

# Rotational energetics in vinyl polymer liquids:

## 2. Other polymers

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The procedures described for poly(vinyl acetate) in the preceding paper are applied to compute the effects of pressure on the Vogel  $T_0$  and  $B$  between  $P^* = -b$  (Tait) and  $P = 2000$  bars for polystyrene, linear polyethylene, polyisobutylene, and polydimethylsiloxane. From these are derived the pressure dependences of the rotational energies  $U$  and  $V$ , where  $U$  is the energy difference between the rotational states and  $V$  is a rotational barrier. The  $U^*$  for the 'isolated' chain is corrected by the factor  $Z^*$ , which appears to be an *intramolecular* cooperative unit, to yield  $U^{**}$ , the energy difference between the rotational states for a single main-chain bond in the 'isolated' chain. A major conclusion of this work is that statistical mechanical calculations of the conformational (i.e. rotational) properties using 'isolated' chain values for  $U$  will give erroneous results when applied to the real polymer liquid. The same conclusion based on a different approach has been reported previously.

### INTRODUCTION

In this paper we derive the pressure dependence of the Vogel  $T_0$  and  $B$ , and the rotational energetics for four additional vinyl-type polymers: polystyrene (PS), linear polyethylene (PE), polyisobutylene (PIB), and polydimethylsiloxane (PDMS), following the procedures reported in detail for PVAc in the preceding work<sup>1</sup>. As mentioned there, for comparisons of 'isolated' chains between the different polymers, a specific isotherm,  $T_{max}$  was chosen for the extrapolations to the negative pressure  $P^* = -b$  (Tait). For PVAc and PS,  $T_{max}$  lies within the range of direct  $p$ - $v$ - $T$  measurements on the liquids. For the remaining three polymers, however,  $T_{max}$  turns out to be well below the experimental range, necessitating additional extrapolations of both  $v_0$  and  $b$ . In the case of  $v_0$ , non-linear  $v$ - $T$  relationships are available while  $b$  will be extrapolated according to equation 3b\*. The extent of these extrapolations will be indicated with the individual polymers.

### RESULTS

#### Pressure dependence of $T_0$ and $B$

**Polystyrene.** For this polymer  $B = 1456^\circ$  and  $T_0 = 50^\circ\text{C}$  from Newtonian viscosity measurements by Plazek<sup>2</sup> on a sample with  $M = 47\,000$  ( $T_g = 97.7^\circ\text{C}$ ). This molecular weight is close enough to  $M_c$  that complications<sup>3</sup> due to 'entanglements' for  $M \gg M_c$  are minimal. With the  $p$ - $v$ - $T$  data and Tait constants reported by Quach and Simha<sup>4</sup> and with  $-10^4 \text{ K} = 17 \text{ cc/gm deg.}$ <sup>3,5</sup> in equation 5, we obtain  $T_{max} = 150^\circ\text{C}$ . The pressure coefficients of mobility  $(\partial \ln \mu / \partial p)_T$  were calculated at  $T_{max}$  and  $T_{max} \pm 10^\circ$  as described for PVAc<sup>1</sup> and from these the pressure dependences of  $T_0$  and  $B$  were derived by equation 6. The results are listed in Table 1.

\* Unless otherwise specified, references to equations and figures are to those in the preceding paper<sup>1</sup>

**Linear polyethylene.** The Vogel constants are<sup>6</sup>  $B = 1548$  and  $T_0 = 160^\circ\text{K}$ . Olabisi and Simha<sup>7</sup> reported  $p$ - $v$ - $T$  measurements and Tait constants for the liquid in the temperature range  $142$ – $200^\circ\text{C}$ . By equation 5, with the  $v_0$  values extrapolated by the Olabisi–Simha equation 3, we find  $T_{max} = 0^\circ\text{C}$  which is  $142^\circ$  below the lowest  $p$ - $v$ - $T$  measurement on the liquid, requiring an extrapolation of this magnitude for both  $v_0$  and for the Tait  $b$  by equation 3b. The pressure coefficients were calculated for  $-10$ ,  $0$ , and  $+10^\circ\text{C}$  leading finally to the results in Table 2.

