpolymer PTCB · 2PEI (*3*): in the glassy state (*AM*), in the highly elastic state (*PR*), and in the range of glass transition (*LN*).

Table 2. Results of the measurements of the enthalpies of the interpolymer reaction, of the dissolution of the initial polymers, and of the swelling of the resulting interpolymer in chloroform at T = 298.15 K

Process*	The number of runs	Concentration of the polymer, C (%, w/w)	Enthalpy/kJ mol^{-1}	
			$\Delta H = f(C)$	C = 2% (w/w)
PTCB(s) + 2PEI(s) → IP(s)	9	0.32—2.53*	$-\Delta H_p{}^\circ$ = 3.22÷4.47	4.44
PTCB(g) →PTCB(s)	9	0.13—2.20	$-\Delta H_1{}^\circ$ = 0.61÷0.84	0.60
PEI(h.e.) →PEI(s)	10	0.36—3.22	$-\Delta H_2{}^\circ$ = 2.18÷5.77	2.80
IP(g) →IP(s.s.)	8	0.32—2.91	$-\Delta H_3{}^\circ$ = 3.31÷3.41	3.24

Note. The letters given in parentheses denote the physical states of the reactants: s, in solution; g, in the glassy state; h.e., in the highly elastic state; s.s., swelled in solution. * The total amount of the reacting polymers taken in a molar ratio of 33 : 67 is given.

and at 100—170 K for IP.[16] The heat capacities of the polymers increase smoothly as the temperature increases. The parameters of glass transition and glassy state are presented in Table 3. The temperatures of the beginning ($T^\circ_{G,0}$) and the end ($T^\circ_G{}'$) of devitrification were found graphically (for example, for IP, these are points L and N in Fig. 1), while glass transition temperatures T°_G were found from the plots of the temperature dependence of the entropy of polymers (see Ref. 17). The increase in the heat capacity during devitrification $\Delta C^\circ_p(T^\circ_G)$ was also determined from plots, namely, by extrapolating the normal course of the heat capacity curves at $T < T^\circ_G$ and $T > T^\circ_G$ up to T°_G. For example, in the case of IP, $\Delta C^\circ_p(T^\circ_G)$ is represented by section PM (see Fig. 1) resulting from extrapolation of curves AL and NR to T°_G. The configurational entropies S°_c of the polymers were estimated based on the $\Delta C^\circ_p(T^\circ_G)$ values using the formula[18]

$$S^\circ_c = \Delta C^\circ_p(T^\circ_G)\ln 1.29, \qquad (1)$$

where 1.29 is a constant found as the ratio of the glass transition temperature $T_G{}^\circ$ to the Kautsman temperature $T_2{}^\circ$.

To calculate thermodynamic functions (Table 4), the temperature dependences of heat capacities of the polymers were extrapolated from the temperature at which the measurement of $C_p{}^\circ$ began to 0 K, according to the Debye function

$$C^\circ_p = nD(\theta_D/T), \qquad (2)$$

where D is the Debye heat capacity function, and n and θ_D are specially selected parameters. For IP and PTCB, $n = 2$ and θ_D = 54.19 and 57.75 K, respectively; for PEI, n = 1.1 and θ_D = 95.10 K. Equation (2) describes the values measured for IP in the 6—9 K temperature range, those measured for PTCB in the 8—12 K range, and the values measured for PEI in the 14—20 K range with an error not exceeding 2%. In the calculations of the functions, we assumed that between the temperature of the beginning of the measurements and 0 K, this equation makes it possible to determine heat capacity with approximately the same accuracy. The $C^\circ_p(T)$ values listed in Table 4 correspond to the $C^\circ_p = f(T)$ plot (see Fig. 1). The enthalpy $H^\circ(T) - H(0)$ and the entropy $S^\circ(T)$ were calculated from Eqs. (3) and (4):

Table 3. Glass transition parameters and glassy-state characteristics of PTCB, PEI, and PTCB · 2 PEI under standard pressure

Polymer	$T^\circ_{G,0} - T^\circ_G{}'$	T°_G	ΔC°_p (T°_G)	S°_c
	K		J mol^{-1} K^{-1}	
PTCB	250—320	304±1	44.0	11
PEI	200—230	216±1	46.9	12
PTCB · 2 PEI	170—260	240±1	63.7	16

