Role of Chain Length in Degradation Process (Chain Breakdown)

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ABSTRACT: The role of molecular weight of a chain in the chain breakdown in diluted solution at a constant concentration of chain molecules and constant temperature is discussed theoretically using the methods of the theory of the activated complex and kinetics of cooperative processes. The reaction starts at the certain molecular weight of the chain. The chain breakdown is the flat increasing function of the chain molecular weight. This function has a limit when chain molecular weight approaches infinity. Such dependence is explained by the increase of flexibility (following two theories) and increase of extra entropy of molecules of different sizes (following kinetics of cooperative processes. Unequal reactivity of chemically identical active centers links to the dependence of chain flexibility on the location of the more flexible part (place of reaction) of the chain. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 84: 1810–1817, 2002; DOI 10.1002/app.10356

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INTRODUCTION

It was found in studying degradation of chain molecules that under definite conditions reaction begins at certain value of molecular weight. This weight is defined by the strength of chemical bonds.[1] Thermodynamic probability of initiation of any process, for example, degradation is defined by the equality of thermodynamic potentials of the initial and final systems. Particularly, it is valid for Gibbs free energy[2]

$$\Delta G = G_f - G_i = 0$$

where ΔG is the Gibbs free energy variation throughout the process, G_f is the free energy of formation of a solution after degradation (final state), and G_i is the free energy of the formation of a solution prior to degradation (initial state).

Gibbs free energy (or free energy) is used to describe the process carrying out at constant temperature (T) and pressure.

A number of examples show that degradation of polymers (infinitely long chains with Gaussian distribution between the end points) can be described by rate constants of elemental chemical reactions. These constants do not depend on molecular weight if the degradation mechanism remains unchanged. Because the molecular weight of a chain reduces continuously throughout the process, it is clear that starting from a certain chain length, the dependence of rate constant on the chain length becomes very weak. Therefore, the dependence of rate constants of degradation on molecular weight is normally observed at moderate values of molecular weight (olygomers).[3]

In olygomers, reactivity should be referred to a molecule as a whole (system) (more correctly to the molecular active center), whereas in polymers reactivity is referred to specific reactivity center (monomer unit). Any chemical reaction of olygomers represents chemico-mechanical process,
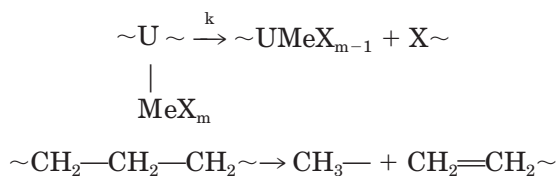
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i.e., the process, where free energy is altered by the change of the system as a whole, not only by chemical processes.[3] If we consider the chain molecule as a system, its change presumes variation of the chain length and/or local rigidity. Breakdown of the chain molecule leads to an increase of the number of molecules and a decrease of their length, thus altering the dependence of the system free energy on the molecular length at a constant concentration of molecules.

For this reason, olygomer chains are characterized by the dependence of the rate constant of the process also on the location of the reaction. If chain breakdown does not occur, the length can be altered only by the ratio of conformers.[4] A variation of the conformer ratio, which can be observed in olygomers due to the variation of molecular weight, may alter the effective rate constant of the process due to the different reactivity of conformers. However, we do not touch this problem in the current work.

The scope of this work is the study of the dependence of the rate of chain breakdown on the chain length. Because breakdown of a relatively long chain (chain length is two times longer than the length of thermally stable chain) can take place several times, we consider the initial rate of degradation of chain molecules of different lengths.

Suppose that we have diluted solution of chain molecules (i.e., we can neglect interaction between chain molecules) at constant conditions (temperature, solvent). We assume that starting from a definite chain length, chemical reaction is carried out, which follows, for instance, the schemes

$$\sim U \sim \xrightarrow{k} \sim UMeX_{m-1} + X\sim$$
$$| $$
$$MeX_m$$

$$\sim CH_2\text{---}CH_2\text{---}CH_2\sim \rightarrow CH_3\text{---} + CH_2\text{=}CH_2\sim$$

The first scheme corresponds of the degradation of the complexes of polyethers (e.g., poly ethyleneoxide) with metals, for example, AlR_3.[3] In this case U = O (atom of oxygen in the chain).

