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J. Leonard[a]; D. Maheux[ab]
[a] Department of Chemistry, Laval University, Quebec 10, Canada [b] Golden Eagle Canada Ltd., Quebec, Canada

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Equilibrium Cationic Polymerization of Tetrahydrofuran in Benzene

J. LEONARD and D. MAHEUX*

Department of Chemistry
Laval University
Quebec 10, Canada

ABSTRACT

The equilibrium cationic polymerization of tetrahydrofuran in benzene is investigated in the 15 to 50°C range. Polymerizations are initiated with triethyloxonium hexafluorophosphate ($Et_3O^+PF_6^-$) and performed using high vacuum techniques. It is shown that, at a given temperature, the equilibrium monomer concentration varies linearly with polymer concentration. Values of $\Delta G_{\ell c}$, the free-energy change upon the polymerization of 1 mole of liquid monomer to 1 base-mole of liquid amorphous polymer of infinite chain length, is deduced from these results. Values of $\Delta G_{\ell c}$ obtained are in good agreement with those found in the literature for the equilibrium polymerization of tetrahydrofuran in bulk. However, there is a large discrepancy between these values of $\Delta G_{\ell c}$ and those computed using χ_{ms}, the monomer-solvent interaction parameter determined from integral heat of mixing.

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*Present address: Golden Eagle Canada Ltd., St-Romuald, Quebec, Canada.

INTRODUCTION

It is well known [1] that for many cyclic ethers a state of equilibrium between monomer and active polymer chains may be attained in the course of their polymerization in solution. This equilibrium is usually worked out through the use of the Dainton-Ivin equation [2]:

$$\ln[M]_e = \Delta H^\circ_{ss}/RT - \Delta S^\circ/R = \Delta G^\circ_{ss}/RT \qquad (1)$$

In this equation ΔG°_{ss} is the free-energy change upon the conversion of 1 mole of monomer in solution to 1 base-mole of polymer in solution, monomer concentration being 1 $\underline{M}$. $[M]_e$ is the equilibrium monomer concentration expressed in moles per liter and T is the absolute temperature. ΔG°_{ss} being unique at a given temperature in a given solvent, Eq. (1) implies that $[M]_e$ is also unique. The equation holds for an ideal system. However, polymer solutions differ from ideal behavior. It has recently been shown that, at a given temperature in the case of anionic polymerization of α-methyl-styrene [3, 4] and cationic polymerization of dioxolane [5], $[M]_e$ is not unique but varies with polymer concentration. Taking into account the nonideal behavior of polymerization systems, the thermodynamic treatment of equilibrium polymerization has been reassessed accordingly [6, 3, 7].

In the present study the cationic polymerization of tetrahydrofuran in benzene is investigated in the 15 to 50°C range and the results are interpreted in the light of recent developments in the thermodynamic treatment. The polymerization is initiated with triethyloxonium hexafluorophosphate ($Et_3O^+PF_6^-$) and proceeds through an opening of the tetrahydrofuran ring to yield a linear polymer [8].

EXPERIMENTAL

Materials

Thiophene-free benzene (Macco) was distilled over calcium hydride, degassed, distilled, and kept over a sodium mirror. The flask containing benzene was covered with aluminum foil. All operations were carried out under high vacuum.

Tetrahydrofuran (Anachemia) was treated in the same manner. A trace of naphtalene was distilled into the flask containing tetrahydrofuran and retention of the green color of sodium naphtalide was used as an indicator for its purity.

Triethyloxonium hexafluorophosphate can be prepared [9] by treating a solution of HPF_6 with ether and epichlorohydrin at low temperature. The initiator is purified in the following way [10]: triethyloxonium hexafluorophosphate is dissolved in CH_2Cl_2 and precipitated by pouring the solution into anhydrous ethyl ether. The ether is decanted off, the precipitate washed with fresh ether, and dried with a stream of nitrogen. The procedure is repeated three or four times. After the final precipitation the initiator is dried under vacuum at room temperature and stored in a vacuum desicator at -10° C. Under these conditions the initiator is relatively stable and may be kept for several months before repurification is needed.

