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CONTRIBUTION TO THE EVALUATION OF THE TENSION OF POLYMERIC CHAINS WITH JUNCTIONS

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Statistical mechanical methods of equilibrium have been used to evaluate the tension of a polymeric chain and then of polymeric chains that are jointed together with permanent junctions, by considering the free energy of the system. The tension is shown to increase when there exist junctions, i.e. when the motion of a chain depends on the motion of other chains. This is also an experimental fact. The dependence of the tension on the position of the junction points has been studied and also the dependence of this tension on the number of molecular units of the macromolecule. The result has been compared to that for the macromolecules without junctions.

1. *Introduction*

The tension of a molecular network has been studied by Treloar[1)] macroscopically by considering the deformations of a solid network. When the positions of the junction points between two macromolecular chains are known, a microscopic point of view is necessary.

In order to obtain a kinetic theory for elastopolymers the bead-rod Kramers' model[2)] has been used, but an elastic restoring force has been allowed on the molecular units with a temperature dependent coefficient of restitution. This restoring force used by Rouse[3)] and Zimm[4)] gives a Gaussian chain.

In the present work we study the tension of a chain with its ends fixed at specified points. Since the tension is proportional to the length of the chain, the molecular chain may be regarded as having an elasticity governed by Hooke's law. The method followed is a statistical mechanical method of equilibrium. This tension has been calculated by Treloar[1)] for a molecular network by considering the deformations of a solid network from a macroscopical point of view.

The method we use allows calculations of the tension of a chain having junctions with other chains and we can see how junctions affect the tension of a polymeric chain from a microscopical point of view.

2. *The tension of a chain*

A Gaussian chain has a potential energy given by

$$U = \frac{\alpha}{2}\left[(x_1 - x_0)^2 + \dots (x_{N-1} - x_{N-2})^2\right], \tag{1}$$

where

$$\alpha = \frac{8kT}{\pi l^2}. \tag{2}$$

$x_0,\ x_1,\ \dots,\ x_{N-1}$ are the position vectors of the N molecular units and l is a mean value of the typical bond length. The coefficient α has been evaluated from

$$\langle r \rangle = \frac{\int\limits_0^\infty r P(r) \mathrm{d}r}{\int\limits_0^\infty P(r) \mathrm{d}r}, \tag{3}$$

where $r = x_j - x_{j-1}$ has been equated to the typical bond length l.

The coefficient α is temperature dependent, as expected, because the restoring force depends on the bond length and the bond length depends on the individual motion of each molecular unit.

If f is the tension of the chain, the potential energy of the chain contains the potential energy due to the tension, i.e.

$$U_f = bkT \sum_{j=0}^{N-2} (x_{j+1} - x_j)^2 - f|x_{N-1} - x_0|, \tag{4}$$

where

$$b = \frac{4}{\pi l^2}. \tag{5}$$

For such a statistical mechanical problem the distribution is a Bolzmann distribution and the probability takes the form

$$P_f[x_j] = C_f \, \exp\left(-\frac{1}{kT}U_f\right) \,, \tag{6}$$

where C_f is the normalizing factor given by

$$C_f = \left[\int \exp\left(-\frac{1}{kT}U_f\right) \prod_{j=0}^{N-1} \mathrm{d}x_f\right]^{-1} \,, \tag{7}$$

and the symbol $P_f[x_j]$ stands for

$$P_f(x_0,\ x_1,\ ,x_2,\ \ldots,\ x_{N-1})\,.$$

Using the probability (6) and integrating with respect to all x_j's except x_0 and x_{N-1}, the probability $P_{2f}(x_{N-1},\ x_0)$ that governs the position vectors of the end points can be calculated (see Appendix A). Therefore, for a Gaussian chain with tension f, the probability that the first molecular unit is at x_0 and the last molecular unit is at x_{N-1} is

$$P_{2f}(x_{N-1}, x_0) = C_{2f} \, \exp\left[-\frac{b}{N-1}(x_{N-1}-x_0)^2 + \frac{f}{kT}|x_{N-1}-x_0|\right], \tag{8}$$

where C_{2f} is the normalizing factor given by

$$C_{2f} = \left(\frac{b}{\pi(N-1)}\right)^{3/2} \frac{1}{V} \left\{\exp\left[\frac{f^2(N-1)}{4k^2T^2b}\right]\right\}^{-1} \,, \tag{9}$$