**Polyisobutylene.** The Vogel constants are<sup>8</sup>  $B = 2856$  and  $T_0 = 123^\circ\text{K}$ . The Tait constants were given by Beret and Prausnitz<sup>9</sup> for the temperature range:  $53$ – $110^\circ\text{C}$ . By equation 5 with  $v_0$  extrapolated according to a quadratic  $p$ - $T$  equation reported by Eichinger and Flory<sup>10</sup> ( $0$ – $150^\circ\text{C}$ ) we obtain  $T_{max} = -40^\circ\text{C}$ . Thus a  $90^\circ$  extrapolation is required for  $b$  via equation 3b. The pressure coefficients of mobility were computed at  $-50$ ,  $-40$ , and  $-30^\circ\text{C}$  with the final results listed in Table 3.

**Polydimethylsiloxane.** The Vogel constants have been recently estimated<sup>11</sup> as  $B = 530^\circ$  and  $T_0 = 136^\circ\text{K}$ . The

Table 1 Pressure dependence of Vogel constants for polystyrene

$P$ , bars	$\Delta T_0$ , deg.	$\Delta B$ , deg.
0	0	0
200	4.39	47
400	7.86	100
600	10.68	156
800	13.02	216
1000	15.00	277
2000	21.51	601
$T_0$ , $^\circ\text{K}$	323	$B(P_0) = 1455 \text{ deg.}$
$10^2 a_1$	2.487	$(dB/dp)_0 = 0.210 \text{ deg/bar}$
$10^6 a_2$	-12.683	
$10^9 a_3$	+2.813	

**Table 2** Pressure dependence of Vogel constants for linear polyethylene

$P$ , bars	$\Delta T_0$ , deg.	$\Delta B$ , deg.
0	0	0
200	2.41	57
400	4.47	117
600	6.25	177
800	7.81	238
1000	9.18	299
2000	14.19	615
$T_0$ , °K	160	$B(P_0) = 1548$ deg.
$10^2 a_1$	1.303	$(dB/d\rho)_0 = 0.281$ deg./bar.
$10^6 a_2$	-4.733	
$10^9 a_3$	0.883	

**Table 3** Pressure dependence of Vogel constants for polyisobutylene

$P$ , bars	$\Delta T_0$ , deg.	$\Delta B$ , deg.
0	0	0
200	2.22	65
400	4.18	132
600	5.95	201
800	7.51	271
1000	8.91	344
2000	14.31	717
$T_0$ , °K	123	$B(P_0) = 2856$ deg.
$10^2 a_1$	1.214	$(dB/d\rho)_0 = 0.325$ deg./bar
$10^6 a_2$	-3.967	
$10^9 a_3$	0.737	

Tait constants based on  $p$ - $v$ - $T$  measurements in the range 25–70°C have been reported by Beret and Prausnitz<sup>9</sup>. The  $v$ - $T$  data (20–200°C) of Shih and Flory<sup>12</sup> were extrapolated to lower temperatures using their quadratic  $\rho$ - $T$  equation, leading to  $T_{max} = -30^\circ\text{C}$  by equation 5. Thus, a 50° extrapolation was required for the Tait  $b$  by equation 3b. The results for PDMS are given in Table 4.

#### Vogel constants at negative pressure $P^*$

The Vogel  $T_0$  was extrapolated to negative pressure  $P^* = -b$ , corresponding to the 'isolated' chain, by use of equation 7 with the appropriate coefficients for each polymer. With this  $T_0^*$ , and  $-\ln\mu^*$  for the  $T_{max}$  isotherm,  $B^*$  was computed as described for PVAc in the preceding paper<sup>1</sup>. All of the results are assembled in Table 5 in which the polymers have been arranged in order of decreasing  $T_0$  (and  $T_{max}$  since as noted earlier  $T_{max}$  is about 100° above  $T_0$ ). It turns out that this is also the order of decreasing  $T_0^*$ .

#### Derived rotational energetics

The values in Table 5 lead directly to the results in Table 6:  $U$ ,  $U^*$  via equation 2a;  $E_0$ ,  $E_0^*$  via equation 2b;  $f$  via equation 14 (calculated for  $U$  and  $U^*$  at temperature  $T_{max}$ ); and  $V$ ,  $V^*$  via equation 15 and 13 respectively. The results for PVAc from the preceding work<sup>1</sup> are also included.

#### DISCUSSION

It should be recalled that aside from the pressure extrapolations to negative  $P^*$  used in deriving the rotational energetics for the 'isolated' chains, temperature extrapolations of the Tait  $b$  were involved for three of the polymers, PDMS, PIB,

and PE, with the latter polymer requiring the largest extrapolation. Consequently the values in Table 6, and indeed the computed effects of pressure in Tables 2–4, for these three polymers must be considered as most tentative. Subject to this qualification, the following features may be noted regarding the results in Table 6.

