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Molecular model for mobilities of copolymer liquids

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Introduction

Earlier papers[1,2] have presented a molecular interpretation of the Vogel equation for polymer liquid mobility:

$$-\ln \mu \sim B/(T - T_0) \tag{1}$$

where B, T_0 are constants which are independent of temperature but increase with pressure[3]. On the basis of a rotational isomeric model it was shown that:

$$U = mRT_0 \tag{2}$$

and

$$E_0 = RB \tag{3}$$

in which U is the energy difference between the rotational states and E_0 is related to the rotational barrier(s) between these states. For the simplest 3-state rotational model (a *trans* state, t, and two equivalent *gauche* states, g^+ and g^-) with independent bond rotations[1], $m = 4.2$ in equation (2). A 3-state model in which transitions between *gauche* states of opposite sign are excluded (the 'pentane interference') gives $m = 4.0$ or 4.4, depending upon which of two rotational partition functions is chosen[2]. The conformational entropy calculated for linear polyethylene (PE) with $m = 4.4$, together with a new calculation of the volume entropy, gave excellent agreement with the experimental entropy of fusion[2].

A procedure for extrapolating U and E_0 from the real polymer liquid to the 'isolated' chain and the relation of E_0 to the barriers against rotation in the 'forward' ($t \rightarrow g^+, g^-$) and 'reverse' ($g^+, g^- \rightarrow t$) directions have also been reported[4].

Combining equations (1)–(3) leads to

$$-\ln \mu \sim E_0/(RT - U/m) \tag{4}$$

The glass transition is considered to be an isomobility state[3,5] with a constant value of the Vogel term for a given polymer:

$$B/(T_g - T_0) = D \tag{5}$$

or

$$T_g = T_0 + B/D \tag{5a}$$

where also $D = 2.303C_1^g$ in the WLF context, its value ranging between 30 and 40 ($1/D = 0.033$–0.025) for different vinyl-type polymers[6,20].

By substituting equations (2) and (3) in equation (5a) we obtain for the glass-transition temperature:

$$T_g = (U + mE_0/D)/mR \tag{6}$$

For a binary copolymer liquid, if both U and E_0 were simply additive in mol fractions, n_a and n_b, of the components and m remained constant over the composition range, then from equations (2) and (3):

$$T_0 = n_a T_{0a} + n_b T_{0b} \tag{7}$$

and

$$B = n_a B_a + n_b B_b \tag{8}$$

By equation (5a) this would also require that T_g of the copolymer be simply additive i.e. T_g would be linear in n_a or n_b.

Usually, however, T_g against mol fraction is nonlinear, showing either a positive or a negative deviation and in some cases even a maximum or a minimum[7,8]. This suggests that equations (7) and (8) cannot apply simultaneously, i.e. either T_0 or B can be linear in n but not both. A choice can be made only on the basis of experimental measurements of the Vogel (or WLF) constants as a function of composition. Only a very few such measurements have been reported in the literature, in contrast to the abundance of data on T_g versus composition for copolymers.

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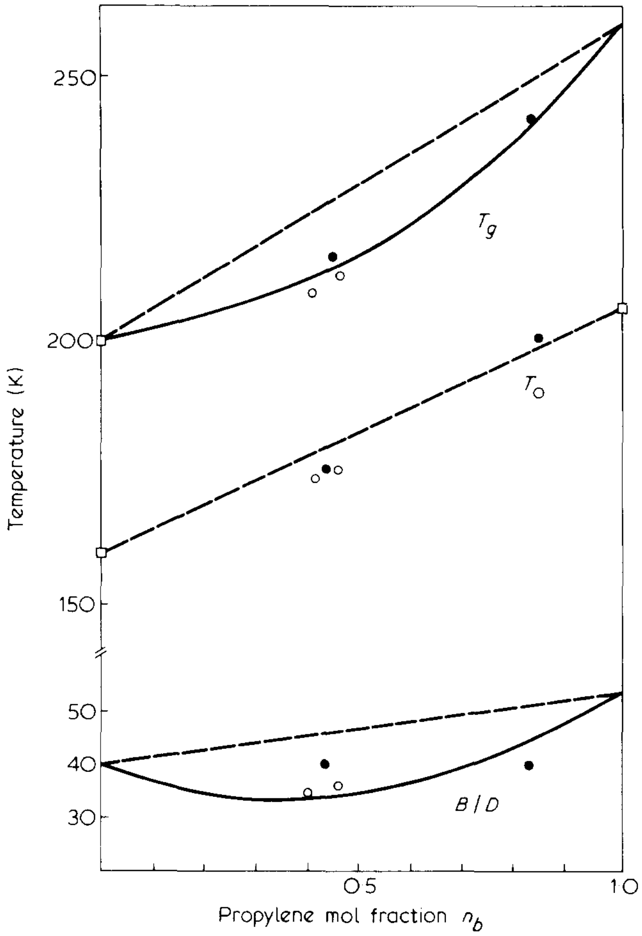