Solvent consists of one kind of nonassociated molecules. Other chemical processes do not take place in the solution. There is no molecular weight distribution in chain molecules, i.e., all chains have the same length. Because we consider only the effect of chain on the process, we assume that all chains have a regular structure and consist of the same conformers, i.e., chain length L is proportional to the number of monomer units n and unit length l ($L = nl$).

Kinetics of this process can be described in terms of the theory of activated complexes (formal kinetics)[5,6] or in terms of kinetics of cooperative processes.[7] Let us assume that system equilibrium can be reached faster at given composition of solution, than degradation process carries out. Then, following formal kinetics we can write equation of reaction rate V in standard form of first order reaction[5]

$$V = -dC/dt - kC$$

where C is current concentration of degrading chain molecules, which is equal:

$$C = C_o \exp(-kt) \qquad (1)$$

Here, C_o is initial concentration of chain molecules, t is time.

The constant rate of reaction is defined by free energies of formation of initial chain and activated complex

$$k = \chi kT/h \ \exp(-\Delta G^+/RT)$$
$$= \chi kT/h \ \exp(-\Delta S^+/RT) \exp(-\Delta H^+/RT)$$

where ΔG^+, ΔS^+, and ΔH^+ are free energy, entropy, and enthalpy of activation, respectively, which are equal to the difference of corresponding functions in the activated complex and initial state, as, for example:

$$\Delta G^+ = G^+ - G$$

where χkT is transmission coefficient, and k and h are Boltzman and Plank constants.

Free energy of the formation of the diluted solution of free molecules prior to degradation (initial state) can be deduced assuming additive character of components[1]

$$G_i = G_{st} + G_s + G_{id} + \Delta G_{ex} + G_b + G_l + \Delta G_{ss}$$

where G_{st} is the free energy of the formation of chain molecules in the stretched state, G_s is the free energy of solvent formation, G_{id} is the free energy of the ideal mixture, ΔG_{ex} is the extra free energy of the mixture of molecules of different

sizes (chain and solvent), G_b is the free energy of the chain bend in the solution, G_l is the free energy of the local interaction between the chain and solvent, ΔG_{ss} is the free energy of the interaction between the solvent molecules during their transport from the bulk to the chain.

If the activated complex if formed by deformation of the breaking bond, then the free energy of the formation of the solution of chains containing the activated complex consists of the same components of free energy of the formation of solution (final state).

Thus, variation of free energy due to the formation of the activated complex is equal to

$$\Delta G_i = \Delta G_{st} + \Delta\Delta G_{ex} + \Delta G_b + \Delta G_l + \Delta\Delta G_{ss}$$

where the symbol Δ characterizes the variation of the corresponding component of free energy, equal to the difference between components of the final and initial state.

Because the number of molecules remains the same during the transition to the activated complex $\Delta G_{id} = 0$, the value $(\Delta G_{st} + \Delta G_l + \Delta G_{ss})$ depends weakly on the chain length (if molecules are relatively large ΔG_{ss} approaches zero) because geometry of an initial part if the reacting chain and activated complex is defined only by local interactions. The amount of solvent molecules that surround the initial chain and activated complex is approximately the same. Therefore, $\Delta\Delta G_{ex}$ decreases with an increase of the polymer chain approaching zero. Taking the above into account we can write

$$\Delta G_i = \Delta G_b + \Delta G_{li}$$

where ΔG_{li} is the variation of the free energy due to local interactions

$$k = k_{li} \exp(-\Delta G_b/RT)$$

i.e., the polymer specifics become obvious due to the changes in the chain bend.

Because free energy of the bend is defined mainly by a change of entropy, the dependence of the rate constant of the degradation on the chain length is due to the change of entropy. This is similar to other processes with participation of the chain molecules.