Polymerization

Polymerizations were carried out in sealed ampoules using high vacuum techniques. Known volumes (±0.005 ml) of monomer and solvent were distilled quantitatively into an ampoule containing from 2 to 3 mg of initiator. The total initial volume was approximately 6 ml. Then the ampoule was frozen in liquid nitrogen and sealed off from the vacuum line.

In order to initiate the reaction, the ampoule was immersed in a bath at 50° C for 30 min and then transferred into a bath set at a desired temperature. Polymerizations were carried out at temperatures ranging from 15 to 50° C. Equilibrium was attained within 5 days in all cases. Reversibility of the polymerization may be checked by following volume change in a dilatometer through variation of the meniscus height in the capillary. This procedure is illustrated in Fig. 1. In section a, the bath is set at a given temperature (25° C) and the meniscus height is followed until it remains constant (equilibrium). Then, in section b, the temperature is lowered (15.2° C) and the procedure is repeated. After equilibrium has been attained, the bath is reset at its original temperature (section c) where, in the case of a reversible polymerization, the meniscus should come back to its initial equilibrium height.

After equilibrium had been reached, the polymerization was terminated with methanol at equilibrium temperature. The solution was quantitatively removed from the ampoule and transferred into a preweighted flask. The bulk of solvent and remaining monomer was removed in a vacuum evaporator. The polymer was dried to constant weight in vacuo at room temperature. The amount of monomer present under equilibrium conditions was determined by subtracting the amount of polymer obtained from the initial amount of monomer. The equilibrium volume of the solution was determined through the difference between the level of the solution and a reference mark on the stem of the ampoule, the volume and the section of the ampoule at the reference mark level being known. The estimated error on concentrations was of the order of 2%.