where V is the volume obtained by the integration over the last variable. Using (8), the mean length of this chain can be calculated

$$\langle|x_{N-1}-x_0|\rangle = \int |x_{N-1}-x_0| \, \exp\Big[-\frac{b}{N-1}(x_{N-1}-x_0)^2$$

$$+\frac{f}{kT}|x_{N-1}-x_0|\Big]\mathrm{d}x_{N-1}\mathrm{d}x_0 = kT\frac{\partial}{\partial f}\int \exp\Big[-\frac{b}{N-1}(x_{N-1}-x_0)^2$$

$$+\frac{f}{kT}|x_{N-1}-x_0|\Big]\mathrm{d}x_{N-1}\mathrm{d}x_0 = \frac{f(N-1)}{2kTb}\,. \tag{10}$$

The dependence of the tension f on the mean length of the chain can be obtained from (10) by substituting b from (5),

$$f = 2kT\,\frac{4}{\pi}\,\frac{1}{(N-1)l^2}\langle|x_{N-1}-x_0|\rangle\,. \tag{11}$$

The tension f depends on temperature T in a linear way (see Anthony, Caston and Guth[5]). The result is similar to that of Treloar[1] but this method can be used to obtain the tension of a chain when there exist junction points.

The shear modulus G is the tension per cm^2 and for polymer samples in the form of flat sheets such as ethylene glycol dimethacrylate (EGDM), triethylene glycol dimethacrylate (TrEGDM) and tetraethylene glycol dimethacrylate (TEGDM) we have experimental results (Katz and Tobolsky[6]). The 10 sec. shear modulus G is linearly dependent upon temperature in the region of room temperature up to 200° C. This experimental result is in full agreement with our theoretical one, which shows this linear dependence of the tension on temperature.

3. *Effect of junctions on the tension of a chain*

According to our model (Flory[7]) a polymer mixture exists in a dynamic state with intermolecular interactions being formed and broken continuously. The equilibrium condition can be expressed by (Howe and Coleman, Ref. 8)

$$\sum_{ij}(R_{Fij} - R_{Dij}) = Q = 0, \qquad \frac{\partial Q}{\partial T} = 0\,,$$

where $R_{Dij} = N_{ij}r_{ij} \Big/ \sum_{ij} N_{ij}r_{ij}$ is the rate of deformation, i. e. the number of $i - j$ contacts multiplied by the relative frequency and

$$R_{Fij} = \varphi'\varphi' \Big/ \sum_{ij} \varphi'_j\varphi'_j$$

is the dissociation rate of the $i - j$ contact.

φ'_i, φ'_j are the effective site fractions of unbonded species. The problem of crosslinking efficiencies was discussed by Lochaek and Fox[9], Shultz[10] and Hwa[11].

The plots of the effect of the position of the crosslinking on the tension of the polymer chain are in agreement with the plots of Howe and Coleman[8], Moonan and Tschoegl[12].

By junction points we mean the interlocking of two molecules that belong to two different chains in such a way that they behave mechanically as one molecule. The number of such junction points will be theoretically two per chain (Treloar[1]).

Treloar, using the original theory of Kuhn, calculated the tension of a vulcanized rubber network by considering the deformation of the rubber using the extension ratios λ_1, λ_2, λ_3 under conditions of constant volume. The problem of polymers with junctions can be treated microscopically by considering a group of polymeric chains, where successive molecules of the same chain are permanently connected to each other by primary chemical bonds, and two molecular units belonging to two different chains are also connected to each other to form permanent junctions.

We begin by considering two macromolecules. Each macromolecule consists of N molecular units with position vectors $x_0^{(1)}$, $x_1^{(1)}$, $\ldots x_{N-1}^{(1)}$, for the first chain and $x_0^{(2)}$, $x_1^{(2)}$, $\ldots x_{N-1}^{(2)}$ for the second chain. The m-th molecule of the first chain is jointed with to the k-th molecule of the second chain. These two molecules can be identified using a δ-function.