Figure 1 Ethylene–propylene copolymers. ●, Ferry *et al.*[9]; ○, Bares[10]; □, see text. Solid T_g line is from Illers[12]. $B/D = T_g - T_0$ equation (5)

Table 1 Ethylene–propylene copolymers

Mol fraction propylene	T_g(K)	T_0(K)	B (deg)	D [b]
0[a]	200	160[11]	1548[16]	38.7
0.41[10]	209	174	1128	32.2
0.44[9]	216	175.3	1229	30.2
0.46[10]	213	176	1278	34.5
0.84[9]	242	201.3	1229	30.2
1.00[a]	259[14]	206[14]	1762[16]	33.2

[a] See text

[b] $D = B/(T_g - T_0)$ by equation (5)

Results

Ethylene–propylene (EP) From the standpoint of chemical structure alone this copolymer is the simplest of the vinyl-type systems. The WLF constants for several compositions have been determined from dynamic compliance[9] and from stress relaxation[10] measurements. These were converted to the Vogel values as follows[6]: $T_0 = T_r - C_2^r$ and $B = 2.303\, C_1^r C_2^r$, where C_1^r and C_2^r are the WLF constants for the reference temperature T_r. The results are listed in *Table 1* including values for amorphous linear polyethylene (PE) and amorphous polypropylene (PP).

The Vogel constants for PE were originally derived by extrapolation of Newtonian viscosities from the lower n-alkanes[11] and the T_g is consistent with 196K, reported by Illers[12] from several ethylene copolymers, and with 197–200K derived recently from progressive hydrogenation of *cis*-1,4-polybutadiene[13].

For PP the Vogel T_0 was identified with $T_2 = 206(\pm 20)$K, the latter derived by Passaglia and Kevorkian[14] from heat capacity measurements on the atactic and isotactic polymers The justification for assuming that $T_0 = T_2$ for PP (as for PE) has been discussed[2, 15]. Despite the large error limits the value $T_0 = 206$K as well as our value of $B = 1762$ are consistent when compared with PE or with T_g for PP. Actually, the Vogel constants for amorphous PP could be determined by direct measurement of Newtonian viscosities on the atactic polymer over a broad temperature range approaching T_g and for a molecular weight not exceeding M_c, the critical 'entanglement' value. To our knowledge such measurements have not yet been reported in the literature.

The results for the E–P copolymers from *Table 1* are displayed in *Figure 1* which includes also T_g values calculated from the Illers work[12] and converted from weight fraction to mol fraction.

n-Hexyl methacrylate–styrene (HMA–S) Ferry and coworkers[17] reported the WLF constant for two compositions of this copolymer from dynamic mechanical measurements and included the values for the two homopolymers. The derived Vogel constants are listed in *Table 2.* The plot of these data in *Figure 2* shows that T_0 is quite linear in mol fraction of styrene, in contrast to the large positive deviation from linearity for T_∞ (i.e. T_0) against *weight* fraction of styrene in *Figure 4* of the original paper[17].

