the observed immiscibility of these two polymers.

Table V summarizes χ_{23}' for PS_L–PnBMA blends at 140 °C. It is apparent that the probe-to-probe variations are considerably smaller than before and that the interaction parameter is now a complex function of composition. In order to represent this concisely, χ_{23}' values for each of the seven blend compositions at 140 °C were averaged for the 11 probes and the resulting values plotted as a function of PS_L content (Figure 4). These interaction parameters are slightly more positive at 120 °C, but a similar composition dependence is observed. In view of the generally positive χ_{23}' values measured (at high PS_L content), there are no strong attractive forces between these two polymers. The miscibility observed with optical and T_g criteria must therefore be due to more favorable combinatorial entropy effects on lowering the molecular weight of the PS. Further work is required in order to determine the generality and the implications of the composition dependence of χ_{23}' in such polymer blends.

Acknowledgment. We wish to acknowledge helpful discussions with Dr. M. Croucher and to thank Dr. M. Breton for helpful comments.

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Main-Chain Rotational Contributions in the Glass–Liquid Transition[1]

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Received January 21, 1981

ABSTRACT: Main-chain rotational contributions to the increments in thermal expansivity and heat capacity in the glass-to-liquid transition, derived via a three-state rotational model, are compared for five vinyl-type polymers. For linear polyethylene and polyisobutylene these contributions are about 40% while for polystyrene and poly(vinyl acetate), both with "articulate" substituents, these contributions are only about 20%. Poly(dimethylsiloxane) gives anomalous results with this rotational model. Considering the glass transition as an isomobility state, it is shown that the second Ehrenfest relation need not apply, but may appear to do so in the limited cases where the pressure coefficients of the Vogel T_0 and B are equal.

In a series of recent papers we have been developing a kinetic model for mobility and the glass transition of polymer[2–4] and copolymer[5] liquids. In this model the important molecular motion is the cooperative rotational isomerization about main-chain bonds. This motion becomes virtually "frozen" when the temperature is lowered to T_g, which we consider to be an isomobility state.[6]

On the other hand, despite the recognized time dependence of this transition there has been much effort on strictly thermodynamic approaches. Intensive discussions of these have recently been reported for polystyrene (PS)[7] and for poly(vinyl acetate) (PVAc).[8–10]

Following the earlier Gibbs and DiMarzio concepts,[11] Adam and Gibbs[12] in 1965 combined the thermodynamic and kinetic aspects of the glass transition in their theory for cooperative relaxation. We have modified[2] (or perhaps clarified) this theory to make it conform to the Vogel or Tammann–Hesse equation[13]

$$-\ln (\mu/\mu_0) = B/(T - T_0) \qquad (1)$$

which still appears to be the best empirical relationship describing the temperature dependence of mobility for polymers.[14]

For a three-state rotational model it was shown[2,3] that $U = mRT_0$ and $E_0 = RB$, where U is the energy difference between the trans (t) state and two equivalent higher gauche (g^+, g^-) states and E_0 is related to the energy barriers against rotation between these states in the for-

0024-9297/81/2214-1460$01.25/0

Table I
Vogel Quantities[4] and Other Data

	PS	PVAc	PIB	PE	PDMS
T_g, K	373	304	203	200	150
T_0, K	323	248	123	160	136
B, K	1455	2183	2856	1548	530
dT_0/dP,[a] K/bar	0.0249	0.0176	0.0121	0.0130	0.0127
dB/dP,[a] K/bar	0.210	0.296	0.325	0.281	0.166
$10^4 V\Delta\alpha$, cm^3/(g K)	2.90[b]	3.50[c]	4.1[d]	6.1[e]	5.0[d]
ΔC_p, cal/(g K)	0.075[f]	0.119[g]	0.0965[d]	0.199[e]	0.12[h]
$M/2$[i]	52	43	28	14	37

[a] At P_0 (atmospheric pressure). [b] Quach, A.; Simha, R. *J. Appl. Phys.* 1971, *42*, 4592. [c] Reference 8, Table 9a. [d] Reference 16, Table 1 ($V\Delta\alpha = \Delta\beta$). [e] Reference 15, Appendix. [f] Karasz, F. E.; Bair, H. E.; O'Reilly, J. M. *J. Phys. Chem.* 1965, *69*, 2657. [g] Reference 10 (see Note Added in Proof). [h] Andrianov, K. A., et al. *J. Polym. Sci., Part A-1* 1972, *10*, 1. [i] Since there are two rotating segments in the main chain per repeating unit M, the factor $M/2$ will convert $V\Delta\alpha$ and ΔC_p into molar units.

Table II
Main-Chain Rotational Properties at T_g

	PS	PVAc	PIB	PE	PDMS
U/RT_g[a]	3.464	3.263	2.424	3.200	3.627
Q	1.0443	1.0541	1.1253	1.0576	1.0376
C_{pc}, cal/(mol K)	0.968	1.030	1.154	1.048	0.913
$10^3(dv/dT)_c$, cm^3/(mol K)	3.12	3.06	4.75	3.56	3.57

[a] $U/RT_g = 4.0T_0/T_g$.

ward and reverse directions,[4] t $\rightleftarrows$ g$^+$, g$^-$.

