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Thermodynamics of Polymerization Involving a Gaseous Monomer-Condensed Polymer Equilibrium

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ABSTRACT: The thermodynamics of polymerization involving an equilibrium between gaseous monomer and active polymer in the "solid" state is reconsidered taking into account the fact that under equilibrium conditions the polymer is not a pure component. A sizable amount of liquid monomer which forms a nonideal mixture with the polymer is then present and its activity is expressed through the Flory–Huggins treatment. An expression for $\Delta G°_{gc}$, the free enthalpy change upon the conversion of 1 mol of gaseous monomer at 1 atm to 1 base mol of pure amorphous polymer, is written in terms of the equilibrium vapor pressure of the monomer and its volume fraction in the condensed phase. This expression is applied to the published data for the polymerizations of dioxolane and tetrahydrofuran. The results are compared with the value of $\Delta G°_{gc}$, $\Delta H°_{gc}$, and $\Delta S°_{gc}$ computed from the free enthalpy of vaporization of the pure monomers and from ΔG_{lc}, the free enthalpy change upon the conversion of 1 mol of pure liquid monomer into 1 base mol of pure amorphous polymer. A good agreement is found in the case of dioxolane whereas the corrections to be applied to the tetrahydrofuran system are discussed.

In a certain number of equilibrium polymerizations it is found that an equilibrium is established between the monomer in the gaseous state and the active polymer in the condensed state. In the classical thermodynamic treatment of such polymerization systems, the gaseous monomer is considered to be in equilibrium with the pure amorphous polymer, which is simply termed "solid" polymer. The activity of the "solid" polymer is set equal to the activity of the gaseous monomer and this leads to the simple relationship:

$$\Delta G°_{gc} = RT \ln p \qquad (1)$$

where $\Delta G°_{gc}$ is the free enthalpy change upon the conversion of 1 mol of gaseous monomer at a pressure of 1 atm (101.325 kPa) into 1 base mol of pure amorphous polymer, p is the vapor pressure of the monomer under equilibrium conditions, and R and T are the gas constant and the temperature, respectively.

However, in many cases the gaseous monomer is in fact in equilibrium with a mixture of monomer and active polymer. Under these conditions the term "solid" polymer becomes inappropriate and the more general term "condensed" polymer or polymer in the condensed state, which applies to polymer in a liquid mixture as well as to pure amorphous polymer, is used in this paper. Since the proportion of monomer in the condensed phase can be large, the thermodynamics of such equilibria ought to be reexamined accordingly.

Theory

In an equilibrium between gaseous monomer and active polymer in the condensed state, the transformation of 1 mol of gaseous monomer at a pressure p into 1 base mol of polymer in a solution made of monomer and polymer takes place. This process may be considered as the sum of the three following steps:

$$\text{monomer (g, }p) \rightarrow \text{monomer (g, 1 atm)} \rightarrow \text{polymer (amorphous)} \rightarrow \text{polymer (solution)}$$

A free enthalpy term can be associated with each of these steps and the sum of these is equal to zero under equilibrium conditions:

$$\Delta G_g + \Delta G°_{gc} + \overline{\Delta G_p}/n = 0 \qquad (2)$$

ΔG_g is the free enthalpy change when the pressure of 1 mol of gaseous monomer is changed from p to 1 atm and, assuming an ideal behavior, is expressed by

$$\Delta G_g = -RT \ln p(\text{atm}) \qquad (3)$$

Table I
Polymerization Data for Dioxolane

t, °C	p,[a] kPa	ϕ_m[b]	t, °C	p,[a] kPa	ϕ_m[b]
48.5	15.3	0.12	69.3	45.3	0.21
55.1	21.4	0.15	70.5	47.7	0.22
58.7	25.8	0.16	74.8	59.2	0.25
60.4	28.5	0.17	76.7	62.3	0.26
66.7	42.0	0.20			

[a] From ref 2. [b] From ref 3.