The probability distribution for the molecules of the two chains will contain the potential energy of the two chains under tension conditions and it will be given by

$$P_{2N}\big[x^{(1)}, x^{(2)}\big] \prod_{j=1}^{N-1} \mathrm{d}x_j^{(1)} \mathrm{d}x_j^{(2)}$$

$$= C_{2N}\, \exp\Bigg[-b \sum_{j=0}^{N-2} \big(x_{j+1}^{(1)} - x_j^{(1)}\big)^2 - b \sum_{j=0}^{N-2} \big(x_{j+1}^{(2)} - x_j^{(2)}\big)^2$$

$$+ \frac{f}{kT}\big|x_{N-1}^{(1)} - x_0^{(1)}\big| + \frac{f}{kT}\big|x_{N-1}^{(2)} - x_0^{(2)}\big|\Bigg] \delta\big(x_m^{(1)} - x_k^{(2)}\big) \prod_{j=0}^{N-1} \mathrm{d}x^{(1)} \mathrm{d}x^{(2)}, \qquad (12)$$

where C_{2N} is the normalizing factor,

$$C_{2N} = \Bigg\{ \int \exp\Bigg[-b \sum_{j=0}^{N-2} \big(x_{j+1}^{(1)} - x_j^{(1)}\big)^2 - b \sum_{j=0}^{N-2} \big(x_{j+1}^{(2)} - x_j^{(2)}\big)^2 \qquad (13)$$

$$+ \frac{f}{kT}\big|x_{N-1}^{(1)} - x_0^{(1)}\big| + \frac{f}{kT}\big|x_{N-1}^{(2)} - x_0^{(2)}\big|\Bigg] \delta\big(x_m^{(1)} - x_k^{(2)}\big) \prod_{j=0}^{N-1} \mathrm{d}x^{(1)} \mathrm{d}x^{(2)} \Bigg\}^{-1}.$$

The probability distribution for the end points of the chains can be evaluated from (12) by Fourier transforming the δ function (See Appendix B) and is shown to be

$$P_2(x_0, x_{N-1})\mathrm{d}x_0 \mathrm{d}x_{N-1} = C_2 \exp\Big[-\frac{2b}{N-1}(x_{N-1} - x_0)^2$$

$$- \frac{b(K-m)^2}{m(N-1)[(N-m-1) + K(N-K-1)}(x_{N-1} - x_0)^2$$

$$+ \frac{f}{kT}|x_{N-1} - x_0|\Big] \mathrm{d}x_0 \mathrm{d}x_{N-1}\,, \qquad (14)$$

where C_2 is the normalizing factor.

The main length of the macromolecule is given by

$$\begin{aligned}\langle|x_{N-1}-x_0|\rangle &= \int |x_{N-1}-x_0| P_2(x_0,x_{N-1})\mathrm{d}x_0\mathrm{d}x_{N-1}\\ &= \frac{kT}{2}\frac{\partial}{\partial f}\int \exp\Bigg\{-\frac{2b}{N-1}(x_{N-1}-x_0)^2\\ &-\frac{b}{N-1}\frac{(K-m)^2}{[m(N-m-1)+K(N-K-1)]}(x_{N-1}-x_0)^2\\ &+\frac{2f}{kT}|x_{N-1}-x_0|\Bigg\}\mathrm{d}x_0\mathrm{d}x_{N-1}\\ &= \frac{f(N-1)}{kTb\Big[2+\dfrac{(K-m)^2}{m(N-m-1)+K(N-K-1)}\Big]}\,. \end{aligned} \tag{15}$$

And the tension f is

$$f=\frac{b}{N-1}kT\left[2+\frac{(K-m)^2}{m(N-m-1)+K(N-K-1)}\right]\langle|x_{N-1}-x_0|\rangle\,. \tag{16}$$

This result in comparison with (11) shows an increase in the tension by the amount

$$\frac{b}{N-1}kT\frac{(K-m)^2}{m(N-m-1)+K(N-K-1)}\,.\langle|x_{N-1}-x_0|\rangle\,.$$

This method can be generalized when there are M chains and each chain has N molecular units. Two molecular units of each chain called $m^{(j)}$ and $n^{(j)}$ ($n^{(j)} > m^{(j)}$) have been jointed with two molecular units belonging to other chains.