The dependence of free energy of the chain bend on the chain length links to the ratio $\overline{R^2}/\overline{R_o^2}$ varying from $L^2/\overline{R_o^2}$ ($S_b/n = 0$, where S_b is the
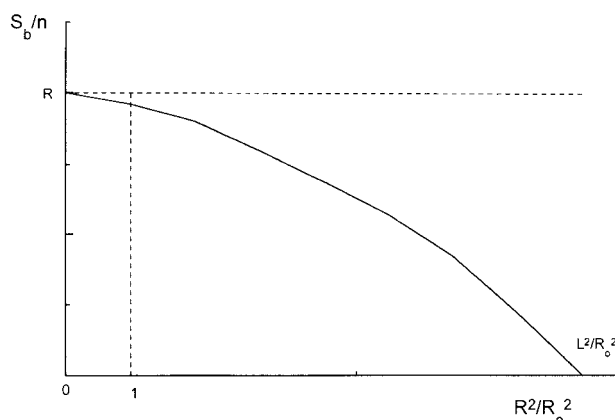

Figure 1 Dependence of the entropy of the chain bend referred to the monomer unit S_b/n on the ratio between average squares of the distance between chain ends in solution and the isolated state R^2/R_o^2.

entropy of the chain bend) to 1 ($S_b/n = R$) (Fig. 1). Because the precise mathematical link between the above ratio and entropy of the bend is not known, we can use the empirical equation

$$S_b/n = \alpha[1 - \beta \exp(-\overline{R^2}/\overline{R_o^2})]$$

where α and β are defined by initial conditions

$$\alpha = R/\{[1 - \exp(L^2 - \overline{R_o^2})/\overline{R_o^2}]\}$$

$$\beta = \exp(L^2/\overline{R_o^2})$$

The empirical equation is chosen for the following reasons: (a) the function has a limit, but the dependence is not linear; (b) function is continuous and flat; and (c) because R^2 is described by the two constant parameters (a/RT and L), it was presumed that the function is also characterized by two parameters.

$\overline{R_o^2}$ can be found by standard methods,[4] and $\overline{R^2}$ can be calculated using a model or measured experimentally. Here we use the Landau-Lifshitz model,[8] where $\overline{R^2}$ is characterized by the chain length L and local rigidity of isolated chain a. $\overline{R^2}$ can be calculated on the basis of experimental data on viscosity.

For infinitely long chains (polymers) $S/n = R$ and $\overline{R^2} = 2\,La/RT$, whereas for short chains R^2 approaches L^2.

In diluted solutions local rigidity of the isolated chain must be substituted by apparent local rigidity a_l, which satisfies the following equation[3]

$$a_l = 40a^2/(40a - L^2p)$$

Here, p is parameter of chain–solvent interaction. Apparent local rigidity of a chain increases with an increase of its length approaching infinity at $L_{\lim} = (40a/p)^{1/2}$. It is one of the reasons of the existence of thermally stable chain lengths in the solution. As a_l approaches infinity, the chain is being stretched, and the chain bend is equal to zero at $L_{\lim}$. Because $\overline{R^2} \approx L^2$ for short chains, dependence of the chain bend entropy on chain length has extreme character (Fig. 2). The extreme value can be calculated finding maximal value of $\overline{R^2}/\overline{R_o^2}$ and substituting a by a_l in the expression for $\overline{R^2}$.[8]

For chains containing an activated complex in a certain place of the chain (say in the middle), the dependence of the bend entropy is similar to that on the chain length of initial molecules. Due to less local rigidity a_l, less local interaction of solvent with that part of the chain that contains an activated complex and longer chain length, the bend entropy will have a larger value, but this value is less than the bend entropy of the isolated chain (Fig. 2).

Hence, the integral case rate constant of the reaction is larger than the rate constant of the degradation of chains that have no bend. Apparently, degradation begins when free energy of the bend has an extreme at a certain value of the chain length. If it is valid, the dependence of the
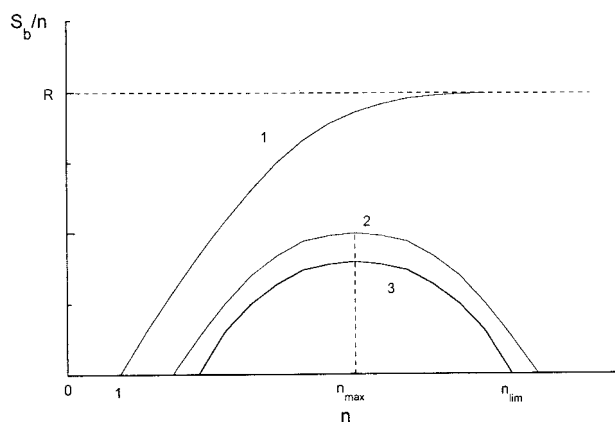

