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Theoretical Considerations on the Possibility of Enhancing the Effect of Temperature upon the Melt Viscosity of Linear Polymers by the Incorporation of Weak Bonds in the Chains. I. Thermodynamic Arguments

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SUMMARY

A basic limitation in the processing of thermoplastics lies in the high viscosity of their melts. Since high viscosity is largely a consequence of high average molecular weight, this problem would be solved if a polymer could be provided in the form of polymer blocks which are essentially independent at elevated temperatures and which bond together reversibly at ambient temperatures. The theoretical possibility of achieving such a system is considered from the point of view of thermodynamic arguments as applied to an idealized system of monodisperse polymer blocks linearly connected by weak chemical bonds. Average molecular weights are expressed in terms of a molar Gibbs function contribution associated with a weak bond in the polymer. Assuming a requirement for substantial decomposition at 500°K, arguments are presented for an entropy contribution of ca. 200 J $^{\circ}K^{-1}$ mole^{-1} for such

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† Correspondence should be sent to this address.

bonds, and on this basis an optimum weak bond energy of 60 ± 20 kJ mole^{-1} is indicated. Possible block terminations giving energies of this magnitude are considered.

INTRODUCTION

The essential property of a thermoplastic polymer lies in its ability to show a reversible decrease in viscosity with increasing temperature. However, even at the highest usable processing temperatures and for the more favorable standard polymers [1], the viscosities of thermoplastic melts are relatively high so that high pressures and comparatively heavy equipment are necessary to make the polymer flow. The basic reason for this lies in the steep dependence of viscosity upon average molecular weight and in the very high molecular weights which are necessary for the establishment of satisfactory mechanical properties in the solid (cold) condition. Ideally, the best thermoplastic would be one which has a low average molecular weight at elevated temperatures and a high average molecular weight at ambient temperatures. This could be achieved in principle by the reversible bonding of polymeric blocks; clearly, the bonding between blocks would need to be weaker than that within blocks.

When this work was initiated, there was no available information on the feasibility of creating such a system. The present study (described in two parts) is concerned with calculating the conditions and limitations which would be expected to apply to the required association-dissociation reaction. Part I is largely concerned with equilibrium thermodynamic arguments. In Part II [2], the reaction rates for fission and block recombination are considered, to ascertain the extent of approach to the predicted equilibria under actual conditions of operation.

(SI units [3] are used throughout. Conversion factors for other units are given in the Appendix.)

FACTORS INFLUENCING MELT VISCOSITY

Temperature

Experimental data are generally in accord with the semi-empirical equation of Williams et al. [4]:

$$\log \frac{\eta_T}{\eta_0} = \frac{-C_1 (T - T_0)}{C_2 + T - T_0}$$

where η_T is the viscosity at temperature T, η_0 is the viscosity at an arbitrary reference temperature T_0, and C_1, C_2 are functions of T_0 and to some extent of the polymer system. In cases where T is significantly greater than $|C_2 - T_0|$, the equation may be approximated to

$$\log [\eta_T/(\text{kg m}^{-1} \text{ sec}^{-1})] = C_3 + C_4/T$$

C_3 and C_4 being characteristics of a particular polymer system. Positive values for C_4 ensure the universal observation that viscosities decrease with increasing temperature.

Shear Stress

Polymers exhibit non-Newtonian behavior, viscosity η decreasing with increasing shear stress. The effect may be exemplified by polyethylene [1] (Table 1).

Table 1. Effect of Shear Stress upon Viscosity of Polyethylene

	$\eta/(\text{kg m}^{-1} \text{ sec}^{-1})$ at shear stress of	
Temp/°K	1.0×10^2 N m^{-2}	1.0×10^3 N m^{-2}
418	3.85×10^3	3.3×10^3
471	1.9×10^3	1.3×10^3

The variations of η with shear stress are not very large, and since this study is concerned with the creation of low viscosity at elevated temperatures, it will be supposed that the situation approximates to Newtonian (shear rate $\propto$ shear stress). Under these conditions, an adequate shear rate in polymer processing equipment would occur at low shear stress. The main concern here is then with low (or in the limit zero) shear stress results.

Average Molecular Weight

For a monodisperse polymer system (at a particular temperature and a particular shear stress) both theory and experiment [5] indicate a relationship of viscosity to molecular weight, M, of the form shown in Fig. 1. There are two distinct relationships here, approximating to

$$\left.\begin{aligned}\log\,[\eta/(\mathrm{kg\ m^{-1}sec^{-1}})] &= 1.0\log M + X\\ \text{and } \log\,[\eta/(\mathrm{kg\ m^{-1}sec^{-1}})] &= 3.5\log M + Y\end{aligned}\right\} \qquad (1)$$

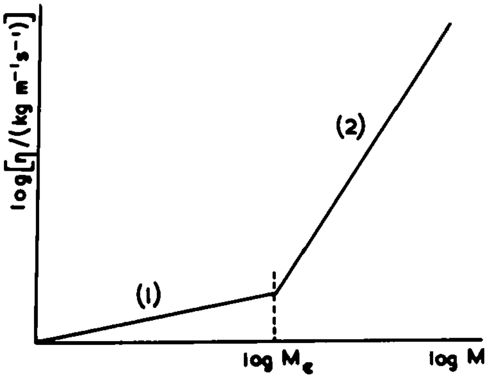

Fig. 1. Dependence of viscosity upon molecular weight.

