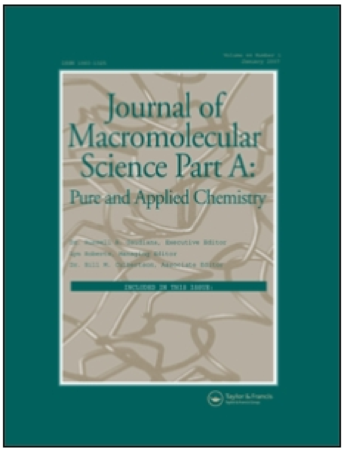

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Theoretical Considerations on the Possibility of Enhancing the Effect of Temperature upon the Melt Viscosity of Linear Polymers by the Incorporation of Weak Bonds in the Chains. II. Kinetic Factors

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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. II. Kinetic Factors

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SUMMARY

On the basis of a realization of thermodynamic requirements as given in part I, simple kinetic considerations are applied to the processes of weak bond fission and block recombination from two distinct bases: (a) independence of rate constants and viscosity (or average molecular weight) of the polymer system; and (b) a diffusion-controlled situation where the rate of block recombination is governed by the viscosity of the medium. On the independent rate constant model, an activation energy for the recombination process of less than 40 kJ [mole (of weak bonds)]$^{-1}$ gives an acceptable rate of equilibration at ambient temperatures; this criterion ought to be readily satisfied in practice. However, considerations of diffusion control suggest that equilibration may be too slow to be practicable,

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and this is probably the major limitation on preparing rigid polymers with temperature-varying molecular weights.

INTRODUCTION

In part I [1] of this series, the possibility of creating a polymer system with a temperature coefficient of viscosity larger than normal in magnitude has been considered in terms of polymer blocks reversibly joined in linear fashion by weak bonds. Several assumptions are implicit in the thermodynamic predictions. Perhaps the more important are (i) monodispersity of polymer blocks, (ii) ideality of polymer "mixtures," and (iii) rapid attainment of chemical equilibrium for both fission and recombination processes. It is not easy to predict the effects of deviation from the first stipulation, but in many cases monodispersity can be experimentally arranged or at least approximately so. The effect of nonideality can be predicted if the simplifying assumption is made that all polymer species have the same activity coefficient, f. Equation (7) of part I would then be modified so that A is replaced by A/f, and this replacement would then persist for later equations involving A. In the light of the definition of A in terms of link Gibbs function and thence in terms of link energy and link entropy, s_l^0, the replacement of A by A/f is equivalent to the replacement of s_l^0 by (s_l^0 + R ln f). For the link entropies considered in part I and for "normal" values of f, this modification ought not to have a radical effect on the conclusions of part I. Some preliminary considerations of the third assumption in multistage processes have already been presented in part I. In the present paper, a more detailed study of single-stage fission and recombination processes is described.

For this purpose, a simple model system has been chosen with the following characteristics: (i) a block molecular weight M_b of 10^5; (ii) free polymer blocks only for equilibrium at 500°K; (iii) a number average molecular weight of 10^6 for the 300°K equilibrium; (iv) a density of 1 g cm^{-3} at all temperatures and states of polymerization; (v) bimolecularity in the recombination process; and (vi) unimolecularity in the fission process. Recombination may be considered from two distinct standpoints:

(a) on the basis of rate constants being independent of viscosity, as reflected by average molecular weight; and

(b) on the basis of the reaction being diffusion-controlled.

APPROACH (a): INDEPENDENCE OF RATE CONSTANTS AND VISCOSITY

Number average molecular weight, density, and molar concentration of polymer molecules (amount/volume) may be simply related; number average molecular weight M_N is given by

M_N g mole^{-1}, the number average molar mass = mass/amount

$$= \frac{\text{density}}{\text{amount/volume}} \qquad (1)$$

Thus, on the basis of features (i) to (iv) of the present model, the molar concentration of polymer at 300 and 500°K is 10^{-3} and 10^{-2} mole dm^{-3}, respectively. From Eq. (16) of part I, the mole fraction of free blocks at 300°K is 0.1 at equilibrium.

Suppose that the higher-temperature, free block system is suddenly cooled to the lower temperature. The question arises as to how long it will take for equilibration. Full treatment of the kinetics would be exceedingly complex and probably intractable. Some simplifying assumptions have therefore been made:

(i) Rate constants are assumed to be independent of the size of polymer molecule involved.

(ii) The mole fraction of free blocks is taken as constant, at the approximate mean of the two extremes, throughout the reaction.

(iii) The attainment of a molar concentration of polymer molecules of 10^{-3} mole dm^{-3} is assumed to mark completion of reaction.