Figure 2 Dependence of the entropy of the chain bend referred to the monomer unit S_b/n on chain length n; n_{max} is the chain length corresponding to the maximum value of S_b/n; $n_{\lim}$ is the chain length corresponding to infinite local rigidity; 1—isolated chain, 2—chain containing activated complex, 3—chain in solution.
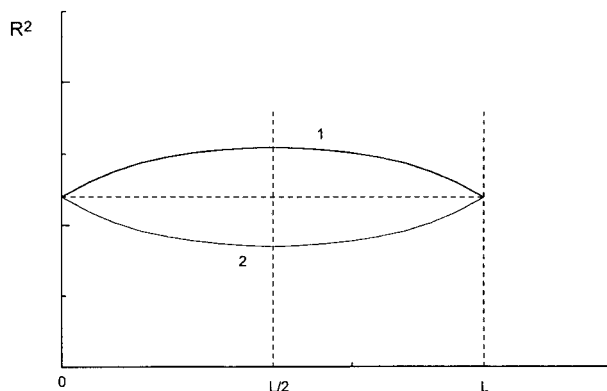

Figure 3 Dependence of the average squares of the distance between chain ends R^2 on location of one flexible or rigid part of constant length in a chain, L is the chain length: 1—local rigidity is less than local rigidity of the main chain; 2—local rigidity is more than local rigidity of the main chain.

rate constant on the chain length approaches a constant value observed in the experiment.

Note that an increase of the chain length provokes association of molecules and an increase of the time required to reach equilibrium macromolecular shape in the initial state and in the activated complex. This makes experimental study of the dependence of the rate of degradation on chain length more difficult.

The values of $\overline{R^2}$ and S are defined by location of rigid and flexible units if the number of these units is equal (Fig. 3). Therefore, for olygomer compounds the reaction, most probably, takes place in the middle of the chain.[3] If the chain has only one break point, the reaction of degradation takes place in the middle of the chain only.

As the length of the degrading chain increases, the degradation process involves parts located far from the middle. If formal kinetics is valid to describing degradation, then variation of the bend and local rigidity can be found, which are due to the deformation of a chemical bond. It can be done by estimating distribution of the products of reaction. The deformation can be calculated assuming a certain structure of the activated complex. For example, here we assume the same angles between bonds. It should also be taken into account that the apparent rate constant is an average of local rate constants.

With a further increase of the chain length (in polymers) nearly all chain parts will degrade with equal probability because reactivity of the end groups can be neglected. Thus, reactivity does not depend on chain length, and the rate constant of

degradation can be estimated by relating the effective rate of process to the overall concentration of active centers.[9]

If degradation follows fluctuation of solvent molecules from the place of reaction to the chain, the most probable place of fluctuation is the middle of the olygomer chain (fluctuation results in p and a_l decrease). The probability of reaction is the same throughout the chain. The activated complex is formed due to the deformation of the degrading bond in the place of fluctuation of the solvent. For this reason the kinetic of the process is similar to the above; however, the initial concentration C_i is less than C_o. Initial concentration is defined by the probability of the fluctuation process.

Because we consider the reaction in the diluted solution of the olygomer and polymer chains (cooperative systems), the equation describing cooperative chemical reactions[7] can be used to describe the kinetics of the irreversible first-order reaction. In this case the equation of the rate of reaction is substituted by the equation of the acceleration of the reaction

$$\partial G/\partial C = M_x d^2 C/dt^2 = f/C d^2 C/dt^2 \qquad (2)$$

where M_x is the parameter characterizing the chemical reaction, and $d^2 C/dt^2$ is the acceleration of the reaction, $f/C = M_x$.