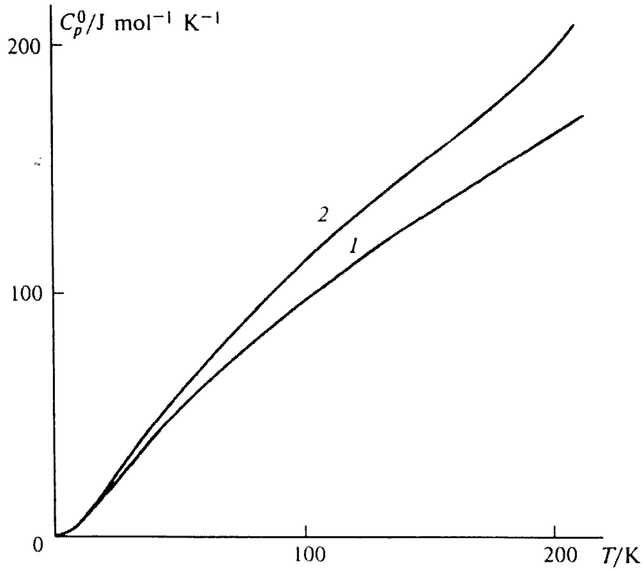

Fig. 2. Temperature dependences of the heat capacity of the interpolymer PTCB · 2 PEI (*1*) and of the PTCB + 2 PEI additive mixture (*2*).

Table 4. Thermodynamic functions of PTCB, PEI, and PTCB · 2 PEI under standard pressure

T/K	$C_p°(T)$	$S°(T)$	$H°(T) - H°(0)$	$C_p°(T)$	$S°(T)$	$H°(T) - H°(0)$	$C_p°(T)$	$S°(T)$	$H°(T) - H°(0)$
	/J mol^{-1} K^{-1}		/kJ mol^{-1}	/J mol^{-1} K^{-1}		/kJ mol^{-1}	/J mol^{-1} K^{-1}		/kJ mol^{-1}
	PTCB (157.427 g mol^{-1})			PEI (43.068 g mol^{-1})			PTCB · 2 PEI (243.563 g mol^{-1})		
0	0	11	0	0	12	0	0	16	0
100	60.84	74	3.322	25.85	34	1.273	119.3	128	6.200
200	99.95	130	11.52	$\underline{49.58}$	$\underline{59}$	$\underline{4.952}$	$\underline{201.7}$	$\underline{237}$	$\underline{22.40}$
298.15	$\underline{133.5}$	$\underline{176}$	$\underline{22.98}$	106.0	95	14.02	355.5	347	50.03
330*	179.4	193	28.43	109.9	106	17.46	381.3	385	61.77

* The values above the dash refer to glassy polymers, those below the dash refer to the polymers in the highly elastic state.

$$H°(T) - H(0) = \int_0^T C_p°(T)\mathrm{d}T\,, \qquad (3)$$

$$S°(T) = S°(0) + \int_0^T C_p°(T)\mathrm{d}\ln T\,, \qquad (4)$$

where $C_p°(T)$ are temperature dependences of heat capacity of the polymers and $S°(0)$ are their zero-point (residual) entropies, which were taken to be equal to $S_c°$ in the calculations of the absolute values of the entropy $S°(T)$ (see Ref. 18).

Comparison of the properties of IP with those of the initial PTCB and PEI indicates that the temperature range of the $C_p° \sim T^1$ dependence for IP is about half those for PTCB and PEI, which is probably due to the fact that IP contains elements of both planar and three-dimensional structures, which, according to a previous paper,[16] are characterized by $C_p° \sim T^2$ and $C_p° \sim T^3$ dependences, respectively. The heat capacity of IP is lower than that of the corresponding mixture of PTCB and PEI having the same composition (see Fig. 2). This difference between the heat capacities increases to 25% as the temperature changes from 10 to 330 K. This is due to the fact that the contribution of the frequencies of deformation vibrations of the PTCB and PEI linear macromolecules to heat capacity decreases, since the number of these vibrations decreases markedly when these linear molecules are bound into IP. The glass transition temperature of IP lies between those of the initial PTCB and PEI (see Table 3), which is typical of systems consisting of thermodynamically compatible polymers (copolymers) or polymer mixtures.[19] The position of $T_G°$ for these systems is determined by the glass transition temperatures of the initial polymers $T_{G,1}°$ and $T_{G,2}°$ and by their weight fractions W_1 and W_2. The dependence for $T_G°$ is described adequately by the Fox[20] (5) and Gordon[21] (6) equations:

$$\frac{1}{T_G°} = \frac{W_1}{T_{G,1}°} + \frac{W_2}{T_{G,2}°}, \qquad (5)$$

$$T_G^{\circ} = \frac{W_1 \cdot T_{G,1}^{\circ} + W_2 \cdot T_{G,2}^{\circ} \cdot (\Delta C_p{}^{\circ}(T_{G,2}^{\circ} / \Delta C_p{}^{\circ}(T_{G,1}^{\circ}))}{W_1 + (\Delta C_p{}^{\circ}(T_{G,2}^{\circ} / \Delta C_p{}^{\circ}(T_{G,1}^{\circ}))}, \qquad (6)$$

where $\Delta C_p°(T_{G,1}°)$ and $\Delta C_p°(T_{G,2}°)$ are the changes in heat capacities upon the devitrification of the polymers.