The two opposing processes (and their associated rate constants) may be schematically represented as

$$\text{(I)}\ \ P + P \xrightarrow{k_r} P$$
$$\text{(II)}\ \ P\ \text{(except free blocks)} \xrightarrow{k_f} P + P$$

In these reactions, P symbolizes any polymer molecule. The rate constants are defined by

d [product P]/dt by (I) = $k_r[P]^2$, and
d [reactant P]/dt by (II) = k_f[P other than free blocks] $= k'_f[P]$

where $(1 - k'_f/k_f)$ is the assumed constant mole fraction of free blocks. The net rate of decrease of polymer concentration

$$-d[P]/dt = k_r[P]^2 - k'_f[P] \qquad (2)$$

At equilibrium $[P] = [P]_e$ and

$$k_r[P] = k_f'$$

Combination of this relationship with Eq. (2), followed by integration, gives reaction time

$$t = \frac{1}{k_r[P]_e} \ln \frac{[P]([P]_e - [P]_i)}{[P]_i([P]_e - [P])}$$

In the present situation, $[P]_e = 10^{-3}$ mole dm^{-3}, and $[P]_i$, the initial concentration, $= 10^{-2}$ mole dm^{-3}. For $[P] = 1.45 \times 10^{-3}$ mole dm^{-3}, corresponding to 95% completion of reaction,

$$t_{95\%} = \ln 2.9/(k_r \times 10^{-3} \text{ mole dm}^{-3})$$

so that for $t_{95\%} = 10$ sec, a reasonable maximum for this quantity, $k_r = 106$ dm^3 $mole^{-1}$ sec^{-1}. This then represents a sensible minimum for the recombination rate constant; in logarithmic terms,

$$\left\{\log\ [k_r/(\text{dm}^3\ \text{mole}^{-1}\ \text{sec}^{-1})]\right\}_{\min} = 2.03$$

If it is assumed that the rate constant satisfies the usual Arrhenius relationship, then

$$\log (k_r/A_r) = -E_r/2.303RT$$

where A_r and E_r are the corresponding preexponential factor and activation energy, respectively. At 300°K

$$\log\ [k_r/(\text{dm}^3\ \text{mole}^{-1}\ \text{sec}^{-1})] = \log\ [A_r/(\text{dm}^3\ \text{mole}^{-1}\ \text{sec}^{-1})]$$
$$- 0.174E_r/(\text{kJ mole}^{-1})$$

For liquid-phase reactions, the preexponential factor is frequently [2] of the order of 10^{11} dm^3 $mole^{-1}$ sec^{-1}, but for the present purpose consider the range 10^8-10^{12} dm^3 $mole^{-1}$ sec^{-1}. A number of reactions [3] have preexponential factors near the lower limit of this range. Values of log $[k_r/(dm^3\ mole^{-1}\ sec^{-1})]$ corresponding to various values of log $[A_r/(dm^3\ mole^{-1}\ sec^{-1})]$ and E_r are presented in Table 1. Positions in the table above the stepped line correspond to satisfactory recombination rates.

Table 1. Values of log $[k_r/(dm^3\ mole^{-1}\ sec^{-1})]$ at 300°K

E_r/ (kJ mole^{-1}	log $[k_r/(dm^3\ mole^{-1}\ sec^{-1})]$ for log $[A_r/(dm^3\ mole^{-1}\ sec^{-1})]$ = 8	9	10	11	12
25	3.65	4.65	5.65	6.65	7.65
30	2.78	3.78	4.78	5.78	6.78
35	1.91	2.91	3.91	4.91	5.91
40	1.04	2.04	3.04	4.04	5.04
45	0.17	1.17	2.17	3.17	4.17
50	-0.70	0.30	1.30	2.30	3.30
55	-1.57	-0.57	0.43	1.43	2.43
60	-2.44	-1.44	-0.44	0.56	1.56
65	-3.31	-2.31	-1.31	-0.31	0.69

Even for the most unfavorable preexponential factor, an activation energy less then 30 kJ mole^{-1} will suffice. Perhaps the nearest, well-established analog of the recombination process is the radical combination termination in polymerization reactions (although the nature of the bonding will generally be different). Kinetic characteristics of this analog for a number of polymers are given [4] in Table 2. Combination with Table 1 indicates that in every case the rate constant exceeds 106 dm^3 mole^{-1} sec^{-1} at 300°K.