$\partial G/\partial C$ represents the chemical potential at constant temperature and pressure, and relatively large concentrations of the reacting compounds.[2,10] This parameter describes the mol variation of free energy in a system. Use of the derivative $\partial G/\partial C$ presumes the existence of chemical potentials in systems, where chemical processes take place, not only at equilibrium. Taking into account the assumption of an additive character of free energy components, we can estimate the effect of any ΔG component on the process.

The barrier of chemical reaction (k) and mol variation of free energy of reaction defines the f value. This value weakly depends on concentration: $f = (G_b - G_a)/k^2$ where k is defined by movement of an intermediate particle through the reaction barrier.[11] In fact, f characterizes kinetic probability of the process that is defined by movement of an intermediate particle along the reaction barrier. Application of thermodynamic potentials (e.g., $\partial G/\partial C$) as a driving force of the process enables application of variation principles for identification of the reaction mechanism.

Condensed phases are characterized by a weak local interaction chain–solvent (energy of local interaction is less than RT). In this case, reaction starts, apparently, from fluctuation of the solvent molecule at the local place of the chain.[7] Due to fluctuation, energetic nonequilibrium is observed, which leads to the reaction. Apparently, the active particle goes up along the reaction barrier. Because the probability of fluctuation is proportional to $\exp(G_s/RT)$ (G_s is the free energy of the formation of local intermolecular bond chain–solvent), the expression for the concentration of active centers C_a is similar to that derived from consideration of formal kinetics.

$$C_a = C_o \exp(G_s/RT) = K_{sf} C_{so}$$

It is clear that larger G_s value results in a bigger difference between energy of the active centers of solvent molecules. On the other hand, it leads to smaller C_o values. As pointed out above, fluctuation has the same probability along the chain molecule in the polymers, and has the variable probability in olygomers. The start of the reaction in the place of fluctuation is further confirmed by a volume increase during the degradation process.

Strong local interaction between the solvent and chain (interaction energy is larger than RT) probably results in a new way for the reaction to starting from the solvent fluctuation. Then activated particles move along reaction coordinates deforming the chemical bond. As the reaction barrier is overcome, chain molecules take a desirable shape. To simplify study of the role of the chain length in the degradation process it is assumed that diffusion is faster than the chemical reaction. The variation of the chain shape in the solution, which is characterized by variation of $\overline{R^2}$, links to the variation of a_l with the chain length. If degradation results in the molecules of the same shape, the rate of this process is very low, and it reduces with an increase of the chain length.

Using variation methods,[7] a conclusion can be drawn about the following successive stages of the degradation process: fluctuation of solvent, chemical degradation, and changes of the shape of forming chains. Applying the same principles the part of the molecules can be estimated, which can be formed out of the basic mechanism. An evaluation showed the low probability of the following reaction: chain fluctuation to the desirable shape with a subsequent chain reaction.
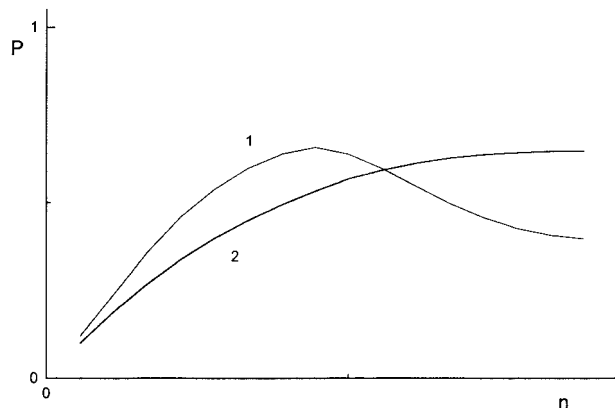
Figure 4   Probability of fluctuation of the molecule of the solvent P in the middle of the chain as it depends on the chain length n: 1—equilibrium chain shape can be reached during the fluctuation period; 2—equilibrium chain shape cannot be reached during fluctuation period.