M_e is twice the "molecular weight" between entanglement points and ranges from ca. 2×10^3 for polyethylene to ca. 4×10^4 for polystyrene [5]. At $M = M_e$

$$\log\,[\eta_e/(\mathrm{kg\ m^{-1}\ sec^{-1}})] \simeq 1.0\log M_e + X \simeq 3.5\log M_e + Y$$

so that

$$X - Y \simeq 2.5\log M_e$$

(X and Y are characteristic of the material, the temperature, and, to a lesser degree, the shear stress.)

For polydisperse systems, M may be replaced in Eq. (1) by the weight average molecular weight, M_w.

PREDICTION OF DEPENDENCE OF VISCOSITY UPON TEMPERATURE FOR A POLYMER SYSTEM IN WHICH M_w IS REVERSIBLY DEPENDENT UPON TEMPERATURE

Compounding the dependences of viscosity upon temperature and molecular weight,

$$\log\,[\eta/(\mathrm{kg\ m^{-1}\ sec^{-1}})] = f(T) + C \log M_W$$

C being ca. 1.0 or 3.5, according to whether $M_W < M_e$ or $M_W > M_e$, respectively. Consider the situations when M_W (a) remains constant at $M_W(1)$ at temperatures less than T′; (b) remains constant at $M_W(2)$ at temperatures less than T′; and (c) decreases reversibly from $M_W(1)$ to $M_W(2)$ as the temperature is increased from a low value to T′. From the schematic representation of these situations in Fig. 2, (a) has too high a viscosity at an elevated temperature T′; (b) has too low a viscosity at ambient temperatures; and (c) has desirable viscous behavior at both extremes. If there is little change in the average molecular weight above T′, the approach of curve (c) to curve (b) may be nearer to asymptotic than is indicated in Fig. 2, but this detail is irrelevant for the present purpose.

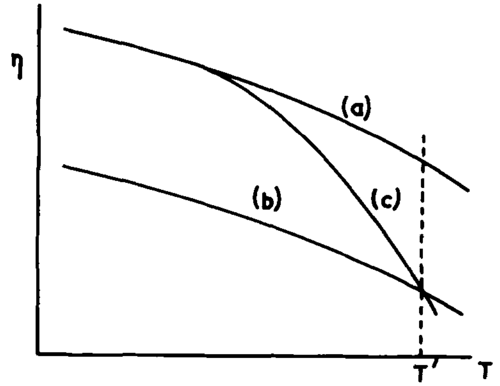

Fig. 2. Dependence of viscosity upon temperature.

If the change in molecular weight arises from the incorporation of bonds of low dissociation energy in the polymer system, there are several questions which must be considered:

(1) What sort of molecular weight variation with temperature is required?

(2) What magnitude of dissociation energy is required for the weak bonds?

(3) How may such bonds be realized in practice?

(4) At what intervals should the bonds be incorporated in the polymer system?

(5) Are the molecular weight changes rapidly established, i.e., are kinetic factors favorable?

Question (1) may be formulated more basically as follows. If curve (a) represents the behavior of a commercial polymer, and if T′ represents the temperature at which it is required to process the polymer melt, what sort of viscosity reduction is desirable at T′? Much will depend upon the particular polymer, but it will be supposed that, for the present considerations, reduction by a factor of ca. 10^3 is required for the viscosity. This figure is presumably appropriate to a constant shear rate. When modified to zero shear stress, the reduction may be rather larger, as indicated in the schematic representation of Fig. 3, where (A) represents a more viscous polymer than (B) and will show the greater deviations from linearity (Newtonian behavior). An estimated viscosity reduction factor (at zero shear stress) of 10^4 is used here. The corresponding molecular weight ratio $[M_W(1)/M_W(2)]$may then be deduced from Eqs. (1), but three distinct cases may be considered:

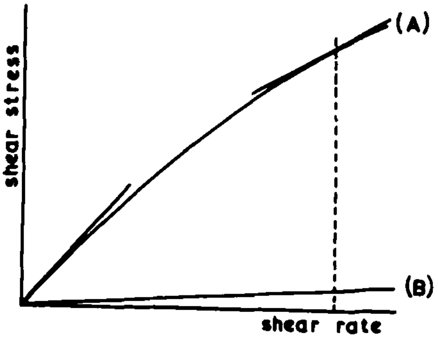

Fig. 3. Non-Newtonian behavior.

(i) Both $M_W(1)$ and $M_W(2) < M_e$:

$$\log [\eta(1)/\eta(2)] \simeq 1.0 \log [M_W(1)/M_W(2)]$$

so that for $\eta(1)/\eta(2) = 10^4, M_W(1)/M_W(2) \simeq 10^4$.