Butadiene–styrene (Bd–S) The Newtonian melt viscosity on a single composition of this copolymer containing 25 weight percent styrene (15 mol percent) was measured by Kraus and Gruver[18]. The distribution of unsaturation of the butadiene component was 19% *cis*, 47% *trans* and 34% vinyl. Their Vogel constants together with those for the two homopolymers give a large positive deviation from linearity for T_0 of the copolymer and a negative deviation of about the same magnitude for B/D. The same conclusion derives from measurements by Ferry and coworkers on a Bd–S copolymer of very similar composition (23.5 weight percent styrene) but of unspecified distribution of unsaturation.

The Bd–S copolymers are complicated by the presence of the *cis*/*trans*/vinyl unsaturation with the corresponding homopolymers, poly-1,4-butadiene and poly-1,2-butadiene, having different T_g, T_0 and B values[20]. Consequently, Bd–S cannot be considered as typical of vinyl-type copolymers, which are better exemplified by E–P and HMA–S.

Discussion

Figures 1 and *2* suggest that for these saturated vinyl-type copolymers T_0 is additive (i.e. linear) in $n_{a,b}$ and that the nonlinearity in T_g is caused by a corresponding nonlinearity in B. Conversely, it might be argued that if experiment shows that T_0 is linear then the m value (equation (2)) must remain constant over the composition range, in turn implying that the two homopolymers conform to the same rotational model. Indeed, the positive deviation in T_0 observed for the Bd–S copolymer may be due in part to differing m values between polystyrene and the polybutadiene isomers.

The effect of the sequential distribution of A–A, A–B,

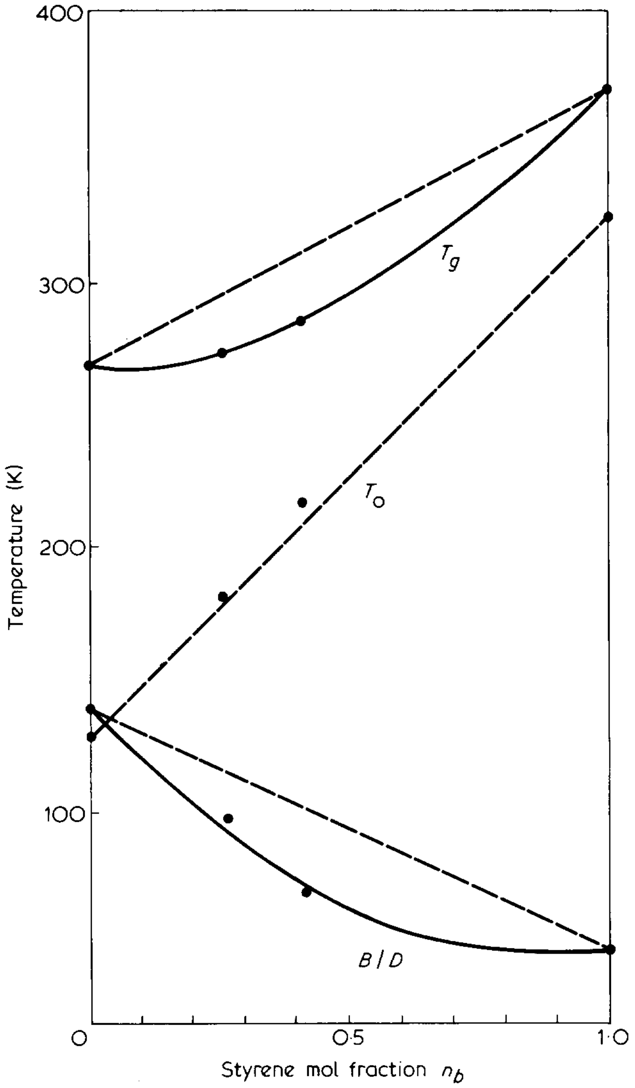

Figure 2 n-Hexylmethacrylate–styrene copolymers[17]. $B/D = T_g - T_0$ (equation (5))

Table 2 n-Hexyl methacrylate–styrene copolymers[17]

Mol fraction styrene	T_g (K)	T_0 (K)	B (deg)	D[a]
0	268	127.8	5928	42.3
0.26	277	180.6	3154	32.7
0.41	287	216.8	2363	33.7
1.0	373	324	1514	30.9