The final stage of the process starts after chain breakdown only, because if the chain is not broken, the place of breakdown has more effect on the chain flexibility than the end group forming. A very long chain may be characterized by nonequilibrium. It is clear that application of initial state thermodynamics requires analysis of the equilibrium shape of initial chains prior to reaction. This is because a rate of chain formation increases with the length of initial chains. The stage of formation of equilibrium shape can be observed experimentally.[12] However, in this case, the experimental techniques can be applied (e.g., calorimetry or molecular weight distribution), which enable skipping the final stage.

Dependence of fluctuation on the chain length can be better viewed for nondegrading chains (Fig. 4). In this case, the most variable parameter is G_b, because concentration of the molecules remains unchanged, and variation of a number of contacts chain–solvent is minor. The specific character of solvent fluctuation links, basically, to the "chain effect."[3] The dependence of free energy of fluctuation on the chain length has an extreme in a definite place of the chain (e.g., in the middle of the chain).

If formation of the equilibrium shape is a slower process than degradation (the most realistic case), free energy is an increasing function of the chain length. This function has a limit. Maximal increase of the free energy of bending is observed if there is no component of free energy, which links to the chain bending at equilibrium.

All intermediate cases are also possible. The far chain is from equilibrium, the more is free energy gain due to fluctuation of solvent molecules. All the above relates to the fluctuation of solvent molecules and chain bending. It is also applicable if kinetics of degradation is considered in terms of formal kinetics.

To estimate kinetics of the process one should find free energy of the formation of the final state, and then the driving force of the process. In contrast to definition of the formal kinetics, here the final state is solution forming, as the result of degradation. The free energy of its formation G_f' is equal to

$$G_f' = G_f' + G_s + G_{st}' + G_{id}' + \Delta G_{ex}'$$
$$+ G_b' + G_l' + \Delta G_{ss}'$$

Here, the symbol "'" refers to free energies of the final state.

To simplify consideration we assume that breakdown has taken place in the middle of the chain (all chain molecules are of the same size). Furthermore, all components depending on chain length are average values.

Values of G_l' and $\Delta G_{ss}'$ are different from G_l and ΔG_{ss} due to the different bends of the initial and final chain and a different number of chain–solvent contacts. The latter is more than the number of contacts of initial chains because of a different free energy of fluctuation and additional contacts of solvent molecules with end groups.

Following the above free energy of the process ΔG can be written as

$$\Delta G = \Delta G_x + \Delta G_{st} + \Delta\Delta G_{ex} + \Delta G_b + \Delta G_l + \Delta\Delta G_{ss}$$

Because components relating to local interactions weakly depend on chain length, it can be aggregated in one item ΔG_o: $\Delta G_o = \Delta G_x + \Delta G_l + \Delta G_{ss}$

Because other components of free energy have entropy character, the dependence of degradation on chain length is of entropy character also. Therefore, enthalpy of the process does not depend on molecular weight of initial chain. When two equal molecules are formed from one,[1] free energy of ideal mixing is equal to

$$\Delta G_{id} = -RT[1/2x_2'x_1 \ln(x_2/x_1) + \ln(1 + x_2)$$
$$- x_2' \ln 2].$$

Here, the symbol "'" refers to mol parts of solvent (x_1) and chain (x_2) molecules in the final state.

Note that the above equation is derived assuming total concentration of chain and solvent molecules no more than 1 mol/L. Therefore, the numerical solution will require normalization to actual concentrations.

If initial concentration of chain molecules remains unchanged and breakdown of each molecule results in formation of a constant number of new molecules, this component of free energy is constant, i.e., it does not depend on molecular weight.

Extra free energy of mixing of molecules of different sizes[1] follows the equation

$$\Delta\Delta G_{id} = -RT[1/2x_2'x_1 \ln r + \ln(1 + x_2) - x_2' \ln 2]$$

where r is the number of places occupied by the chain molecule in the quasi-crystal cell assuming that one solvent molecule occupies one place in this cell. The above equation is obtained using the Flory-Huggins assumption.[13,14] It was assumed that the number of places in the quasi-crystal cell, in which the chain molecule is occupied is equal to $r/2$. Additional contacts of solvent with chain ends are neglected. The first approximation of r dependence on molecular weight of initial chain values is linear. The accuracy of this linear approximation increases with an increase of molecular weight. Therefore, ΔG_{id} is the flat function of the chain length, which has a limit (Fig. 5).