(ii) Both $M_W(1)$ and $M_W(2) > M_e$:

$$\log[\eta(1)/\eta(2)] \simeq 3.5 \log [M_W(1)/M_W(2)]$$

so that $M_W(1)/M_W(2) \simeq 14$.

(iii) $M_W(1) > M_e, M_W(2) < M_e$:

$$\log [\eta(1)/\eta(2)] \simeq \log \{M_W(1)^{3.5}/[M_W(2) \times M_e^{2.5}]\}$$

so that $M_W(1)/M_W(2) \simeq 10^4 \; [M_e/M_W(1)]^{2.5}$. This ranges between the two extremes of (i) and (ii).

For most polymer systems, situation (ii) will be the one which obtains in practice, i.e., commercial polymers correspond to portion (2) of Fig. 1 and a molecular weight reduction of ca. 14 is insufficient for passage onto portion (1). Summarizing, then, a reduction of molecular weight average by a factor of about 14 from ambient to processing temperature is desirable.

THERMODYNAMIC TREATMENT OF POLYMER CHAINS WITH REGULAR WEAK LINKS

General Theory

For normal paraffins of high molecular weight, it is well known [6] that the molar standard Gibbs function g^0 at corresponding temperatures increases regularly for each additional methylene group.† It will be assumed that this applies also to polymer chains in which monodisperse blocks are linearly connected by weak, chemical bonds. For an assembly of polymer chains, each having n blocks and therefore n - 1 weak bonds (henceforth designated links), the standard molar Gibbs function (relative to constituent elements in their normal states) is therefore

$$g_n^0 = ng_b^0 + (n - 1)g_l^0 \qquad (2)$$

where g_b^0 and g_l^0 are the contributions per block and per link, respectively.

Now consider a system comprising a variety of molecular sizes but all built from the same monodisperse blocks. On the basis of the existence of general chemical equilibrium, the system will present a large number of individual chemical equilibria. If each molecular species is represeented by the number of blocks it contains, i.e., by (n), chemical equilibria may be represented by the general chemical equation

$$\sum_{n=1}^{\infty} \nu_n(n) = 0$$

ν_n are the stoichiometric coefficients (positive for products, negative for reactants). For mass conservation, it will be necessary for

$$\sum_n \nu_n n = 0 \qquad (3)$$

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†After n-pentane, there is a virtually constant increase of 8.6 kJ mole^{-1} in the Gibbs function of formation per CH_2 in gaseous normal hydrocarbons [6].

At equilibrium, under conditions of constant temperature and pressure, the thermodynamic relationship,

$$\sum_n \nu_n \mu_n = 0 \tag{4}$$

must be satisfied; μ_n is the chemical potential of species (n) in the mixture. By one definition of activity a_n of this species,

$$\mu_n = g_n^0 + RT \ln a_n$$

(R being the gas constant) so that, combining with Eq. (4),

$$\sum_n \nu_n g_n^0 = -RT \ln (a_1^{\nu_1} a_2^{\nu_2} \ldots .) = -RT \ln [\Pi^n (a_n^{\nu_n})]$$

If ideality is assumed for simplicity, activity (on the present definition) may be replaced by mole fraction, x_n, so that

$$\sum_n \nu_n g_n^0 = -RT \ln [\Pi^n (x_n^{\nu_n})]$$

If this equation is combined with Eq. (2),

$$\sum_n \nu_n [ng_b^0 + (n - 1)g_l^0] = -RT \ln [\Pi^n (x_n^{\nu_n})]$$

which in conjunction with Eq. (3) yields

$$g_l^0 \sum_n \nu_n = RT \ln [\Pi^n (x_n^{\nu_n})]$$

This equation may be written in the parametric form

$$\left\{ \begin{array}{ll} \Pi^n (x_n^{\nu_n}) = A^{\sum_n \nu_n} & (5) \\ A = \exp(g_l^0/RT) & (6) \end{array} \right.$$

A is a function of temperature and is positive.

Equation (5) may be exemplified by species with small n as follows. For

$1(2) = 2(1)$ or $2(1) - 1(2) = 0$, $x_1^2 x_2^{-1} = A$;

$1(3) = 3(1)$ or $3(1) - 1(3) = 0$, $x_1^3 x_3^{-1} = A^2$;

$2(3) = 3(2)$ or $3(2) - 2(3) = 0$, $x_2^3 x_3^{-2} = A$.

These three results are not independent, and, in general, it is sufficient to restrict considerations to chemical equilibria of the type n(1) - 1(n) = 0, with n = 2 to ∞; the case of n = 1 is trivial. For such equilibria

$$x_1{}^n x_n{}^{-1} = A^{n-1} \tag{7}$$

From the definition of mole fraction, it then follows that

$$\sum_{n=1}^{\infty} x_n = 1 = \sum_{n=1}^{\infty} A^{1-n} x_1{}^n = A \sum_n (x_1/A)^n$$

The last summation is an infinite geometric progression and is clearly convergent. Thus

$$\begin{aligned} x_1/(1 - x_1/A) &= 1 \\ x_1 &= (1 + 1/A)^{-1} \end{aligned} \tag{8}$$

which, in combination with Eq. (7), gives

$$x_n = A(A + 1)^{-n} \tag{9}$$

On this basis, x_n diminishes with increasing n. This gives some validity to the approximation implicit in this treatment of an infinite range of polymer chain length, i.e., of n.

