

Effect of Radiation on the Persistent Length of a Chain

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The effect of radiation on the persistent length of a chain in a water solution of polymer is considered in the work. This effect is suggested to be related to the breaking of the hydrogen bonds in hydrate layers around the chain. The kinetic equation of the breakage of the hydrogen bonds is defined and the stationary solution is found with the help of the equation. The expression of average value of the persistent length of the chain at a fixed average number of broken bonds is determined by means of the Poisson distribution. We found that the persistent length of the chain at irradiation is smaller than that of one without irradiation. Therefore we suggest that this effect of the “softening” of conformations by irradiation which breaks hydrogen bonds has to be revealed experimentally in situations where macroeffects depend on the persistent length of the chain.

Introduction

Taking into account the influence of different factors on a conformation of polymers is of great importance as conformational properties define most peculiarities of synthetic polymers as well as of bio-polymers. The temperature dependence of flexibility, and the influence of solution quality and the presence of various salts on flexibility are well known. In our theoretical model we consider conformational change in the polymer chain under the external factor irradiation. In polymers of the condensed state radiation usually causes radiation-stimulated polymerisation and degradation¹, radiation-stimulated cross-linking and network formation², increase in the crystallinity degree³. In this work we will discuss changing the polymer chain conformation under irradiation (for instance, infrared laser) in a water solution of polymer.

Theoretical Model

We can suppose that the bonded water^{4,5} around a macromolecule in a water solution of polymers hardens a chain and results in an increase in the persistent length of the chain \bar{l}_p . We can suppose that the persistent length of the chain has to change at irradiation of such a solution. On the basis of this effect, a breakage of hydrogen bonds in hydrate layers around the chain is suggested to take place⁶.

The kinetic equation for the breakage of the hydrogen bonds is defined as

$$\frac{dN_p}{dt} = \lambda - \alpha N_p^2 \quad (1)$$

Here N_p is the concentration of the hydrogen bonds in the hydrate layers, the first term on the right is the contribution to the rate of the breakage of the hydrogen bonds from irradiation (λ - irradiation power) and the second term takes into account their restoration, the rate of which is characterised by α .

The kinetic equation is solved and we receive the following solution (Fig. 1):

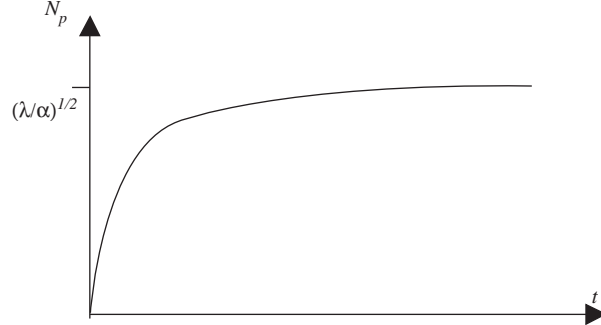


Figure 1. Kinetics of the breakage of hydrogen bonds in water solution of polymer.

$$N_p = \sqrt{\frac{\lambda}{\alpha} \left[\frac{e^{2t\sqrt{\lambda\alpha}} + 1}{e^{2t\sqrt{\lambda\alpha}} - 1} \right]} \quad (2)$$

The stationary solution of equation (1) is the following:

$$N_p = \sqrt{\frac{\lambda}{\alpha}} \text{ at } t \rightarrow \infty \quad (3)$$

An orientation of the chain is supposed to change where a breakage of the hydrogen bonds takes place. In this case the persistent length of the chain is defined by $l_p \approx N_p^{-1/3}$. If the average number of broken hydrogen bonds \bar{M}_p is known the Poisson distribution will be used for determining the probability of the breakage of the M_p hydrogen bonds

$$W(\bar{M}_p, M_p) = \frac{(\bar{M}_p)^{M_p} e^{-\bar{M}_p}}{M_p!} \quad (4)$$

Then we can define the following expression for the average persistent length of the chain

$$\bar{l}_p = \sum_{M_p} W(\bar{M}_p, M_p) \times N_p^{-1/3} \quad (5)$$

Accounting for $N_p^{-1/3} = \left(\frac{M_p}{V}\right)^{-1/3}$, (where V is the volume of bonded water around the chain) the following expression has to be determined as

$$\bar{l}_p = V^{1/3} \sum_{M_p^*}^{M_p^{\max}} \frac{(\bar{M}_p)^{M_p} e^{-\bar{M}_p}}{M_p!} \times M_p^{-1/3} \quad (6)$$

The evaluation of the average number of broken hydrogen bonds has indicated that \bar{M}_p is smaller than 1. Therefore the following term, which is the largest contribution to the sum, is preserved

$$\bar{l}_p \approx V^{1/3} \frac{(\bar{M}_p)^{M_p^*} e^{-\bar{M}_p}}{M_p^*} \quad (7)$$

where M_p^* is the parameter defining the minimum number of broken hydrogen bonds at which the persistent length of the chain begins to change. The analysis showed that the persistent length of the chain upon irradiation is smaller than that without it (Fig. 2).