To estimate ΔG_b one should find R_j^2 values at final $(j = f)$ and initial $(j = i)$ states. Then using the ratio $\overline{R^2}/\overline{R_o^2}$, the entropy of the bend can be found. The dependence of ΔG_b on chain length
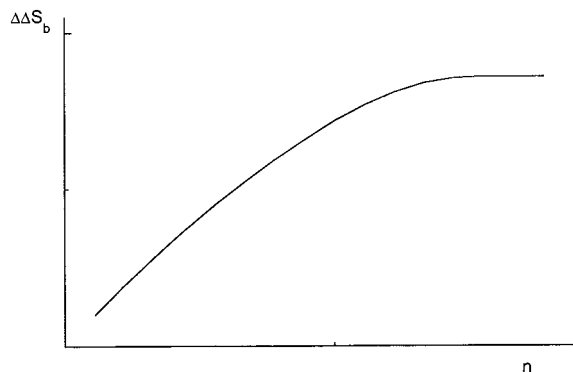

Figure 5   Dependence of free energy $\Delta\Delta G_{id}$ of mixing of molecules of different sizes (chain and solvent) on the chain length n.
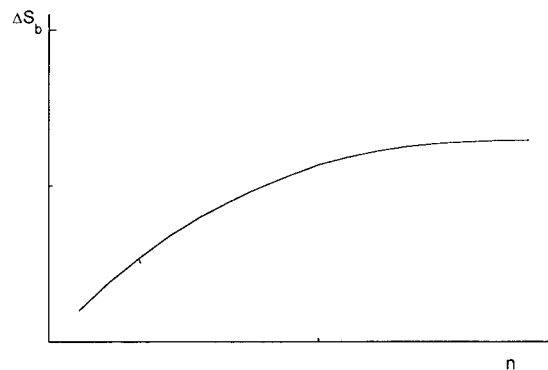

Figure 6   Dependence of free energy of the chain bend in solution ΔS_b on the chain length n.

approaches a limit as is shown in Figure 6, because solution is uneasily formed at certain chain lengths. An increase of degradation rate due to the sharp increase of thermodynamic instability of the initial chains is similar to polymer decomposition in the condensed phase.[15] Degradation, which takes several places, is out of current consideration.

Therefore, the dependence of degradation on molecular weight links to a variation of the entropy of mixing of the molecules of different sizes.

Because $\Delta\Delta G_b$ and ΔG_b are flat functions having a limit, the rate constant is a flat function of the chain length, and it has a limit that is justified experimentally.

Note that the parameter f required to solve the kinetic problem can be found from

$$f = (G_b - G_a)/k^2 = \Delta G_{chem}/k^2$$

where ΔG_{chem} is the free energy of varying particles (molecules).

Because we consider the breakdown of chains of a specific size, the partial derivative $\partial G/\partial C$ can be substituted by a finite difference $\Delta G/\Delta C$, and ΔG can be represented as a sum of two items

$$\Delta G = \Delta G_{chem} + \Delta G_c$$

where ΔG_c is the free energy of the system throughout the process.

Hence, the rate constant, which is observed in the cooperative system, can be characterized as the production of the rate constant of the process considered in terms of formal kinetics and function of the system as a whole.

In a general case following from the thermodynamics, the partial derivative of thermodynamic potential in respect to concentration can be the function of concentration (chemical potential μ). For this reason, the second-order differential equation should be considered for proper solution. The solution of such equations is described in details in the handbooks on mathematics (see refs. 16 and 17 for examples):

$$t + q_2 = \pm \int dC/2 \int f(C)dC + q_1$$

where $f = \mu C/f$, q_1 and q_2 are constants of integration.

Therefore, using both approaches we obtain the same result: the dependence rate constant of degradation (chain breakdown) is a flat function of molecular weight having a limit. We presume that consideration of the process in terms of cooperative kinetics is more correct because it takes into account all changes in the system. Following this method, the rate constant depends on concentration of initial molecules due to the dependence of $\Delta\Delta G_{id}$ on concentration. However, consideration of this dependence is beyond the current article.

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