Average Molecular Weights

If the molecular weight of each monodisperse block is M_b, the molecular weight of an n-block polymer will be nM_b and the weight average molecular weight

$$M_w = \sum_n w_n n M_b \tag{10}$$

w_n is the weight fraction of the n-block polymer, and is given by

$$w_n = x_n n M_b / \sum_n (x_n n M_b)$$

Substituting in Eq. (10)

$$M_w = M_b \sum_n (x_n n^2) / \sum_n (x_n n)$$

which in conjunction with Eq. (9) gives

$$M_w = M_b \sum_n [n^2(A+1)^{-n}] / \sum_n [n(A+1)^{-n}]$$

The two summations are standard series [obtained by successive differentiations of the infinite geometric progression $\Sigma\,(A+1)^{-n}$ with respect to $(A+1)$]. The numerator and denominator series are, respectively, $(A+1)(A+2)/A^3$ and $(A+1)/A^2$, so that

$$M_w = M_b\,(1 + 2/A)$$

Use of Eq. (6) allows this expression to be rewritten as

$$\log\,(M_w/M_b - 1) = \log 2 - g_l^0/2.303RT \qquad (11)$$

g_l^0, the single-link contribution to the molar standard Gibbs function, may be expressed in terms of a molar standard enthalpy, h_l^0, and a molar standard entropy, s_l^0, by

$$g_l^0 = h_l^0 - Ts_l^0 \qquad (12)$$

The three molar quantities in Eq. (12) may be essentially defined in terms of the chemical change

$$n(1) \rightarrow (n)$$

If ΔG^0, ΔH^0, and ΔS^0 are the increases in standard Gibbs function, enthalpy and entropy per unit (or mole of) reaction,

$$z_l^0 = \Delta Z_l^0/(n-1)$$

$$z, Z = g, G \text{ or } h, H \text{ or } s, S$$

For condensed phases, h_l^0 may be approximated to the molar bond energy of the weak links, u (defined in such a way as to be negative). Thus, Eq. (12) may be approximated to

$$g_l^0 = u - Ts_l^0 \qquad (13)$$

allowing Eq. (11) to be rewritten as

$$\log\,(M_w/M_b - 1) = \log 2 + s_l^0/2.303R - u/2.303RT \qquad (14)$$

In this treatment, it is implicitly assumed that the bonds within blocks are much stronger than those between them, so that fission need only be considered at the latter. It will be further assumed that the quantities s_l^0 and u are temperature-independents. Values of M_W as a function of u and T may be deduced from Eq. (14), but unfortunately this equation involves the unknown quantity, s_l^0.

The number average molecular weight is expressed by

$$M_N = \sum_n x_n n M_b$$

which in combination with Eq. (9) gives

$$M_N = AM_b \sum_n n(A + 1)^{-n} = M_b (1 + 1/A) \tag{15}$$

Substitution of (1 + 1/A) from Eq. (8) then results in

$$x_1 = M_b/M_N \tag{16}$$

Combination of Eqs. (6), (13), and (15) gives

$$\log (M_N/M_b - 1) = s_l^0/2.303R - u/2.303RT$$

and comparison of this result with Eq. (14) yields

$$M_W/M_N = 2 - M_b/M_N$$

The Choice of a Value for the Link Entropy s_l^0

Dainton and Ivin [7, 8] have reviewed the thermodynamics of addition polymerization as determined both by direct measurements on monomer and polymer and by determination of the ceiling temperature. For olefin polymerizations, the following generalizations emerge.

(a) For (hypothetical) gas phase polymerizations, it is supposed that the loss of molecular rotational entropy is approximately equal to the composite gain in vibrational and internal rotational entropy. This appears to be equivalent to saying that the additional vibrational and internal rotational modes in the polymer are such that pseudorotation of the monomer segments arising from motion in these modes is, at least as far as entropy contribution is concerned, as free as the rotation of separate monomer molecules. As a consequence of this and the further approximation that the translational entropy of the monomer segment in the polymer molecule is zero, Δs^0_{gg}, the increase in standard entropy per mole of polymer bonds formed, may be equated to the negative of the standard-state translational entropy (including indistinguishability term) for the monomer molecule.

(b) Δs^0_{lc} (corresponding to Δs^0_{gg} but with liquid monomer and condensed-state polymer) - Δs^0_{gg} is approximately constant for corresponding materials: 44-59 J °K^{-1} mole^{-1} at 298°K.