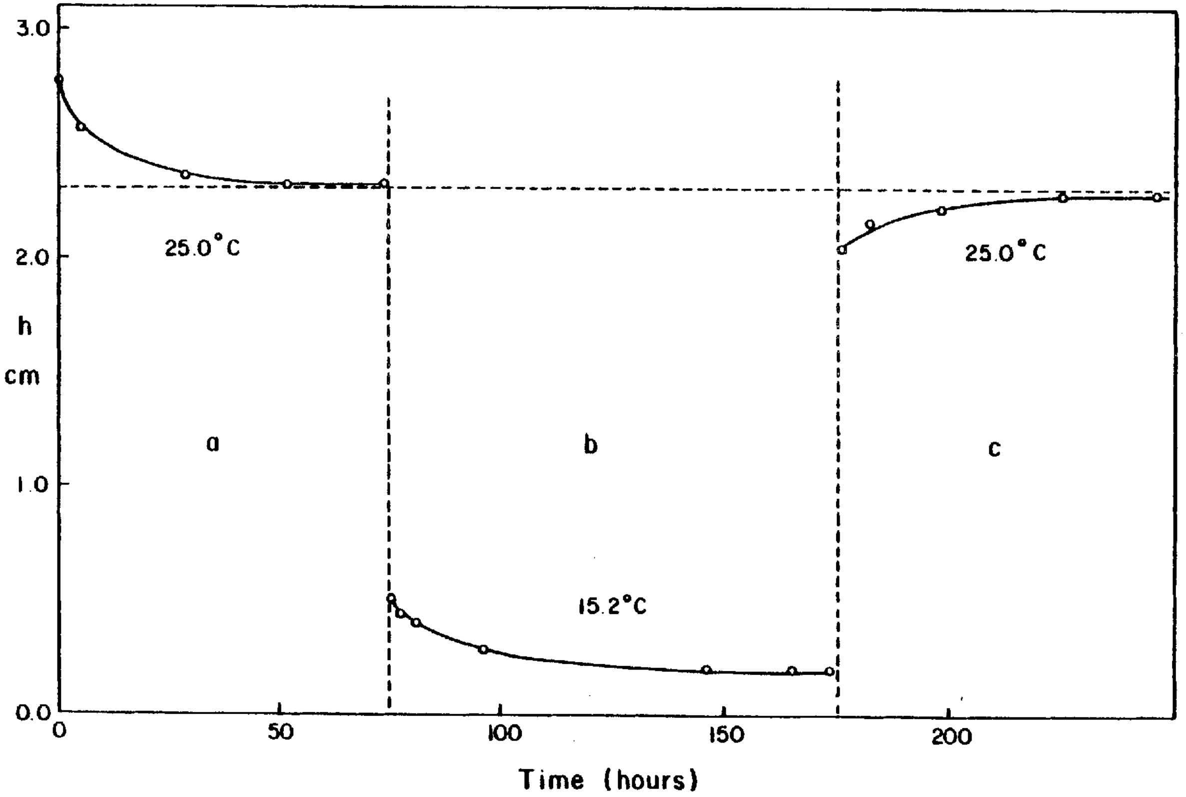

FIG. 1. Reversibility of the polymerization of tetrahydrofuran. Variation of meniscus height h with time for a polymerization in a dilatometer.

Molecular Weights

Average molecular weights of polytetrahydrofuran were determined by viscometry in benzene at 30°C in a modified Ubbelohde viscometer [11]. Molecular weights were computed from the relation [12]

$$[\eta] = 1.31 \times 10^{-3}\, \overline{M}_v^{\,0.60}$$

where $\overline{M}_v$ is the average molecular weight. The intrinsic viscosity $[\eta]$ was determined by a one-point method [13]. For the present system, results obtained by the one-point method and those obtained through the extrapolation of η_{sp}/c agree within 1%.

RESULTS

Equilibrium monomer concentrations $[M]_e$ and equilibrium polymer concentrations $[P]$ for the cationic polymerization of tetrahydrofuran in benzene at various temperatures are shown in Table 1, together with molecular weights $\overline{M}_v$. In some cases, the amount of polymer collected was too small and its molecular weight too low in order to determine it through viscometry; consequently, no values of $\overline{M}_v$ are reported in Table 1 for these samples of polymer.

From Fig. 2 it can be seen that, as in the case of the anionic polymerization of α-methylstyrene in tetrahydrofuran [3] and in p-dioxane [4], the variation of $[M]_e$ with $[P]$ is linear for the concentration range under investigation. This variation may be expressed by

$$[M]_e = A + B[P] = [M]_e^\circ + B[P] \tag{2}$$

Parameters A and B are computed by the method of least squares and results are shown in Table 2. Empty circles and squares in Fig. 2 correspond to values obtained for low molecular weight polymer (see Table 1) and were not used for the computation of A and B. It has recently been shown [7, 14] that for equilibrium between monomer and short-chain polymer at low polymer concentration, the value of $[M]_e$ is lower than it would be with long-chain polymer at the same $[P]$.

In order to relate the experimental results to the thermodynamic properties of the polymerization system, Eq. (2) is written in terms

TABLE 1. Equilibrium Values of Monomer and Polymer Concentrations and Molecular Weights at Various Temperatures

t (°C)	$[M_e]$ (mole/liter)	[P] (base-mole/liter)	$\overline{M}_v \times 10^{-4}$ (g/mole)
15	3.56	0.964	14.3
	3.51	1.243	17.6
	3.44	1.525	15.5
	3.42	1.952	26.0
20	3.90	0.596	2.5
	3.87	0.803	1.3
	3.78	1.126	9.1
	3.74	1.416	1.5
	3.76	1.631	8.7
25	4.34	0.143	-
	4.40	0.313	-
	4.33	0.594	0.82
	4.38	0.786	1.1
	4.28	1.040	0.84
	4.28	1.356	38.9
	4.14	1.825	31.6
30	4.70	0.228	-
	4.84	0.299	0.82
	4.79	0.544	4.1
	4.58	0.974	10.8
	4.63	1.095	15.3
	4.52	1.615	43.7
	4.41	2.089	27.6