In the most recent paper[15] the main-chain rotational contributions to the increments in thermal expansivity, $V\Delta\alpha$, and heat capacity, ΔC_p, in the glass-to-liquid transition were derived for PVAc and linear polyethylene (PE). The present work compares three additional vinyl-type polymers: polystyrene (PS), polyisobutylene (PIB), and poly(dimethylsiloxane) (PDMS). Also, a correlation of the $V\Delta\alpha/\Delta C_p$ ratio reported by Boyer[16] and the second Ehrenfest relation are reexamined within the context of the present model.

The appropriate literature data and their sources are listed in Table I for the five polymers.

Results

Conformational (i.e., Rotational) Properties.[2,3] We adopt the three-state rotational model with "pentane interference" (g$^\pm$g$^\mp$ transitions excluded) using the simpler of the two partition functions,[3] Q. Thus

$$U = 4.0RT_0 \tag{2}$$

and

$$Q = 1 + 2^{1/2}\exp(-U/RT) \tag{3}$$

For the conformational heat capacity we have

$$C_{pc} = R(U/RT)^2(Q-1)/Q^2 \tag{4}$$

and for the temperature dependence of the flex volume[15]

$$(dv/dT)_c = C_{pc}(d\ln T_0/dP) \tag{5}$$

Table II lists these results for the five polymers, calculated at T_g and atmospheric pressure using the T_0 and dT_0/dP data from Table I.

Table III
Main-Chain Rotational Contributions in Glass-Liquid Transition

	PS	PVAc	PIB	PE	PDMS
$(dv/dT)_c/V\Delta\alpha$	0.207	0.203	0.414	0.417	0.193
$C_{pc}/\Delta C_p$	0.248	0.201	0.427	0.376	0.210
$10^5 d\ln T_0/dP$, bar^{-1}	7.71	7.10	9.84	8.13	9.34
$10^5 V\Delta\alpha/\Delta C_p$, bar^{-1}	9.24	7.03	10.15	7.32	9.96
$T_g V\Delta\alpha/\Delta C_p$, K/bar	0.0345	0.0214	0.0206	0.0146	0.0149
dT_g/dP, K/bar					
calcd[a]	0.0321	0.0252	0.0212	0.0202	0.017
obsd	0.0316[b]	0.0266[c]			

[a] Calculated with eq 10. [b] Quach, A.; Simha, R. *J. Appl. Phys.* 1971, *42*, 4592. [c] Reference 8, Table 9a.

Main-Chain Rotational Contributions at T_g. On the basis of the results for PE and PVAc in the earlier paper[15] it was proposed that

$$(dv/dT)_c/V\Delta\alpha = C_{pc}/\Delta C_p \tag{6}$$

and thus via eq 5

$$V\Delta\alpha/\Delta C_p = d\ln T_0/dP \tag{7}$$

For all five polymers eq 6 is reasonably well confirmed by the results in the first two lines of Table III, as is eq 7 by the third and fourth lines.

Boyer[16] has reported inverse correlations between T_g and both $\Delta\alpha$ and ΔC_p for a variety of amorphous polymers and he suggested such correlations as a means of resolving conflicting literature data. This would be particularly useful for semicrystalline polymers measured on different samples by different investigators. Figure 3 of Boyer's paper[16] shows a straight line represented by $V\Delta\alpha/\Delta C_p = 1/K_5$, with $K_5 = 270$ cal/cm^3. Thus, $1/K_5 = 8.85 \times 10^{-5}$ bar^{-1}. According to eq 7, the $V\Delta\alpha/\Delta C_p$ ratio is determined by $d\ln T_0/dP$, which may in some cases be close to Boyer's $1/K_5$, as Table III shows, but not necessarily coincide with it.

The two most pronounced discrepancies in Boyer's Figure 3 are for PE and PDMS, for both of which he used results of measurements on the partially crystalline polymers. For completely *amorphous* PE our values for $V\Delta\alpha$ and ΔC_p, as listed in Table I, are much more consistent with eq 6 and 7 than are the values used by Boyer. Similarly, our cited ΔC_p for PDMS was for a rapidly quenched amorphous sample and it is more consistent with eq 6 and 7, as well as with Boyer's Figure 3.

Second Ehrenfest Relation.[17] The Gibbs–DiMarzio theory[11] proposed a second-order thermodynamic transition temperature, $T_2 > 0$ K, lying below T_g but sufficiently close that T_g itself could be treated as a quasi-thermodynamic transition to which the two Ehrenfest relations might apply:

$$dT_g/dP = \Delta\beta/\Delta\alpha \tag{8}$$

$$dT_g/dP = T_g V\Delta\alpha/\Delta C_p \tag{9}$$

The experimental evidence has completely eliminated eq 8 while "agreement" with eq 9 is considerably better.[17]

The present kinetic approach, considering the glass transition as an isomobility state, permits a critical reexamination of the second Ehrenfest relation, eq 9. We have shown,[18] for example, that in the formation of PVAc glass at elevated pressures up to 800 bars ($\Delta T_g = 17$ K), the Vogel term remains precisely constant: $B/(T_g - T_0) = 38.5$.