If the rate of block recombination is adequate at 300°K, the question then arises as to whether the rate of fission is satisfactory at the higher temperature of 500°K. On the basis of an equilibrium constitution of 100% free blocks at this temperature, recombination by chemical reaction (I) may be neglected, and as a result of reaction (II) only,

$$d[P]/dt = k_f' [P]$$

subject again to the approximation of constant mole fraction of free blocks during the process. Integration of the first-order rate law yields

$$t = k_f'^{\,-1} \ln ([P]/[P]_i) \qquad (3)$$

If the initial state has the constitution of the 300°K equilibrium system,

Table 2. Kinetic Characteristics of Radical Combination Terminations

Monomer	Activation energy/ (kJ mole^{-1})	log [preexponential factor/ (dm^3 mole^{-1} sec^{-1})]
Vinyl acetate	13	9.6
Methyl methacrylate	5	8.0
Styrene	8	7.8
Methyl acrylate	ca. 2	ca. 8.2
Vinyl chloride	18	11.8
Methacrylonitrile	21	10.7

$[P]_i = 10^{-3}$ mole dm^{-3}, and the time for 95% conversion, corresponding to $[P] = 9.55 \times 10^{-3}$ mole dm^{-3}, is

$$t_{95\%} = 2.26/k_f'$$

(The fact that Eq. (3) gives a finite time for 100% conversion arises from the approximation used.) For $t_{95\%} < 10$ sec (again taken as a reasonable maximum), $k_f' > 0.23$ sec^{-1} or $\log (k_f'/\text{sec}^{-1}) > -0.64$.

If it is assumed that the internal energy change for the process is 60 kJ mole^{-1}, conforming to the theoretical requirements of part I, the fission activation energy will be E_r + 60 kJ mole^{-1}. Then, on the basis of the Arrhenius equation at 500°K,

$$\log (k_f'/\text{sec}^{-1}) = \log (A_f'/\text{sec}^{-1}) - 6.3 - 0.104E_r/(\text{kJ mole}^{-1})$$

For unimolecular reactions, the preexponential factor A_f' is commonly in the range 10^{13}-10^{15} sec^{-1}, the lower value being in accord with transition-state theory; the difference between k_f and k_f' should not affect the range significantly. Table 3 presents values of $\log (k_f'/\text{sec}^{-1})$ corresponding to various values of the recombination activation energy and $\log (A_f'/\text{sec}^{-1})$ within the specified range. The table shows that recombination activation energies less than 70 kJ mole^{-1} result in satisfactory fission (corresponding to positions above the stepped line). On the basis of analogy with combination termination in polymerization, this would seem likely.

The activation energy [5] for homolytic fission in a paraffinic chain is of the order 300 kJ mole^{-1}. If this is the first stage of a fission process for such materials, the high activation energy is clearly prohibitive.

Table 3. Values of $\log(k'_f/s^{-1})$ at 500°K

E_r/	$\log(k'_f/\mathrm{sec}^{-1})$ for $\log(A'_f/\mathrm{sec}^{-1})$ =		
(kJ mole^{-1})	13	14	15
55	1.0	2.0	3.0
60	0.5	1.5	2.5
65	-0.1	0.9	1.9
70	-0.6	0.4	1.4
75	-1.1	-0.1	0.9
80	-1.6	-0.6	0.4
85	-2.1	-1.1	-0.1
90	-2.7	-1.7	-0.7
95	-3.2	-2.2	-1.2

APPROACH (b): DIFFUSION-CONTROLLED RECOMBINATION

There is evidence for diffusion control [6] in polymerization termination reactions when the medium has high viscosity [7, 8]. By analogy, it seems quite likely that recombination in the present systems may also be diffusion-controlled. According to North [8], the rate constant for radical combination in a diffusion-controlled situation is given by†

$$k_r = 2RT\ [(1 + r_A^2/r_B^2)^{\frac{1}{2}} + (1 + r_B^2/r_A^2)^{\frac{1}{2}}]/3\eta \qquad (4)$$

where R is the gas constant, η is the viscosity of the medium (solution), and r_A, r_B are the "hydrodynamic radii" of the two combining polymer molecules A,B. On the basis of the simplifying assumption that $r_A = r_B$,

$$k_r = 4\sqrt{2}RT/3\eta$$

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†In Ref. [8], reactant concentration is defined in molecular terms and the gas constant is replaced by Boltzmann's constant.

and at 300°K

$$\mathrm{kr} = 4.70 \times 10^3\ \mathrm{J\ mole^{-1}}/\eta$$
$$= 4.70 \times 10^6\ \mathrm{dm^3\ mole^{-1}\ sec^{-1}\ kg\ m^{-1}\ sec^{-1}}/\eta$$
$$\log\ [\mathrm{k_r/(dm^3\ mole^{-1}\ sec^{-1})}] = 6.67 - \log\ [\eta/(\mathrm{kg\ m^{-1}\ sec^{-1}})] \qquad (5)$$