$\overline{\Delta G_p}$ is the partial molar free enthalpy change for the addition of 1 mol of polymer to the mixture. This term is divided by n, the average degree of polymerization, in order to express it in terms of base mol. From the Flory–Huggins expression,[1] assuming n is large, we obtain

$$\overline{\Delta G_p}/n = RT[-\phi_m + \chi\phi_m^2] \tag{4}$$

where ϕ_m is the monomer volume fraction in the mixture and χ is the polymer–monomer interaction parameter. Making use of eq 3 and 4, eq 2 becomes:

$$\Delta G°_{gc} = RT[\ln p + \phi_m - \chi\phi_m^2] \tag{5}$$

By comparing eq 1 and 5 it is obvious that the presence of a large amount of monomer under equilibrium conditions brings about an important correction in the computation of $\Delta G°_{gc}$. On the other hand if the equilibrium really involves the gaseous monomer and the pure active polymer in the condensed state, ϕ_m is then equal to naught and eq 5 becomes identical to eq 1.

In the case of an equilibrium where the average degree of polymerization is low (smaller than 100), eq 5 then becomes:

$$\Delta G°_{gc} = RT\left[\ln p + \frac{(n-1)}{n}\phi_m - \chi\phi_m^2 - \frac{\ln\phi_p}{n}\right] \tag{6}$$

where ϕ_p is the polymer volume fraction in the condensed phase ($\phi_p + \phi_m = 1$).

Application to Polymerization Systems

In order to check the relevancy of eq 5 one needs data on equilibrium polymerizations where the vapor pressure of the monomer and the amount of monomer in the condensed phase are known. These data are available for the polymerizations of dioxolane (DOL) and tetrahydrofuran (THF). Busfield, Lee, and Merigold[2] measured what they claimed to be the vapor pressure of gaseous DOL and THF in equilibrium with their "solid" polymer. For the DOL system they obtained for the 48.5 to 76.7 °C temperature range:

$$\log p\ ,\ -(2.49 \pm 0.04) \times 10^3/T + (8.92 \pm 0.10) \tag{7}$$

For the THF system the results were:

$$\log p = -(1.97 \pm 0.12) \times 10^3/T + (7.50 \pm 0.36) \tag{8}$$

in the 37.2 to 87.0 °C temperature range. In both equations p is expressed in kPa (kNm^{-2}). The equilibrium bulk polymerizations of dioxolane[3] and tetrahydrofuran[4] have been studied in the same temperature ranges. From the values of p and ϕ_m for each temperature, $\Delta G°_{gc}$ can be computed from eq 5 using χ values of 0.4 and 0.3 for dioxolane[3] and tetrahydrofuran,[5] respectively. These constant concentration- and temperature-independent values of χ were found to give the best curve fit for the equilibrium bulk polymerizations and the best agreement with other methods for the computation of free enthalpy of polymerization.

The values of $\Delta G°_{gc}$ obtained through eq 1 and 5 can be compared with values computed from

$$\Delta G°_{gc} = \Delta G_{1c} - \Delta G°_{vap} \tag{9}$$

Table II
Polymerization Data for Tetrahydrofuran

t, °C	p,[a,d] kPa	ϕ_m[b]	p,[c] kPa	t, °C	p,[a,d] kPa	ϕ_m[b]	p,[c] kPa
37.2	14.7	0.35	24.5	70.4	48.8	0.72	111.3
47.3	20.0	0.42	41.3	76.5	70.1	0.83	140.2
48.4	29.1	0.43	43.5	76.7	74.5	0.83	141.2
54.7	30.7	0.53	56.9	87.0	101.9		
68.5	48.5	0.71	102.1				

[a] From ref 2. [b] From ref 4. [c] From eq 12. [d] These data are not used for computation.