Hence, differentiating this term at T_g with respect to pressure

$$dT_g/dP = dT_0/dP + [(T_g - T_0)/B]\ dB/dP \quad (10)$$

Substituting eq 7 and rearranging

$$dT_g/dP = T_0 V\Delta\alpha/\Delta C_p + [(T_g - T_0)/B]\ dB/dP \quad (11)$$

The second term in this equation will always be somewhat less than the corresponding term in eq 9 since $T_0 < T_g$, but there is an additional positive contribution by the third term. The second Ehrenfest relation, eq 9, can become identical with eq 11 only under the condition that $d \ln T_0/dP = d \ln B/dP$. Of the five polymers being considered here, only PIB comes close to this criterion, $d \ln T_0/d \ln B = 1.16$, while for the remaining polymers this ratio ranges between 1.9 and 3.3. The results in the last lines of Table III show these discrepancies of eq 9, except for the case of PIB. In a note added in proof, McKinney and Goldstein[8] reported $\Delta C_p = 0.097$ cal/(g K) for PVAc and hence apparently better agreement with eq 9. However, the higher value of ΔC_p cited in Table I of the present work was subsequently obtained by two independent groups on the same sample (cf. Note Added in Proof in ref 10).

DiMarzio and co-workers[19] have extended the Gibbs–DiMarzio theory of the glass transition to include the effects of pressure. They derived $dT_2/dP = T_2 V\Delta\alpha/\Delta C_p$, which appears to be identical with our eq 7. However, our interpretation of T_0 (Vogel) differs from the Gibbs–DiMarzio T_2 (calorimetric) and the two values are not necessarily the same.[2,3]

Discussion

The present work supports the conclusions reported earlier[15] regarding the contributions by rotational isomerization about main-chain bonds to the increments in thermal expansivity and heat capacity in the glass-to-liquid transition. In Table III, PS and PVAc show a rotational contribution to both $V\Delta\alpha$ and ΔC_p of about 20% while PE and PIB both show about 40%. The two former polymers each have "articulate" substituents whose enhanced motions in the liquid can contribute to $V\Delta\alpha$ and ΔC_p but not to $(dv/dT)_c$ or C_{pc} since the latter two quantities refer only to rotations about main-chain bonds. (The similarity of the values between PS and PVAc may be a coincidence since there is no "a priori" reason that the nonconformational contributions by the phenyl and the acetate substituents should be the same.)

PIB shows about the same rotational contributions as PE, which has no "articulate" substituent. This indicates that the *gem*-dimethyl makes no noticeable additional contribution to $V\Delta\alpha$ or ΔC_p in the transition to the liquid state, as was previously concluded for a single methyl substituent (cf. Discussion in ref 3). In this respect PDMS appears to be anomalous. While it also has *gem*-dimethyl substituents, its main-chain rotational contributions to $V\Delta\alpha$ and ΔC_p are found to be far less than for PIB. It should be noted that the agreement already observed with eq 6 and 7 permits little margin for experimental error in the independently determined values of $V\Delta\alpha$, ΔC_p, and $d \ln T_0/dP$. A remaining possibility is that, owing to the marked difference in chemical composition of the main-chain (–Si–O– vs. –C–C–), the rotational statistics of PDMS may differ from those of the other four polymers.[20]

In related work, Roe and Tonelli have calculated the main-chain rotational contribution to ΔC_p at T_g for a variety of polymers[21a] and also substituent contributions for some of these.[21b] Focusing on the main-chain only, the values for C_{pc} in Table II are to be compared with those in Table I of ref 21a. However, it should be noted that a conceptual difference arises here. Roe and Tonelli use an *intra*molecular U^* applying to the isolated chain and this is appreciably lower than our U, defined by eq 2 and applying to the real polymer liquid. For polyethylene it was shown that U^* gives a physically unrealistic result in the calculation of the rotational entropy and its temperature derivative, $dS_c/dT = C_{pc}/T$, at low temperatures (see Figure 3 in ref 3). Indeed, we have suggested a physical rationale for an *inter*molecular perturbation on U^*, raising it to U in the real liquid.[15] It turns out that a plot of C_{pc} against U/RT (eq 4) has a maximum in C_{pc} at $U/RT \simeq 2.5$, with or without the "pentane interference". As a consequence, in some cases a deceptive "agreement" may be observed between the C_{pc} at T_g calculated with the lower U^* ($U^*/RT_g < 2.5$) and that calculated with the higher U ($U/RT_g > 2.5$).

Conclusion

In this model the equilibrium conformational (i.e., rotational) properties of the main-chain are governed solely by $U(T_0)$ while dynamical properties such as viscosity, the α process in dielectric relaxation, and the glass transition are influenced also by $E_0(B)$. These rotational energetics are uniquely defined by the Vogel (Tammann–Hesse) equation, with no adjustable parameters. Thus far this model has provided a unified molecular explanation for the effects of chemical structure,[2] pressure,[3,4] and copolymer sequence distribution[5] on polymer liquid mobility. Other seemingly diverse effects will be examined in future work.

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