For the present purpose, it will be assumed that these generalizations are still appropriate. The first of these assumptions is probably reasonable in view of the weakness of the links, where presumably internal rotation is essentially free and vibrational frequencies, particularly for bending modes, are low. On this basis, using propene as a convenient standard,

Δs^0_{gg} (present system) - Δs^0_{gg} (propene) $\simeq$ standard-state molar translational entropy (propene) - standard-state molar translational entropy (block)

and by use of standard statistical mechanical formulas for translational entropy [9], this equation may be written simply as

$$\Delta s^0_{gg}\text{ (present)} - \Delta s^0_{gg}\text{ (propene)} \simeq -\frac{3}{2} R \ln (M_b/M_{\text{propene}}) \qquad (17)$$

M_{propene} being the molecular weight of propene.

On the basis of applicability of generalization (b),

$$\Delta s^0_{lc}\text{ (present)} - \Delta s^0_{gg}\text{ (present)} \simeq \Delta s^0_{lc}\text{ (propene)} - \Delta s^0_{gg}\text{ (propene)}$$

Combination with Eq. (17) then yields

$$\Delta s^0_{lc}\text{ (present)} \simeq \Delta s^0_{lc}\text{ (propene)} - 3.455R \log (M_b/M_{\text{propene}})$$

$$\simeq (-113 - 29 \log (M_b/M_{\text{propene}})\text{ J °K}^{-1}\text{ mole}^{-1}$$

The standard state appropriate to these considerations is 1 mole (of monomer or monomer segments) dm^{-3}, but on the basis of the simplifying assumptions of (i) solution ideality, and (ii) zero volume change on polymerization, the same value of Δs^0_{lc} may be used when standard states are pure materials. Hence, Δs^0_{lc} (present) may be approximated to s^0_l. The value of the latter depends upon M_b/M_{propene} but not critically so. If the size of polymer block is chosen so that an assembly of unbonded blocks has a suitable low viscosity at the optimum processing temperature, then a value of 10^3 for the ratio is probably of the correct order of magnitude, in which case $s^0_l \simeq -200$ J °K^{-1} mole^{-1}. In view of the crudeness of this entropy calculation, some latitude is necessary, and a range from

-275 to -125 J °K^{-1} $mole^{-1}$ has been considered here. Table 2 presents the values of M_w/M_b at three temperatures (300, 400, and 500°K) for this range of s_l^0 and for values of u within the range -20 to -120 kJ $mole^{-1}$. Results for the lower values of the molecular weight ratio are also presented in graphical form in Fig. 4; for the sake of clarity, only the three central values of s_l^0 (-175, -200, and -225 J °K^{-1} $mole^{-1}$) are represented in the figure.

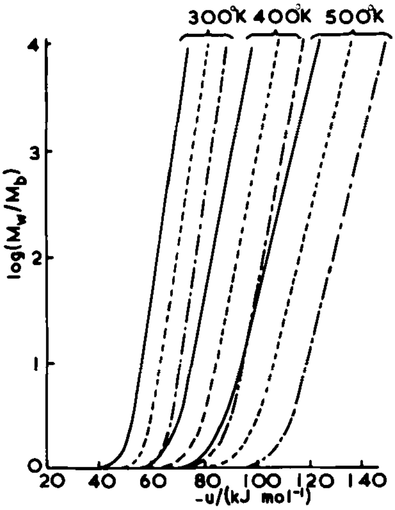


Fig. 4. Dependence of weight average molecular weight upon bond energy and link entropy: ——— s_l^0 = -175 J °K^{-1} $mole^{-1}$; - - - - - - s_l^0 = -200 J °K^{-1} $mole^{-1}$; — - — - s_l^0 = -225 J °K^{-1} $mole^{-1}$.

Conclusions

(a) A dissociation energy (-u) of 60 ± 20 kJ $mole^{-1}$ gives the right sort of change in average molecular weight on the basis of 400-500°K as optimum processing temperature.

(b) The size of block should be such as to give the desired high-temperature viscosity in an assembly of unbonded blocks.

(c) (i) For a particular link entropy, the optimum value of dissociation energy is fairly critical, as indicated in Table 3 appropriate for s_l^0 = -200 J °K^{-1} $mole^{-1}$. In this case -65 kJ $mole^{-1}$ represents the optimum value and even a deviation of 5 kJ $mole^{-1}$ may be larger than desirable.