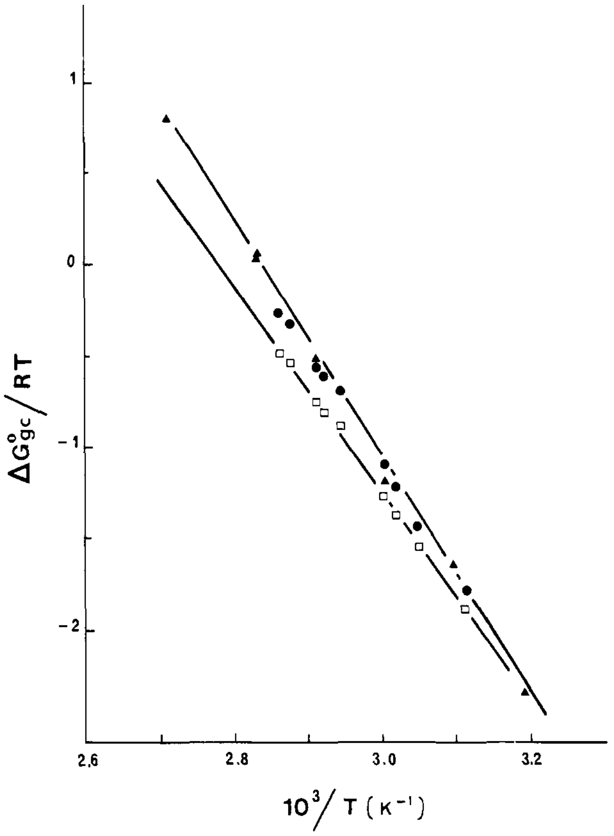

Figure 1. Polymerization of dioxolane. Computation of $\Delta G°_{gc}/RT$ according to eq 1 (empty squares), eq 5 (dots), and eq 9 (triangles).

where ΔG_{1c} is the free enthalpy change upon the conversion of 1 mol of pure liquid monomer into 1 base mol of pure amorphous polymer and $\Delta G°_{vap}$ is the free enthalpy of vaporization of the monomer, the vapor being at 1 atm. The free enthalpy of vaporization[2] for dioxolane is

$$\Delta G°_{vap} = RT[(4.15 \pm 0.02) \times 10^3/T - (11.92 \pm 0.06)] \tag{10}$$

and for tetrahydrofuran

$$\Delta G°_{vap} = RT[(3.80 \pm 0.02) \times 10^3/T - (11.18 \pm 0.06)] \tag{11}$$

Tables I and II show the data used for the DOL and THF systems. The vapor pressure data are taken from ref 2 and the values of ϕ_m are the corresponding smoothed values obtained from the bulk polymerizations for the same temperatures. The error on ϕ_m is estimated to be ± 0.01. Figures 1 and 2 show the variation of $\Delta G°_{gc}/RT$ with $1/T$ according to eq 1 for both the DOL and THF systems and according to eq 5 for the DOL system. Values of $\Delta G°_{gc}/RT$ computed through eq 9 are also plotted against $1/T$ in Figures 1 and 2. Values of ΔG_{1c} are obtained from the bulk polymerizations of dioxolane[3] and tetrahydrofuran[4] and from the polymerization of tetrahy-

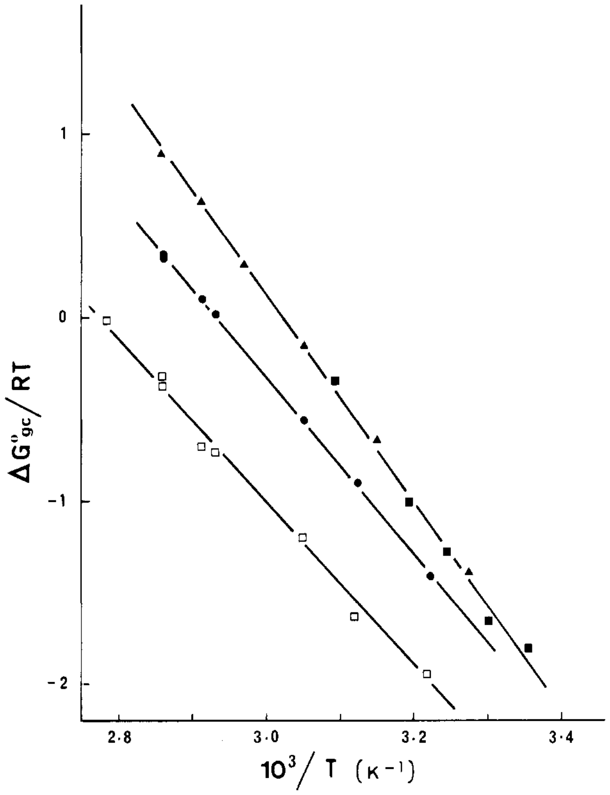

Figure 2. Polymerization of tetrahydrofuran. Computation of $\Delta G^\circ_{gc}/RT$ according to eq 1 (empty squares), eq 12 (dots), and eq 9 (triangles, ref 4; full squares, ref 5).