If we substitute the mole fractions of PTCB ($W_1 = 0.35$) and of PEI ($W_2 = 0.65$), corresponding to the composition of IP, instead of the weight fractions of the polymers, into Eqs. (5) and (6) and the corresponding $\Delta C_p°(T_G°)$ values (see Table 3) into Eq. (6), we obtain $T_G° = 239$ and 243 K. These values are quite close to the value of 240±1 K found experimentally (see Table 3). The $\Delta C_p°(T_G°)$ values for the polymers are related to the energy of excitation of the motion of segments of macromolecules during devitrification. It can be seen from Table 3 that $\Delta C_p°(T_G°) = 137.8$ J mol^{-1} K^{-1} for an additive mixture of PTCB and PEI corresponding to the stoichiometry of IP, whereas the actual $\Delta C_p°(T_G°)$ value for IP is 63.7 J mol^{-1} K^{-1}. The difference between these values characterizes the loss of segmential motion caused by binding PTCB and PEI into IP, which is also matched by a ~20 J mol^{-1} K^{-1} decrease in the configurational entropy.

Thermodynamic parameters of the interpolymer reaction in the bulk (m) are given in Table 5

$$\text{PTCB} + 2\text{PEI} \rightarrow \text{PTCB} \cdot 2\,\text{PEI (IP)}$$

Table 5. Thermodynamic functions for the formation of interpolymer in the reaction between PTCB and PEI in a molar ratio of repeating units of 1 : 2 under standard pressure

T/K	Reagents, PI*	$-\Delta S_m°$ /kJ mol^{-1} K^{-1}	$-\Delta H_m°$	$-\Delta G_m°$
			/kJ mol^{-1}	
0	g,g; g	19	6.4	6.4
100	g,g; g	15	6.1	4.6
200	g,g; g	10	5.4	3.4
298.15	g,h.e.; h.e.	19	7.4	1.7
330	h.e.,h.e.; h.e.	20	8.0	1.4

* Physical state of the reactants: g, glassy; h.e., highly elastic.

The enthalpy of the reaction $\Delta H_m{}^\circ$ at $T = 298.15$ K under standard pressure was calculated from experimental data (see Table 2) using the following cycle of transformations:

$$\begin{tikzcd}
\text{PTCB(G)} \arrow[d, "\Delta H_1^\circ"] & + 2\ \text{PEI (h.e.)} \arrow[r, "\Delta H_m^\circ"] \arrow[d, "\Delta H_2^\circ"] & \text{ИП (h.e.)} \arrow[d, "\Delta H_3^\circ"] \\
\text{PTCB(s)} & + 2\ \text{PEI (s)} \arrow[r, "\Delta H_p^\circ"] & \text{IP (s.s.)}
\end{tikzcd}$$

According to the equation of the first principle of thermodynamics

$$\oint \mathrm{d}H \equiv 0 . \tag{7}$$

As applied to this particular case, Eq. (7) can be represented as follows:

$$\Delta H_1{}^\circ + 2\ \Delta H_2 + \Delta H_p - \Delta H_m = 0. \tag{8}$$

If we solve Eq. (8) for ΔH_m and substitute the numerical values into it, we obtain $\Delta H_1 = -7.5$ kJ mol^{-1}. The enthalphies for other temperatures were calculated using the Kirchhoff formula

$$\Delta H_m{}^\circ(T) = \Delta H_m(298.15\ \text{K}) + \int_{298.15\text{K}}^{T} \Delta C_p{}^\circ(T)\mathrm{d}T , \tag{9}$$

where $\Delta C_p{}^\circ(T)$ are temperature dependences for the difference between the heat capacity of IP and those of the initial PTCB and PEI (the heat capacities of the reactants are given in Table 4). The entropy of the process $\Delta S_m{}^\circ(T)$ was calculated from the absolute entropies of the reactants, and the Gibbs free energy $\Delta G_m{}^\circ(T)$ was found from the enthalpy and entropy according to Eq. (10)

$$\Delta G_m{}^\circ(T) = \Delta H_m{}^\circ(T) - T\cdot \Delta S_m{}^\circ(T). \tag{10}$$

The calculations led to negative values of all the thermodynamic parameters. As the temperature increases, the absolute values of ΔH_m° and ΔS_m° increase, because the $\Delta C_m^\circ(T)$ values are negative, whereas the values of ΔG_m° decrease. In general, the manner in which thermodynamic parameters of the interpolymer reaction considered vary as functions of the temperature is similar to that observed for additive polymerization at multiple bonds or involving opening of strained rings.[22]

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