35	5.17	0.143	-
	5.17	0.308	-
	5.25	0.460	2.3
	5.14	0.744	3.3
	5.11	0.988	5.5
	5.07	1.372	11.4
	4.90	1.917	14.5
40	5.74	0.581	4.6
	5.62	0.956	3.5
	5.63	1.272	6.7
	5.43	1.641	9.4
50	6.55	0.247	-
	6.56	0.637	1.1
	6.65	0.728	2.5
	6.55	1.016	8.6
	6.50	1.475	7.4
	6.47	1.807	9.8
	6.38	2.035	5.7

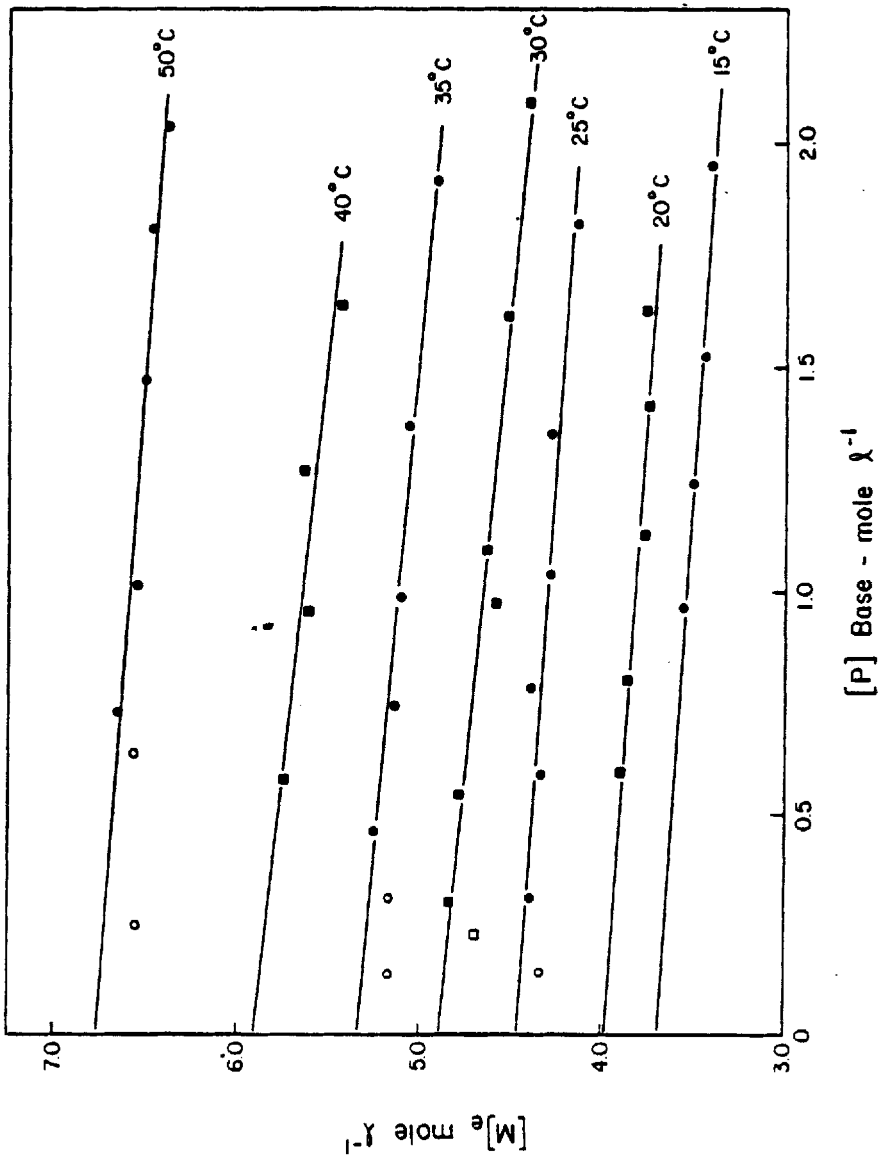

FIG. 2. Variation of equilibrium monomer concentration $[M]_e$ with polymer concentration [P] for the polymerization of tetrahydrofuran in benzene. (o,□) Short chain polymers; (●,■) long chain