In the present context the quantity  $(U - U^*)$  may be interpreted as the extent to which  $U^*$  for the 'isolated' chain is perturbed by intermolecular interactions in the real polymer liquid at  $P_0$  (atmospheric pressure). The fractional change  $(U - U^*)/U^*$ , which is more significant for the comparisons, increases as  $U^*$  itself decreases, except for PDMS.

Between  $P^*$  and 2000 bars the rotational energy diagrams are all qualitatively similar to Figure 5 for PVAc<sup>1</sup>. The greatest increment in  $U$  occurs between  $P^*$  and  $P_0$  with relatively little increase above  $P_0$ . This, of course, directly reflects the  $T_0$  behaviour with pressure as depicted in Figure 3

**Table 4** Pressure dependence of Vogel constants for polydimethylsiloxane

$P$ , bars	$\Delta T_0$ deg	$\Delta B$ , deg
0	0	0
200	2.22	34
400	4.02	69
600	5.55	104
800	6.84	139
1000	7.92	175
2000	11.65	354
$T_0$ , °K	136	$B(P_0) = 530$ deg.
$10^2 a_1$	1.267	$(dB/d\rho)_0 = 0.166$ deg./bar
$10^6 a_2$	-6.078	
$10^9 a_3$	1.327	

**Table 5** Summary of Vogel constants<sup>a</sup>

	PS	PE	PDMS	PIB
$T_0$ , °K	323	160	136	123
$B$ , deg.	1456	1548	530	2856
$T_{max}$ , °K	423	273	243	233
$P^*$ , bars	-1318	-1767	-1240	-2250
$T_0^*$ , °K	262	117	108	67
$-\ln\mu^*$	6.87	6.46	2.27	13.16
$B^*$ , deg.	1109	1006	306	2183

<sup>a</sup>  $T_0$  and  $B$  are for  $P_0$  (atmospheric pressure);  $T_0^*$  and  $B^*$  are for 'isolated' chains at  $P^* = -b$  (Tait)

**Table 6** Derived rotational energetics<sup>a</sup> at  $P^*$  and  $P_0$ 

	PS	PVAc	PE	PDMS	PIB
$U^*$	2184	1607	979	904	561
$E_0^*$	2203	3238	1998	607	4336
$f$	0.129	0.168	0.247	0.235	0.373
$V^*$	2486	3508	2240	820	4546
$U$	2695	2069	1335	1135	1026
$E_0$	2890	4336	3075	1053	5667
$f$	0.075	0.095	0.146	0.160	0.179
$V$	3092	4532	3269	1235	5851
$U - U^*$	511	462	356	231	465
$(U - U^*)/U^*$	0.23	0.29	0.36	0.26	0.83

<sup>a</sup> All energy units are cal/mol.

Table 7 Estimates of  $U^{**}$  for a Single Main-chain bond

	PS	PVAc	PE	PDMS	PIB
$T_{max}, ^\circ K$	423	353 <sup>a</sup>	273	243	233
$T_0, ^\circ K$	262	193 <sup>a</sup>	117	108	67
$Z^*$	2.63	2.20	1.75	1.80	1.40
$U^*, \text{cal/mol.}^b$	2184	1607	979	904	561
$U^{**}$	830	730	558	501	398

<sup>a</sup> From preceding paper; remaining values from Table 5, this paper

<sup>b</sup> From Table 6

of the preceding paper. On the other hand,  $V$  shows a more regular increase with pressure, indirectly reflecting the almost linear increase in  $B$  (c.f. Figure 3).

According to the discussion of the rotational kinetics<sup>1</sup> the quantity  $(V^* - U^*)$  represents the energy barrier to rotation in the  $g^+, g^- \rightarrow t$  direction for the 'isolated' chain. For PS (Table 6) this quantity is relatively small (300 cal/mol) indicating much shallower minima for the  $g^+$  and  $g^-$  states than the remaining polymers, except PDMS. For PDMS,  $V^*$  and  $U^*$  have about the same values which, if correct, implies that there are no real minima at the  $g^+$  and  $g^-$  states.