Table 2. Values of M_w/M_b at 300, 400, and 500°K

$-u/(\mathrm{kJ\ mole^{-1}})$	M_w/M_b for $-s_1^0/(\mathrm{J\ {}^\circ K^{-1}\ mole^{-1}})$ = 125	150	175	200	225	275	275
20[a]	1.0	1.0	1.0	1.0	1.0	1.0	1.0
20[b]	1.0	1.0	1.0	1.0	1.0	1.0	1.0
20[c]	1.0	1.0	1.0	1.0	1.0	1.0	1.0
40[a]	6.5	1.3	1.0	1.0	1.0	1.0	1.0
40[b]	1.1	1.0	1.0	1.0	1.0	1.0	1.0
40[c]	1.0	1.0	1.0	1.0	1.0	1.0	1.0
60[a]	1.7×10^4	8.1×10^2	42	3.0	1.1	1.0	1.0
60[b]	45	3.1	1.1	1.0	1.0	1.0	1.0
60[c]	2.0	1.0	1.0	1.0	1.0	1.0	1.0
80[a]	5.0×10^7	2.5×10^6	1.2×10^5	6.2×10^3	3.1×10^2	16	1.7
80[b]	1.8×10^4	8.9×10^2	46	3.2	1.1	1.0	1.0
80[c]	1.3×10^2	7.2	1.3	1.0	1.0	1.0	1.0
100[a]	1.5×10^{11}	7.4×10^9	3.7×10^8	1.9×10^7	9.3×10^5	4.6×10^4	2.2×10^3
100[b]	7.6×10^6	3.7×10^5	1.9×10^4	9.3×10^2	48	3.3	1.1
100[c]	1.5×10^4	7.4×10^2	38	2.9	1.1	1.0	1.0
120[a]	4.6×10^{14}	2.2×10^{13}	1.1×10^{12}	5.6×10^{10}	2.8×10^9	1.4×10^8	6.8×10^6
120[b]	3.2×10^9	1.5×10^8	7.8×10^6	3.9×10^5	1.9×10^4	9.6×10^2	48
120[c]	1.8×10^6	8.9×10^4	4.5×10^3	2.2×10^2	12	1.6	1.0

[a] At 300°K.
[b] At 400°K.
[c] At 500°K.

Table 3. Values of M_w/M_b for $s_l^0 = -200$ J °K^{-1} mole^{-1}

Temp/°K	M_w/M_b for $-u$/(kJ mole^{-1}) = 55	60	65	70	75	80
300	1.3	3.0	16	1.1 $\times 10^2$	8.3 $\times 10^2$	6.2 $\times 10^3$
400	1.0	1.0	1.0	1.0	1.5	3.2
500	1.0	1.0	1.0	1.0	1.0	1.0

(ii) For a particular dissociation energy, the optimum value of link entropy is likewise fairly critical, as indicated in Table 4 appropriate for $u = -60$ kJ mole^{-1}. In this case, -185 ± 10 J °K^{-1} represents the optimum value and possible limits for the link entropy.

Table 4. Values of M_w/M_b for $u = -60$ kJ mole^{-1}

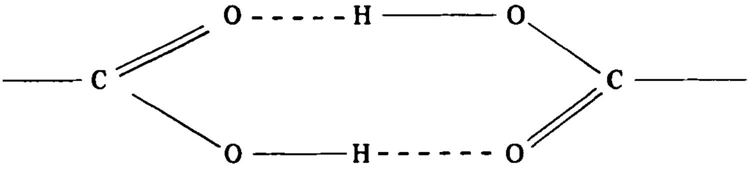
Temp/°K	M_w/M_b for $-s_l^0$/(J °K^{-1} mole^{-1}) = 165	175	185	195	205	215
300	1.3 $\times 10^2$	42	13	4.7	2.1	1.3
400	1.4	1.1	1.0	1.0	1.0	1.0
500	1.0	1.0	1.0	1.0	1.0	1.0

POSSIBLE BLOCK TERMINATIONS

Two types of termination are suggested here:

Strong Hydrogen-Bonding

The importance of intramolecular hydrogen-bonding in natural polymer systems is well established [10, 11]. In general, however, single hydrogen bonds are too weak for the present purpose; the order of magnitude of the energy [12] is 20 kJ mole^{-1}. The possibility of multiple hydrogen-bonding is nevertheless worthy of consideration, e.g.,



The energy involved in this double hydrogen bond may be judged from the data in Table 5 [13, 14].

Table 5. Standard Enthalpy Change for Dimer ⟶ Monomer (Gas Phase)

Acid	$\Delta H°$/ [kJ mole (of dimer)$^{-1}$]
Formic	59
Acetic	61
Trifluoroacetic	59
Benzoic	68

Donor-Acceptor Complexation

A number of donor-acceptor complexes have a dissociation energy (DA → D + A) around 60 kJ mole^{-1}. A comprehensive list has been given by Mortimer [15], but the values in Table 6 are representative.

Table 6. Stability of Donor-Acceptor Complexes

Complex	Dissociation enthalpy/ (kJ mole^{-1})
$MeNH_2 \cdot BMe_3$	73.8
$Me_2NH \cdot BMe_3$	80.6
$Me_3N \cdot BMe_3$	73.8
$EtNH_2 \cdot BMe_3$	75.4
$py \cdot MeSO_3H$	71.5
$py \cdot BF_3$	104.6
$Me_2S \cdot AlMe_3$	80.0
$Me_3P \cdot BF_3$	79.1
$Me_2O \cdot BF_3$	55.7

GENERALLY UNSUITABLE INTERBLOCK BONDING

Several other kinds of block termination have been considered and rejected as generally unsuitable, but there are some interesting qualifications which are probably worthy of consideration.