of monomer volume fraction ϕ_m and polymer volume fraction ϕ_p:

$$\phi_m = AV_m + B(V_m/V_p)\phi_p = \phi_m^\circ + b\phi_p \tag{3}$$

where V_m is the monomer molar volume and V_p is the volume of 1 base-mole of polymer. The values of V_m used are those obtained previously [3]. V_p was computed from the reported density [15] (1.036^{20}) of the amorphous polymer, taking 5×10^{-4} cm^3 g^{-1} deg^{-1} for the coefficient of thermal expansion. Values of V_m, V_p, ϕ_m°, and b are shown in Table 2.

Taking into account the nonideal behavior of the system on the equilibrium position, the variation of ϕ_m with ϕ_p may be expressed [7] by

$$\phi_m = \frac{-(\Delta G_{\ell c}/RT) + \ln \alpha + \beta}{\beta + \chi_{mp} - (1/\alpha)} + \frac{\chi_{mp} - \beta}{\beta + \chi_{mp} - (1/\alpha)}\phi_p \tag{4}$$

with

$$\beta = \chi_{ms} - \chi_{sp}(V_m/V_s) \tag{5}$$

where χ is the free-energy interaction parameter between any two components, and the subscripts m, s, and p refer to monomer, solvent, and polymer, respectively. V_s is the solvent molar volume and $\Delta G_{\ell c}$ is the free-energy change upon conversion of 1 mole of liquid monomer to 1 base-mole of liquid amorphous polymer of infinite chain length. Since values used for the computation of A and B, and hence ϕ_m° and b, are for polymer with a DP above 100 ($\overline{M}_v > 7200$), the infinite chain length assumption is valid [3]. α is a constant which, ideally, should coincide with ϕ_m°. Assuming $\alpha = \phi_m^\circ$ and $\chi_{mp} = 0.3$ for the present range of polymer concentration, β and $-\Delta G_{\ell c}/RT$ may be computed by comparing Eq. (4) with Eq. (3). Results are given in Table 3.

DISCUSSION

As $\Delta G_{\ell c}/RT$ refers essentially to the conversion of 1 mole of liquid monomer to 1 base-mole of amorphous polymer for a given monomer at

TABLE 2. Experimental Values of A, B, ϕ°_m, and b at Various Temperatures

Temperature (°C)	A (mole/liter)	-B (mole/base-mole)	V_m (liter/mole)	V_p (liter/base-mole)	ϕ°_m	-b
15	3.69	0.146	0.0807	0.0694	0.297	0.170
20	3.98	0.156	0.0812	0.0696	0.323	0.182
25	4.46	0.160	0.0816	0.0698	0.364	0.187
30	4.89	0.238	0.0821	0.0700	0.401	0.278
35	5.33	0.219	0.0825	0.0701	0.439	0.257
40	5.90	0.266	0.0830	0.0703	0.489	0.314
50	6.76	0.178	0.0839	0.0707	0.567	0.211

TABLE 3

Temperature (°C)	Values of $\Delta G_{\ell c}/RT$ deduced			
	From Eqs. (3) and (4)		From Eqs. (7), (5), and (8)	
	β	$-\Delta G_{\ell c}/RT$	χ_{ms}	$-\Delta G_{\ell c}/RT$
15	-0.27	0.49	-0.55	0.88
20	-0.25	0.40	-0.55	0.78
25	-0.19	0.24	-0.55	0.64
30	-0.43	0.29	-0.55	0.53
35	-0.28	0.11	-0.54	0.41
40	-0.36	0.05	-0.54	0.28
50	-0.01	-0.26	-0.53	0.09

a given temperature, the value of $\Delta G_{\ell c}/RT$ should be independent of the polymerization system. The validity of Eq. (4) has recently [4] been checked for the anionic polymerization of α-methylstyrene in two different solvents, and values of $\Delta G_{\ell c}/RT$ computed from both systems were in good agreement.