It was shown previously<sup>11</sup> that the size of the cooperative unit is given by  $Z^* = T/(T - T_0)$ . In an *isobaric* (i.e. thermal) expansion to the 'isolated' chain the limiting value of  $Z^*$  is unity since  $T_0$  remains fixed while  $T \gg T_0$  and  $(T - T_0) \simeq T$ . Thus under these conditions the lower limit of  $Z^*$  is one main-chain segment, referring to rotation about a single main-chain bond. On the other hand, in the *isothermal* expansion (by negative pressure)  $T$  now remains fixed while  $T_0$  has a lower limiting value which is still above 0°K. Hence for this type of expansion to the 'isolated' chain the limiting value of  $Z^*$  will be greater than unity, which must be interpreted as a purely *intramolecular* cooperation between contiguous segments in the main-chain. By a statistical probability argument, if a *random* main-chain bond has the probability  $\exp(-U^{**}/RT)$  of being in the higher energy state  $U^{**}$ , then the probability of  $Z^*$  *contiguous* bonds being in state  $U^{**}$  will be the product of the individual probabilities,  $\exp(-Z^*U^{**}/RT)$ . Thus,

$$U^{**} = U^*/Z^* \quad (1)$$

This calculation was made at the temperature  $T_{max}$  for the five polymers, with the results given in Table 7.

Of the polymers in Table 7 linear polyethylene (PE) has been studied the most intensively. Estimates of the *trans*  $\rightarrow$  *gauche* energy by a variety of methods for this polymer lead to  $U_g = 500$ – $600$  cal/bond<sup>13,14</sup>, with which  $U^{**}$

in Table 7 is consistent. Unfortunately, however, this is just the polymer requiring the longest extrapolation below the experimental  $p$ – $v$ – $T$  range for the liquid, as pointed out earlier, so that the agreement may be fortuitous and similar comparisons for the other polymers should ultimately be made. Nevertheless, it may be noted that if  $Z^*$  in Table 7 is indeed the *intramolecular* cooperative unit, then within the present context this implies that  $U^*$ , rather than  $U^{**}$ , should be taken as the *trans*–*gauche* energy differences in any 'isolated' chain calculations that are directly sensitive to the value of this parameter.

Regardless of the absolute accuracy of the values, comparisons of the respective  $U^*$  and  $U(P_0)$  in Table 6 consistently show that significant errors can result when the *intramolecular*  $U^*$ , applying to the 'isolated' chain, is used in statistical mechanical calculations of the conformational (i.e. rotational) properties for the real polymer liquid and this error is even greater if  $U^{**}$  (Table 7) is used. The earlier conclusion<sup>11</sup> that the intermolecular perturbation is minor was based on the relatively small change in  $U(T_0)$  only in the positive pressure region. It has already been shown<sup>11,15</sup> that 'isolated' chain values computed for the conformational entropy  $S_c$  at the melting points of crystalline polymers may be high by about 0.3 e.u. per main-chain bond. In a forthcoming publication (c.f. Ref. 10 in preceding paper), it will be shown that this error in the computed  $S_c$  increases with decreasing temperature.

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#### REFERENCES

- 1 Miller, A. A. preceding paper
- 2 Plazek, D. J. *J. Phys. Chem.* 1965, **69**, 3480
- 3 Miller, A. A. *Macromolecules* 1978, **11**, 134
- 4 Quach, A. and Simha, R. *J. App. Phys.* 1971, **42**, 4592
- 5 Miller, A. A. *Polymer* 1978, **19**, 899,
- 6 Miller, A. A. *Macromolecules* 1969, **2**, 365
- 7 Olabisi, O. and Simha, R. *Macromolecules* 1975, **8**, 206
- 8 Miller, A. A. *J. Polym. Sci. (A)* 1963, **1**, 1865
- 9 Beret, S. and Prausnitz, J. M. *Macromolecules* 1975, **8**, 536
- 10 Eichinger, B. E. and Flory, P. J. *Macromolecules* 1968, **1**, 285
- 11 Miller, A. A. *Macromolecules* 1978, **11**, 859
- 12 Shih, H. and Flory, P. J. *Macromolecules* 1972, **5**, 758
- 13 Flory, P. J. 'Statistical Mechanics of Polymer Chains' Interscience, New York (1969)
- 14 Yoon, D. Y. and Flory, P. J. *J. Chem. Phys.* 1978, **69**, 2536
- 15 Miller, A. A. *Polym. Prepr.* 1978, **19** (2) 779