The tension in the case of M chains with two junctions per chain, can be evaluated using the same method and it is

$$f=\frac{b}{N-1}kT\left\{2+\frac{2}{M}\frac{\left[\sum_{j=0}^{N-1}(n^{(j)}-m^{(j)})\right]^2}{\sum_{j=0}^{N-1}(n^{(j)}-m^{(j)})(N+m^{(j)}-n^{(j)})}\right\}\cdot\langle|x_{N-1}-x_0|\rangle\,. \tag{17}$$

The tension f for the two chains can be plotted using (16) as a function of the molecular K of one chain that is jointed together with a molecular of the other chain. The plots are shown in Fig. 1 for $N = 10$.

In Fig. 2 the tension f from (16) is plotted as a function of N. All junction points have been considered to be equally probable and a mean value has been taken. The dotted line shows the tension f as a function of N – the number of molecules of the chain – in the case that no junction points exist. The increase can be seen from the graphs up to $N = 10$.

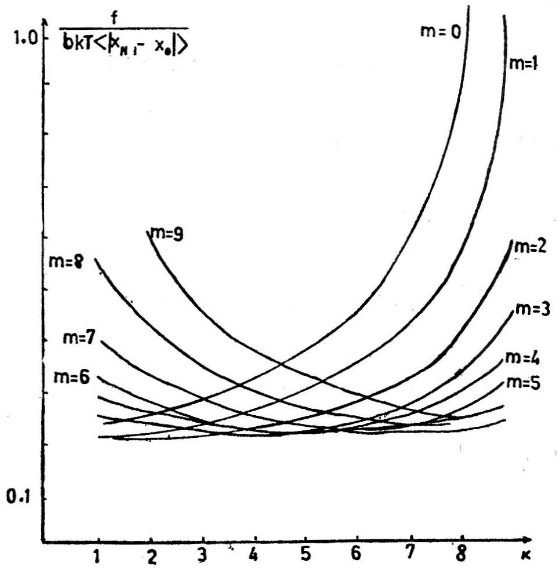

Fig. 1. The tension f as a function of K, where K is the molecule of one chain that is jointed together with the m-th molecule of the other chain ($m = 0,\ 1, ..., 9$).

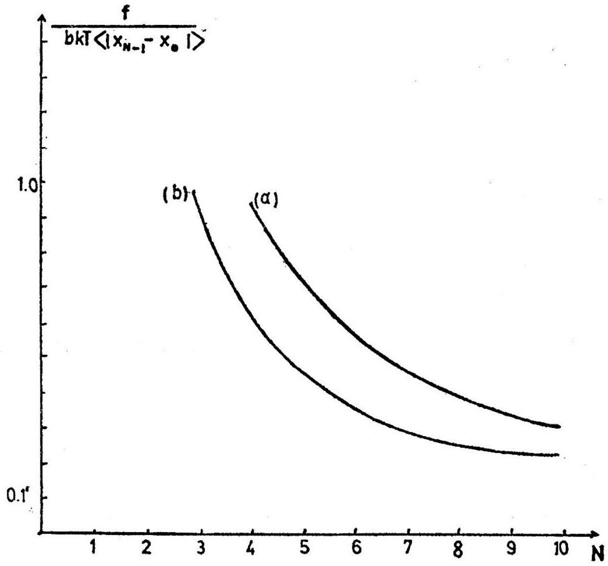

Fig. 2. a) The tension f as a function of the number N of molecular units of the macromolecular chain in the case when there exist junction points, b) The tension f as a function of the number N of molecular units of the macromolecular chain when no junction points exist.

Appendix A

The integrations in (6) can be done step by step. The first integration over x_1 gives

$$\int \exp\{-b[(x_1 - x_0)^2 + (x_2 - x_1)^2]\}\mathrm{d}x_1 = \left(\frac{\pi}{2b}\right)^{3/2} \exp\left[-b\frac{1}{2}(x_2 - x_0)^2\right]. \quad (18)$$

The second integration over x_2 gives

$$\int \exp\left\{-b\left[\frac{1}{2}(x_2 - x_0)^2 + (x_3 - x_2)^2\right]\right\} \mathrm{d}x_2 = \left(\frac{2\pi}{3b}\right)^{3/2} \exp\left[-b\frac{1}{3}(x_3 - x_0)^2\right], \quad (19)$$

and by using the method of mathematical induction the last integration over x_{N-2} gives

$$\int \exp\left(-b\left[\frac{1}{N-1}(x_{N-2} - x_0)^2 + (x_{N-1} - x_{N-2})^2\right]\right) \mathrm{d}x_{N-2}$$

$$= \left(\frac{(N-2)\pi}{(N-1)b}\right)^{3/2} \exp\left[-b\frac{1}{N-1}(x_{N-1} - x_0)^2\right]. \quad (20)$$