In the present case the equilibrium polymerization of tetrahydrofuran in benzene may be compared with results obtained for the bulk polymerization of tetrahydrofuran [16]. In the latter case the polymerization is performed in the absence of solvent, the monomer being the solvent for its own polymer. Thermodynamic properties of these two polymerization systems differ considerably and this is reflected in their equilibrium monomer concentrations. At 20° C the equilibrium monomer concentration for the bulk polymerization is 2.71 and 3.98 moles/liter for the polymerization in benzene; at 50° C the concentrations are 5.08 and 6.76 moles/liter, respectively. Nevertheless, despite large differences in $[M]_e$, values of $\Delta G_{\ell c}/RT$ for both polymerizations should coincide.

Values of $\Delta G_{\ell c}/RT$ computed from Eqs. (3) and (4) are shown in Fig. 3, together with values computed by Dreyfuss and Dreyfuss for the bulk polymerization, using [17]

$$\Delta G_{\ell c}/RT = \ln \phi_m + \chi_{mp} (\phi_p - \phi_m) \tag{6}$$

The best fit between computed and experimental values through the use of Eq. (6) was obtained for $\chi_{mp} = 0.3$ and we use the same value in Eq. (4). From Fig. 3 it can be seen that agreement between the two sets of values is fairly good. From the combined results (omitting our value at 30° C), a value of -3.6 ± 0.2 kcal for $\Delta H_{\ell c}$ is deduced from the slope of $\Delta G_{\ell c}/RT$ against 1/T, and a value of -11.7 ± 0.6 eu is found for $\Delta S_{\ell c}$. These values are in good agreement with $\Delta H_{\ell c}$ = -3.3 kcal and $\Delta S_{\ell c}$ = -10.7 eu found from the bulk polymerization, and with $\Delta H_{\ell c}$ = -3.5 kcal estimated from heat of combustion of monomer [2]

It has recently [7] been suggested that $\Delta G_{\ell c}/RT$ may be computed from χ_{ms} which is defined as

$$\chi_{ms} = \frac{\Delta H_M}{x'_m RT \phi'_s} \tag{7}$$

where ΔH_M is the integral heat of mixing of monomer and solvent,

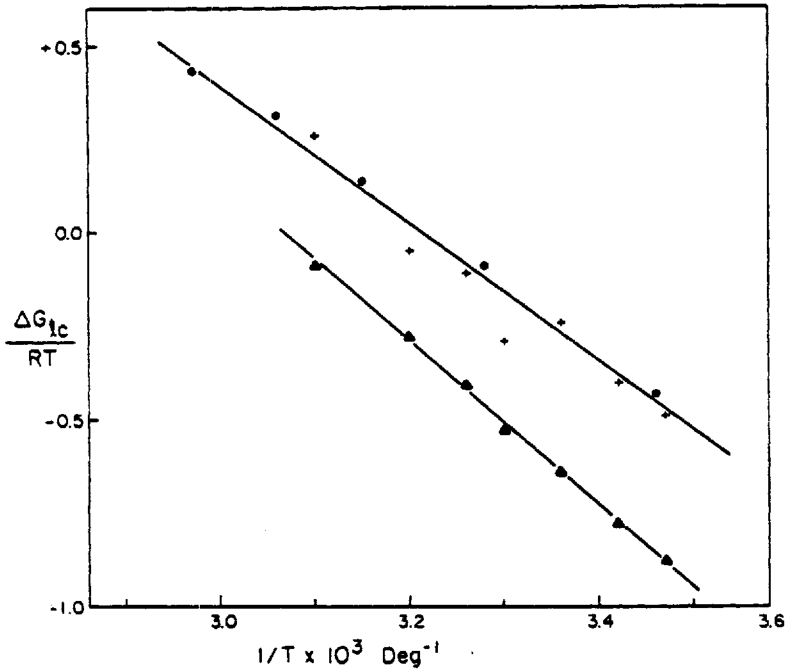

FIG. 3. Variation of $\Delta G_{\ell c}/RT$ with $1/T$ for the polymerization of tetrahydrofuran: Upper curve: (●) in bulk, (+) in benzene from Eqs. (3) and (4). Lower curve: (▲) in benzene from Eqs. (7), (5), and (8).