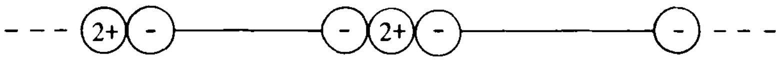
Ionic Forces [16]

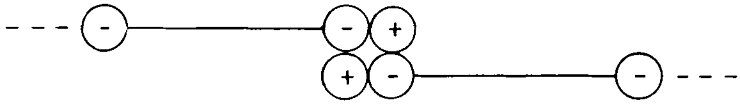
Several kinds of polymeric system may be examined when chain terminations are polar:

(a) All ions may be polymeric; within this category there are two possibilities represented schematically as

and

(b) Ions of one charge may be macromolecular, while those of opposite sign are small counterions, e.g.,

(i) 

(ii) 

The energy required for fission at the block terminations is a function of (1) the distance between "ionic centers," r; (2) the nature of the Born repulsion term, assumed for the present purpose to be proportional to an inverse power, q, of r; and (3) in the case of polymeric systems exemplified under (b) above, the nature of the fission process:

(i) ⟶ completely separated ions .... (I)

(i) ⟶ ion pairs  .... (II)

(ii) ⟶ completely separated ions .... (III)

(ii) ⟶ ions triplets  .... (IV)

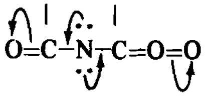
Table 7. Ionic Bond Energies

		$-u/(\mathrm{kJ\ mole^{-1}})$				
			(b)			
q	r/nm	(a)	I	II	III	IV
6	0.20	590	2050	880	1510	340
6	0.40	290	1020	440	760	170
9	0.20	620	2170	930	1600	360
9	0.40	310	1090	470	800	180
6	[a]	117	409	176	302	64
9	[a]	124	434	186	321	73

[a]Values of $-ur/(\mathrm{kJ\ mole^{-1}\ nm})$ are tabulated.

The energies involved in the fission processes for q = 6 and 9 are shown in Table 7 as a function of r, the smallest "ion center" spacing [it is assumed that this does not change in processes (II) and (IV)]. The following conclusions may be drawn from the figures in the table.

(1) The energies involved are much too large, particularly when doubly charged ions are concerned. In the most favorable cases, "ion center" separations would need to exceed 1 nm. In this respect, ions such as $-\overset{+}{N}R_3$ or $-SO_2\bar{N}R$, in which R is a large alkyl group, may be worth considering. Charge delocalization might also facilitate matters, e.g.,

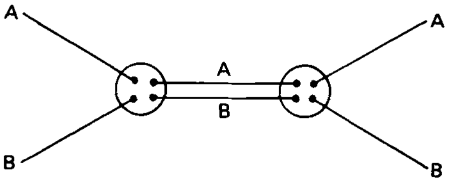


(2) Dissociation of aggregates into ion pairs, as in process (IV), gives a lower and more favorable energy. Ion aggregation occurs in soaps, which form layer lattices [17]. Quite probably, this is also the situation in "ionomers [18], i.e., linear, covalently bonded polymer units cross-linked by ionic bonds, commonly carboxylate anions and alkali metal cations.

There are several complications which could conceivably arise from ionic terminations and which would affect the simple model used here. Thermodynamic predictions may be correspondingly affected. These complications are discussed below.

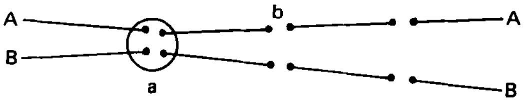
Variability of Link Energy Caused by Ion Aggregation. The following schematic diagrams illustrate some of the complications arising from this situation. Each circle represents an aggregate of four block terminations.

1.



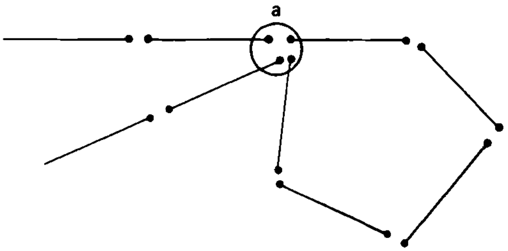
The energy required to separate chains A and B may be large due to multiple links between them.

2.



The energy required to separate chains A and B at a will be different from the energy required for fission at b.

3.



Dissociation at a in such a way as to open the loop produced no change in molecular weight. In fact, the viscosity might increase by virtue of an increase in the radius of gyration of the molecule [19].

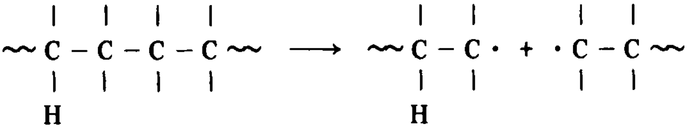
Cyclization. If polymer chains are cyclized both before and after block scission, zero energy change will be involved. There are probably kinetic objections to this, but the consequences are interesting. Equation (14) indicates an invariant M_W when u is zero.