So the probability $P_{2f}(x_{N-1},\ x_0)$ is given by

$$P_{2f}(x_{N-1}, x_0) = C_{2f}\left[-\frac{b}{N-1}(x_{N-1} - x_0)^2 + \frac{f}{kT}|x_{N-1} - x_0|\right], \quad (21)$$

where

$$C_{2f} = \left\{\int \exp\left[-\frac{b}{N-1}(x_{N-1} - x_0)^2 + \frac{f}{kT}|x_{N-1} - x_0|\right] \mathrm{d}x_0 \mathrm{d}x_{N-1}\right\}^{-1}$$

$$= \left(\frac{b}{\pi(N-1)}\right)^{3/2} \frac{1}{V} \left\{\exp\left[\frac{f^2(N-1)}{4k^2T^2b}\right]\right\}^{-1}, \quad (22)$$

where V is the volume obtained by the integration over the last variable.

Appendix B

The probability distribution (12) will be evaluated by Fourier transforming the δ-function,

$$\delta\big(x_m^{(1)} - x_k^{(2)}\big) = \int\limits_{-\infty}^{\infty} \exp\big[-\mathrm{i}q\big(x_m^{(1)} - x_k^{(2)}\big)\mathrm{d}q\,. \quad (23)$$

The probability distribution $P_2(x_0,\ x_{N-1})\mathrm{d}x_0\mathrm{d}x_{N-1}$ for the end points of the two macromolecular chains will be evaluated by integrating over the variables $x_1^{((1)}$, $\ldots x_{N-2}^{((1)}$, $x_1^{((2)}$, $\ldots x_{N-2}^{((2)}$ and q. The integrations can be done by making the following transformations:

$$x_i^{(1)} = X_i^{(1)} + y_i^{(1)}\,,$$

$$x_j^{(2)} = X_j^{(2)} + y_j^{(2)}\,, \tag{24}$$

$$y_0^{(1)} = y_0^{(2)} = y_{N-1}^{(1)} = y_{N-1}^{(2)} = 0\,.$$

The $X_i^{(1)}$ and $X_j^{(2)}$ are solutions of the following differential equations:

$$\ddot{X}_i^{(1)} = \frac{\mathrm{i}q}{2b}\,\delta(\tau - \tau')\,, \tag{25}$$

$$\ddot{X}_j^{(2)} = \frac{\mathrm{i}q}{2b}\,\delta(\tau - \tau'')\,,$$

where the continuous variables τ, τ', τ'' correspond to the discrete variables j, m, k. The boundary conditions are:

$$X_0^{(1)} = x_0^{(1)}, \quad X_0^{(2)} = x_0^{(2)}, \quad X_{N-1}^{(1)} = x_{N-1}^{(1)}, \quad X_{N-1}^{(2)} = x_{N-1}^{(2)}.$$

The solutions are:

$$X_j^{(1)} = \left(\frac{x_{N-1}^{(1)} - x_0^{(1)}}{N-1}\right) j + x_0^{(1)} - \frac{\mathrm{i}q}{2b(N-1)}(N-1-m)j$$

$$+\frac{\mathrm{i}q}{2b}(j-m)\Theta(j-m)\,,$$

$$X_j^{(2)} = \left(\frac{x_{N-1}^{(2)} - x_0^{(2)}}{N-1}\right) j + x_0^{(2)} - \frac{\mathrm{i}q}{2b(N-1)}(N-1-K)j$$

$$-\frac{\mathrm{i}q}{2b}(j-K)\Theta(j-K)\,. \tag{26}$$

$\Theta(j-m)$, $\Theta(j-K)$ are step functions.