[a] $D = B(T_g - T_0)$ by equation (5)

B–A, and B–B dyads on the glass-transition temperatures of random copolymers has been successfully correlated by the introduction of the parameter T_{ab}, which corresponds to the T_g of the regularly alternating copolymers[7,8]. Such copolymers can be synthesized by special polymerization techniques[21]. In terms of the present model measurement of the Vogel B and T_0 on the alternating copolymer, where the sequence distribution has been eliminated as a variable, would permit the evaluation of E_{0ab} applying to the hetero-linkages A–B and B–A, and at the same time test the linearity of T_0 if this quantity is known for both homopolymers.

In the absence of such measurements E_0 for the hetero-linkages can be estimated as follows. We *assume* T_0 to be linear in $n_{a,b}$ and hence the nonlinearity in T_g to be caused exclusively by a corresponding nonlinearity in B/D (c.f. *Figures 1* and *2*). It then follows that:

$$T_{ab} - (T_a + T_b)/2 = B_{ab}/D_{ab} - (B_a/D + B_b/D)/2 \qquad (9)$$

where T_{ab}, T_a and T_b are the glass-transition temperatures for the alternating copolymer and the two homopolymers, respectively. If B_a/D and B_b/D are known for the two homopolymers equation (9) can be solved for B_{ab}/D_{ab} and, with $D_{ab} = (D_a + D_b)/2$ as an approximation, leading finally to E_{0ab} by equation (3).

To illustrate this procedure for a styrene-methyl methacrylate copolymer we adopt the values reported by Furukawa[21] $T_{ab} - (T_a + T_b)/2 = -18$. For polystyrene[20] $B_a/D = T_g - T_0 = 50°$ and similarly for 'ideally atactic' polymethyl methacrylate[20] $B_b/D = 80°$, giving, by equation (9), $B_{ab}/D_{ab} = 47$. But $D_a = 31.5$ and $D_b = 34.1$ and thus $D_{ab} = 32.8$, leading to $E_{0ab} = 3.1$ kcal/mol for the hetero-linkages A–B and B–A. Since $E_{0a} = 3.1$ for PS[16] and $E_{0b} = 5.4$ for PMMA[16], $(E_{0a} + E_{0b})/2 = 4.25$ kcal/mol. Thus the rotational barrier for the hetero-linkages is about 1.1 kcal/mol less than what would be expected on the basis of simple molar additivity.

The determination of E_{0ab} for a variety of vinyl-type copolymers may ultimately permit the effects of such factors as polarity and steric hindrance on the rotational barriers to be assessed quantitatively.

For some vinyl-type polymers (e.g. polyacrylonitrile or polyvinylidene chloride) the melting points are too high for measurements to determine directly their Vogel constants. In these cases such measurements could be made on their amorphous copolymers in a lower temperature range. For example, at least two amorphous acrylonitrile–styrene copolymer compositions would give at least two T_0 values which, with the known T_0 for polystyrene itself, would establish whether a linear extrapolation to T_0 for polyacrylonitrile was justified. If so, B could then also be estimated by equation (5) using an 'average' $D \simeq 35$. These values of T_0 and B for polyacrylonitrile should then coincide with those obtained by the same measurements on acrylonitrile with other comonomers (e.g. methyl methacrylate, polyvinyl acetate, etc.) for whose homopolymers the T_0 and B are known.

Conclusion

Theories for the glass transition have been reviewed by Shen and Eisenberg[22], by Barton[7] for copolymers, and most recently by Lipatov[23] (free-volume). Generally these theories have been based on thermodynamic approaches, neglecting the time-dependent kinetic nature of this transition. These two aspects were reconciled and combined by Adam and Gibbs[24] in their theory for the cooperative relaxation in polymer liquids, following the earlier Gibbs and DiMarzio[25,26] thermodynamic treatments. With an additional modification[1] to make the Adam–Gibbs theory conform to the experimental Vogel equation, this has been the basis for the present model.

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