Freedom of Bending Movement. The nondirectional character of an ionic bond will presumably lead to high bending mobility of these bonds. On the basis of complete freedom to this motion, one might compare the resultant zero bending force constant with typical values [20] of 10-100 N m^{-1} for covalent systems (at the atom adjacent to that involved in the bending). This difference may result in different temperature-viscosity behavior.

Covalent Bonds

Most common covalent bonds have a much higher dissociation energy [15] than 60 kJ mole^{-1}. Furthermore, bonds within the blocks would certainly be covalent, and it is assumed that these are not involved in the fission process. However, it should be noted that the energy required to separate two blocks at a covalent link is not necessarily the dissociation energy of the bond. A process akin to depolymerization, and exemplified here by a polymer system with a backbone carbon chain, may be considered in terms of three consecutive (but not necessarily mechanistic) stages, as follows:

(a)



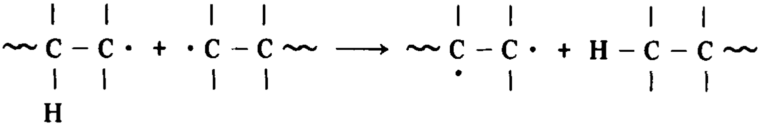
$$\sim\!\sim \overset{|}{\underset{\underset{\textstyle H}{|}}{C}} - \overset{|}{\underset{|}{C}} - \overset{|}{\underset{|}{C}} - \overset{|}{\underset{|}{C}} \sim\!\sim \longrightarrow \sim\!\sim \overset{|}{\underset{\underset{\textstyle H}{|}}{C}} - \overset{|}{\underset{|}{C}}\cdot + \cdot\overset{|}{\underset{|}{C}} - \overset{|}{\underset{|}{C}} \sim\!\sim$$

A typical example is

$$n\text{-}C_{24}H_{50} \longrightarrow 2(n\text{-}C_{12}H_{25})$$

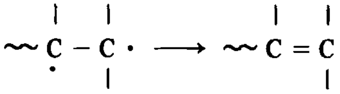
for which $\Delta H = 300$ kJ mole^{-1}. This has been deduced from data on polymerization termination [21].

(b)



$$\sim\!\sim \overset{|}{\underset{\underset{\textstyle H}{|}}{C}} - \overset{|}{\underset{|}{C}}\cdot + \cdot\overset{|}{\underset{|}{C}} - \overset{|}{\underset{|}{C}} \sim\!\sim \longrightarrow \sim\!\sim \overset{|}{\underset{\bullet}{C}} - \overset{|}{\underset{|}{C}}\cdot + H - \overset{|}{\underset{|}{C}} - \overset{|}{\underset{|}{C}} \sim\!\sim$$

(c)



$$\sim\!\sim \overset{|}{\underset{\bullet}{C}} - \overset{|}{\underset{|}{C}}\cdot \longrightarrow \sim\!\sim \overset{|}{C} = \overset{|}{\underset{|}{C}}$$

A typical example of composite (b), (c) is

$$2(n\text{-}C_{12}H_{25}) \longrightarrow n\text{-}C_{12}H_{24} + n\text{-}C_{12}H_{26}$$

for which $\Delta H = -218$ kJ mole^{-1}.

Thus, for the overall process

$$n\text{-}C_{24}H_{50} \longrightarrow n\text{-}C_{12}H_{24} + n\text{-}C_{12}H_{26}$$

$\Delta H = 84$ kJ mole^{-1}. This figure is surprisingly near to theoretical requirement. One must assume that there are adverse kinetic factors arising from (i) a multistage nature of the fission process and (ii) a high activation energy and/or low preexponential factors for one or more of the stages. Small steric factors seem very likely for the recombination process, but this ought not to be specific to covalent bonds.

An even lower "depolymerization" energy occurs in certain urethane and polyurethane systems, e.g., for [22]

$$\text{PhNHCON(Ph)CO}_2\text{Et} \longrightarrow \text{PhNCO} + \text{PhNHCO}_2\text{Et}$$

$\Delta H = 28$ kJ mole^{-1}. Furthermore, the activation energy for the decomposition of some polyurethanes is small [23], but the process is not normally a reversible one, carbon dioxide being evolved. The whole question of kinetic factors in single-stage fission and recombination is considered in part II of this study [2].

Molecular Forces

The presence of strong molecular (van der Waals) forces between polymer chains is responsible for the existence of condensed phases and for their viscous behavior. In practice, however, molecular forces are not capable of localization at specific (and in particular, terminal) sites as is the requirement here; indeed, the nonlocalizability allows a high degree of mobility of one chain relative to another in polymer melts. Except insofar as the presence of molecular forces will affect the assumption of ideality, the thermodynamic model used here does not exclude molecular aggregation.

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APPENDIX

Conversion Factors between SI and Other Units

1 thermochemical calorie = 4.184 J (exactly)
1 poise ≡ 1 g cm^{-1} sec^{-1} = 0.1 kg m^{-1} sec^{-1} (exactly)
1 dyn cm^{-2} = 0.1 N m^{-2} (exactly)
1 liter = 1 dm^3 (exactly)

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