By substituting $x_j^{(1)}$, $x_j^{(2)}$ from the transformation (24) in (12) and by integrating over $y_j^{(1)}$ andy $y_j^{(2)}$ the probability distribution for the end points is given by

$$P_4(x_0^{(1)}, x_{N-1}^{(1)}, x_0^{(2)}, x_{N-1}^{(2)})\mathrm{d}x_0^{(1)}\mathrm{d}x_{N-1}^{(1)}\mathrm{d}x_0^{(2)}\mathrm{d}x_{N-1}^{(2)}$$

$$= \mathrm{d}x_0^{(1)}\mathrm{d}x_{N-1}^{(1)}\mathrm{d}x_0^{(2)}\mathrm{d}x_{N-1}^{(2)}C_4\int \exp\Big[-b\sum_{j=0}^{N-2}(X_{j+1}^{(1)}-X_j^{(1)})^2$$

$$-b\sum_{j=0}^{N-2}(X_{j+1}^{(2)}-X_j^{(2)})^2 - \mathrm{i}qX_m^{(1)} + \mathrm{i}qX_k^{(2)} + \frac{f}{kT}\big(|X_{N-1}^{(1)}-X_0^{(1)}|$$

$$+|X_{N-1}^{(2)}-X_0^{(2)}|\big)\Big]\mathrm{d}q\,. \tag{27}$$

where C_4 is the normalizing factor.

From (26) the following relations are valid:

$$X_{j+1}^{(1)}-X_j^{(1)} = \frac{x_{j+1}^{(1)}-x_j^{(1)}}{N-1} + \frac{\mathrm{i}q}{2b}A_j^{(1)}\,,$$

$$X_{j+1}^{(2)}-X_j^{(2)} = \frac{x_{j+1}^{(2)}-x_j^{(2)}}{N-1} - \frac{\mathrm{i}q}{2b}A_j^{(2)}\,, \tag{28}$$

where

$$A_j^{(1)} = (j+1-m)\Theta(j+1-m) - (j-m)\Theta(j-m) - \frac{N-1-m}{N-1}\,,$$

$$A_j^{(2)} = (j+1-K)\Theta(j+1-K) - (j-K)\Theta(j-K) - \frac{N-1-K}{N-1}\,, \tag{29}$$

$$A_j^{(1)} = \frac{m-N+1}{N-1} \quad \text{for} \quad j \le m-1\,,$$

$$A_j^{(1)} = \frac{m}{N-1} \quad \text{for} \quad j \ge m\,,$$

$$A_j^{(2)} = \frac{K-N+1}{N-1} \quad \text{for} \quad j \le K-1\,,$$

$$A_j^{(2)} = \frac{K}{N-1} \quad \text{for} \quad j \ge K\,, \tag{30}$$

$$\sum_{j=0}^{N-2}A_j^{(1)} = \sum_{j=0}^{N-2}A_j^{(2)} = 0\,,$$

$$\sum_{j=0}^{N-2} \left(A_j^{(1)}\right)^2 = \frac{m(N-m-1)}{N-1}\,,$$

$$\sum_{j=0}^{N-2} \left(A_j^{(2)}\right)^2 = \frac{K(N-K-1)}{N-1}\,. \tag{31}$$

The probability distribution $P_2(x_0,\ x_{N-1})$, after the integration over q and the identification of the end points, becomes

$$P_2(x_0, x_{N-1})\mathrm{d}x_0\mathrm{d}x_{N-1} = C_2 \exp\Bigg[-\frac{2b}{N-1}(x_{N-1}-x_0)^2$$

$$-\frac{b(K-m)^2}{(N-1)[m(N-m-1)+K(N-K-1)]}(x_{N-1}-x_0)^2$$

$$+\frac{2f}{kT}|x_{N-1}-x_0|\Bigg]\mathrm{d}x_0\mathrm{d}x_{N-1}\,,$$

where C_2 is the normalizing factor.

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DOPRINOS PRORAČUNU NAPETOSTI POLIMERNIH LANACA SA SPOJEM

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Koristeći metode statističke mehanike za ravnotežne sisteme izračunata je napetost polimerskog lanca a zatim i sistema povezanih lanaca s trajnim spojem. To je učinjeno razmatranjem slobodne energije sistema. Pokazano je da napetost raste kad postoji spoj što je u skladu s iskustvom. Također je određena ovisnost napetosti o položaju spoja kao i o broju molekulskih jedinica u makromolekuli. Rezultat je uspoređen s onim za makromolekulu bez spoja.