For a typical polymer melt [9], polystyrene at 473°K and a shear stress of $4.6 \times 10^4\ \mathrm{N\ m^{-2}}$,

$$\log\ [\eta/(\mathrm{kg\ m^{-1}\ sec^{-1}})] = 3.32 \log M_V - 13.85$$

This equation has been transformed to one appertaining to 300°K by using the known variation of polystyrene viscosity with temperature [10] and assuming (i) that this variation is essentially independent of average molecular weight, (ii) that molecular weight dependence of viscosity is the same at the two temperatures, and (iii) Newtonian behavior. The resultant equation is

$$\log\ [\eta/(\mathrm{kg\ m^{-1}\ sec^{-1}})] = 3.32 \log M_V - 12.88 \qquad (6)$$

M_V is the viscosity average molecular weight, but it will be supposed that this may be approximated by the number average, M_N. Then combination of Eq. (5)—assuming that this may be transferred to the present system—and Eq. (6) gives

$$\log\ [\mathrm{k_r/(dm^3\ mole^{-1}\ sec^{-1})}] = 19.55 - 3.32 \log M_N \qquad (7)$$

For values of M_N of 10^5 and 10^6, this equation results in k_r values of 8.9×10^2 and $4.3 \times 10^{-1}\ \mathrm{dm^3\ mole^{-1}\ sec^{-1}}$, respectively. This would suggest that the initial rate of recombination at 300°K is quite adequate, but that the process is considerably retarded as the average molecular weight and melt viscosity increase.

For a density of $1\ \mathrm{g\ cm^{-3}}$, Eq. (1) may be written

$$\log M_N = 3 - \log \left\{ [\mathrm{P}]/(\mathrm{mole\ dm^{-3}}) \right\}$$

and combination with Eq. (7) then gives a relationship between k_r and [P], viz.,

$$\log\ [\mathrm{k_r/(dm^3\ mole^{-1}\ sec^{-1})}] = 9.59 + 3.32 \log \left\{ [\mathrm{P}]/(\mathrm{mole\ dm^{-3}}) \right\}$$

or

$$k_r = 3.9 \times 10^9 \text{ dm}^3 \text{ mole}^{-1} \text{ sec}^{-1} ([P]/\text{mole dm}^{-3})^{3.32} \qquad (8)$$

If for simplicity the reverse process of fission is ignored in the approach to equilibrium, Eq. (2) may be simplified to

$$-d[P]/dt = k_r[P]^2$$

Association of this relationship with Eq. (8) yields

$$-d[P]/dt = 3.9 \times 10^9 (\text{mole dm}^{-3})^{-4.32} \text{ sec}^{-1} [P]^{5.32}$$

which integrates to

$$[P]^{-4.32} - [P]_i^{-4.32} = 1.69 \times 10^{10} (\text{mole dm}^{-3})^{-4.32} \text{ sec}^{-1} t$$

If $[P]_i = 10^{-2}$ mole dm^{-3} and $[P] = 10^{-3}$ mole dm^{-3}, the reaction time $t = 540$ sec, which is rather excessive. After 10 sec, $[P] = 2.5 \times 10^{-3}$ mole dm^{-3} corresponding to 83% conversion, but this will not be adequate for the present purpose since it will correspond to attainment of only 5% of the final viscosity ($\eta \propto [P]^{-3.32}$). This may be compared with 95% conversion, which corresponds to 29% attainment of the final viscosity.

It is well known that polyfunctional polymer molecules (in contrast to the bifunctional ones required by the present model) react together at an adequate rate. An n-fold increase in the functionality of polymeric blocks might be expected to increase the probability of intermolecular reaction, as measured by the rate constant k_r, by a factor of about n^2 and thus to reduce the reaction time by this factor. Clearly, a fairly small value of n would effect a satisfactory reduction. However, complications would arise from the possibilities of (i) intramolecular reaction, (ii) multiple intermolecular linkages (and a resultant variability in block-to-block bonding energy), and (iii) cross-linking.

On the whole, then, these considerations of diffusion control oppose the feasibility of rapid equilibration at near-ambient temperatures. This is enhanced by the experimental finding [8] that Eq. (4) predicts rate constants for termination processes in radical polymerizations which are too large by a factor of about 200. On the other hand, the present conclusions are specific to a particular system. Other situations may behave more or less favorably. For example, when the temperature falls below the glass transition temperature, very high viscosities must result. Indeed, under these conditions the mobility of the polymeric species may become effectively zero. The possibility of using reversible linkages would therefore appear to be greater in a noncrystalline rubber than in a polymeric glass.

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