$\phi'_s = \phi_s/(\phi_s + \phi_m) = 1 - \phi^\circ_m$, and x'_m is the corresponding monomer mole fraction. Values of χ_{ms} are computed from reported integral heat of mixing of tetrahydrofuran with benzene at 25°C [18], assuming that $\Delta H_M/RT$ is independent of temperatures. Values of χ_{ms} at various temperatures are shown in Table 3. Values of β are obtained from Eq. (5) assuming $\chi_{sp} = 0.3$ and taking $V_m/V_s = 0.912$. β and ϕ°_m being known, $\Delta G_{\ell c}/RT$ is deduced from Eq. (4) by solving

$$\phi^\circ_m = \frac{-\Delta G_{\ell c}/RT + \ln \phi^\circ_m + \beta}{\beta + \chi_{mp} - (1/\phi^\circ_m)} \qquad (8)$$

Values of $\Delta G_{\ell c}/RT$ computed with the use of Eq. (8) are given in Table 3 and are plotted in Fig. 3 (lower curve). Although these values fall on a straight line, they differ to a considerable extent from the values computed from Eqs. (4) and (6), and they yield $\Delta H_{\ell c} = -4.3 \pm 0.1$ kcal and $\Delta S_{\ell c} = -13.1 \pm 0.03$ e.u. The same discrepancy can be observed in the case of the polymerization of α-methylstyrene in tetrahydrofuran, so that the use of heat of mixing for the determination of χ_{ms}, and hence $\Delta G_{\ell c}/RT$, is questionable. The use of excess free energy of mixing would probably be more appropriate for the determination of χ_{ms}.

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REFERENCES

[1] K. C. Frisch and S. L. Reegen, Ring-Opening Polymerization, Dekker, New York, 1969, p. 7.
[2] F. S. Dainton and K. J. Ivin, Quart. Rev., 12, 82 (1958).
[3] K. J. Ivin and J. Leonard, Eur. Polym. J., 6, 331 (1970).
[4] J. Leonard and S. L. Malhotra, J. Polym. Sci., A-1, 9, 1983 (1971).
[5] L. I. Kuzub, M. A. Markevich, A. A. Berlin, and N. S. Yenikolopyan, Polym. Sci. USSR, 10, 2332 (1968).
[6] S. Bywater, Makromol. Chem., 52, 120 (1962).
[7] J. Leonard, Macromolecules, 2, 661 (1969).
[8] P. Dreyfuss and M. P. Dreyfuss, Advan. Polym. Sci., 4, 528 (1967).
[9] M. P. Dreyfuss, U.S. Patent 3,585,227 (June 15, 1971).
[10] M. P. Dreyfuss, Private Communication.
[11] D. A. Henderson and N. R. Legge, J. Polym Sci., 19, 215 (1956).
[12] J. Brandrup and E. H. Immergut, Polymer Handbook, Interscience, New York, 1966, p. IV-34.
[13] A. A. Berlin, Vysokomol. Soedin., 8, 1336 (1966).
[14] P. E. Harvey and J. Leonard, To Be Published.
[15] O. G. Lewis, Physical Constants of Linear Homopolymers, Springer, New York, 1968, p. 81.
[16] M. P. Dreyfuss and P. Dreyfuss, J. Polym. Sci., A-1, 4, 2179 (1966).
[17] K. J. Ivin and J. Leonard, Polymer, 6, 621 (1965).
[18] J. Erva, Suomen Kemistilehti, 28B, 131 (1955).