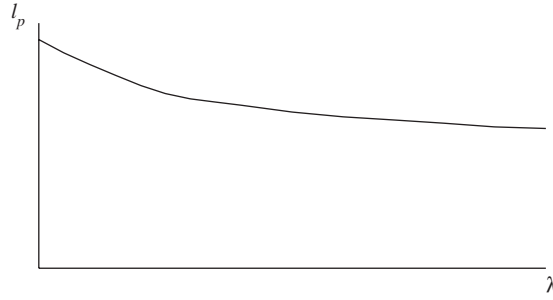


Figure 2. Schematic plot of the persistent length as a function of irradiation power.

Discussion of the results

The discussed effect of the “softening” of macromolecule conformations during irradiation which breaks hydrogen bonds should be revealed experimentally in many situations when macroeffects depend on the persistent length of the chain.

We can show that the hydrodynamic viscosity of the solution depends on this effect. In fact the viscosity of the solution in θ -solvent depends on the size of a macromolecule⁷

$$\eta_o = \frac{\Phi_0}{M} (\bar{h}^2)^{3/2} \quad (8)$$

In (8) Φ_0 is the universal constant, and M is the molecular weight. On the other hand, the size of the macromolecule depends on the persistent length of a chain in the following way

$$\bar{h}^2 = 2Ll_p \quad \text{at } l_p \ll L \quad (9)$$

Therefore the hydrodynamic viscosity of the solution after irradiation should be written as

$$\eta_{eff} = \frac{\Phi_o}{M} (\bar{h}_{eff}^2)^{3/2} \quad (10)$$

If we define the persistent length of the chain in an irradiated solution as $l_p^* = l_p - \delta l_p$, then $\bar{h}_{eff}^2 = \bar{h}^2 \left(1 - \frac{\delta l_p}{l_p}\right)$. The viscosity of the irradiated solution was rewritten in the following way:

$$\eta_{eff} = \eta_0 \left(1 - \frac{\delta l_p}{l_p}\right)^{3/2} \quad (11)$$

It is clear from this that the viscosity of the solution is decreased by irradiation (Fig. 3)

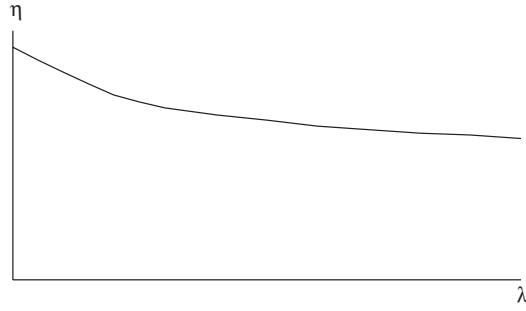


Figure 3. Schematic plot of hydrodynamic viscosity as a function of irradiation.

Generally there are 2 available mechanisms by which the breakage of the hydrogen bonds can take place:

- mechanism of vibrations excitation⁶;
- excitonic mechanism⁸.

These mechanisms correspond to different values of the cross-section of breaking hydrogen bonds

$$\lambda = N_o \sigma I \quad (12)$$

where N_o is the concentration of the hydrogen bonds, σ is the cross-section of the process of breaking hydrogen bonds, and I is the intensity of the irradiation.

This effect is realised by modern laser techniques. The first mechanism is preferable with irradiation by infrared laser. In that case the cross-section of the breakage of the hydrogen bond is defined by the probability of exciting n -level vibrations at the certain meaning of the external field⁶

$$\sigma \rightarrow w_n = \frac{1}{n!} (\varepsilon(t) / \hbar\omega)^n \exp(-\varepsilon(t) / \hbar\omega) \quad (13)$$

where $\varepsilon(t)$ is the quasi-classical work done under the system, and $\hbar\omega$ is the energy of the phonon. In the case of exciting a hydrogen bond to n -oscillation level, that is $\varepsilon(t) = n\hbar\omega$, we obtain the following estimation of the probability of exciting n -number of phonons

$$w_n \approx \frac{1}{n!} n^n \exp(-n) \quad (14)$$

Conclusion

Note that the discussed mechanisms of the persistent length decrease may be important for biological evolution (“softening” the macromolecular conformation leads to an increase in available polymer conformations). A different effect of the conformation change seems to be revealed in polymer solution under ionised irradiation. Here the ionised electrons under irradiation are trapped on a chain and result in an increase in the persistent length of the chain because of the coulomb repulsion of negatively charged links of the chain that displayed polyelectrolyte properties⁹. Such effects must be taken into account in the analysis of experiments of polymer irradiation in which the situation depends upon conformation.

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