drofuran in benzene[5] for the same temperature range. For each corresponding temperature, ΔG°_{vap} is computed through eq 10 or 11. Enthalpies and entropies of polymerization for DOL and THF computed according to eq 1, 5, and 9 are given in Table III.

Discussion

Values of ΔG°_{gc} obtained through eq 9 are independent of vapor pressure measured over a polymerization system and hence may be used as a reference for the results obtained from eq 1 and 5. From Table III and Figure 1 it can be seen that, in the case of dioxolane, values of ΔH°_{gc} and ΔS°_{gc} obtained through eq 5 and 9 are in good agreement. Even the agreement between the values obtained from eq 1 and 9 remains acceptable. This result is expected since Table I shows the amount of monomer present in the condensed phase is small in this polymerization so that the correction brought about to ln p is small.

Table III
Values of ΔH°_{gc} and ΔS°_{gc} for the Polymerizations of DOL and THF

		ΔH°_{gc}, kJ mol^{-1}	ΔS°_{gc}, JK^{-1} mol^{-1}	Data used
DOL	Eq 1	-47.5 ± 0.7	-132 ± 2	Ref 2
	Eq 5	-52.0 ± 1.5	-147 ± 4	Ref 2 and 3
	Eq 9	-54.1 ± 0.8	-154 ± 2	Ref 2 and 3
THF	Eq 1	-36.7 ± 2.3	-102 ± 7	Ref 2
	Eq 9	-47.1 ± 0.6	-143 ± 2	Ref 2, 4, and 5
	Eq 12	-39.7 ± 0.4	-116 ± 1	Ref 4 and eq 9

In the case of tetrahydrofuran, the discrepancy between values obtained from eq 1 and from eq 9 is very large and there is no good agreement between values computed using eq 5 and 9. This may be caused either by the inadequacy of eq 5 or by the inaccuracy of the results used for calculation. Values of $\Delta G_{1c}/RT$ computed from the present set of ϕ_m values have been shown to be consistent with other values obtained with other methods.[3,5] These values together with the precise vapor pressure measurements of pure dioxolane and tetrahydrofuran would yield reliable thermodynamic values through eq 9. Since eq 5 yields systematically values close to those generated through eq 9, the parameters left to our attention are the measurement of p and the use of a constant χ. It has been mentioned earlier that in the present case the use of a constant χ yielded good results. Moreover allowing slight variations of χ would have minor effect since it is multiplied by ϕ_m^2 in eq 5. In the case of the bulk polymerization of tetrahydrofuran, under equilibrium conditions above 50 °C the condensed phase should contain more than 50% of monomer (see Table II). If measurements are carried out with all the liquid monomer pumped out, then the system is not in equilibrium and the values of p should be higher than the ones reported. Under these conditions the values obtained through eq 5 are of little use. However, with the present set of data, it is possible to compute back the vapor pressure values above the polymerization system. Using the values of $\Delta G^\circ_{gc}/RT$ obtained through eq 9 and known values of ϕ_m, p is readily found from eq 12:

$$\ln p(\text{atm}) = \Delta G^\circ_{gc}/RT_{(\text{eq }9)} - \phi_m + \chi\phi_m^2 = \Delta G^\circ_{gc}/RT_{(\text{eq }1)} \qquad (12)$$

New values of p are listed in Table II. ln p is also equal to $\Delta G^\circ_{gc}/RT$ according to eq 1 and is plotted in Figure 2. The difference between the curve from eq 12 and the curve from eq 9 represents the correction applied through eq 5 to the vapor pressure measurements for the polymerization of tetrahydrofuran. This can also be illustrated through the difference in the computed values of ΔH°_{gc} and ΔS°_{gc} given in Table III.

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