Theory of Electric Birefringence of Long Flexible Polymer Chains with Transverse Bond Dipole Moments: Tetrahedral Lattice Model

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ABSTRACT: We describe the Kerr effect in a strong electric field for a polymer chain having only a transverse component of the dipole moment (type B chain). The theory is based on a rotational-isomeric-state model for a tetrahedral lattice which was applied previously for chains with a longitudinal component of the dipole moment (type A chain). We calculate various conformational properties and orientational parameters as functions of the electric field magnitude. The overall chain behavior in a strong electric field can be described as the orientation of "effective" segments by the applied field. The "effective" segment length increases with the field strength. The field dependence of the electric birefringence for type B chains is shown to be stronger than that for type A chains with the same dipole moment per monomer unit. The initial polymer chain rigidity and conformational rearrangements strongly influence the Kerr effect for any type of dipole moment distribution.

1. Introduction

The electric birefringence or Kerr effect is a very powerful experimental method usually used to obtain an information about molecular structure for molecules under the influence of a strong electric field.[1,2] In particular, the Kerr effect in a weak electric field allows one to define experimentally the product of the dipole moment and optical anisotropy. The Kerr effect in a strong field can be used to obtain these two characteristics independently.[2−4]

It is known that the maximum Kerr effect is exhibited by polymers with a permanent longitudinal dipole moment. In our previous paper[3] the Kerr effect in a strong electric field for polymer chains containing only a permanent longitudinal component of the dipole moment (type A chains, according to the Stockmayer classification,[5,6] for example, poly(butyl isocyanate)[2,4]) has been considered using the rotational isomeric state (RIS) model on a tetrahedral lattice. Up to now there has been little experimental and theoretical information concerning the Kerr effect for long polymer chains of the type, considered by the authors, in strong electric fields. Recently Lezov et al.[7] obtained experimental data on the Kerr effect for long molecules of poly(butyl isocyanate) in a strong electric field. The theoretical results of our previous paper[3] may be compared with the experimental data in the near future. At the same time, there are experimental results on the Kerr effect for polymers with both longitudinal and transverse components of dipole moment. In some cases the transverse component is predominant,[8,9] and it is necessary to develop a theory of the Kerr effect for long polymer chains (with numbers of Kuhn segments larger than 10) for this case. Such a theory is developed in the present paper.

It was previously shown[3] that, for type A polymers, the orientation of the chain on the lattice can be interpreted in terms of an "effective" freely jointed chain (FJC) with a field-dependent segment length. To a good approximation, this effective segment is equal to the average length of the trans sequence of the lattice chain. In practice, the case where the direction of the dipole moments is transverse to the backbone (i.e., type B chains[5,6]) is more common.[2] A class of polymers with symmetric side groups belongs to type B, including $-(CH_2-CR_2)_n-$ type chains. The most common examples are poly(vinylidene bromide) $-(CH_2-CBr_2)_n-$ and poly(vinylidene chloride) $-(CH_2-CCl_2)_n-$. The transverse dipole moment of the side group can be represented as a vector sum of two alternating dipole moments of backbone bonds (Figure 1). As a first approximation we consider polymers with symmetrical dipole moments and without helical structure. This means that in this case the results are not affected by stereoregularity.

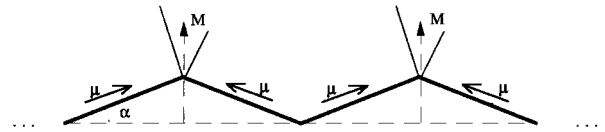

Figure 1. Distribution of dipole moments along the chain. Monomer units of the polymer chain: μ, dipole moment of a bond; M, dipole moment of a monomer unit (dashed lines). cos $\alpha = \sqrt{2/3}$.

In a weak field, a linear dependence of the electric birefringence on the square of the external field magnitude is obtained. This dependence corresponds to the well-known Kerr law.[1−6] In a strong field, a deviation from the linear dependence is observed. This nonlinear dependence was explained by Yoshioka,[10] V. Tsvetkov,[2] and others by using a simple model of a freely jointed chain (FJC). However, in a real flexible polymer chain subjected to an external field, both orientational effects and conformational rearrangements (i.e., redistribution between trans and gauche isomers) occur. These rearrangements cannot be explained by means of the FJC model, which takes into account only orientational effects.

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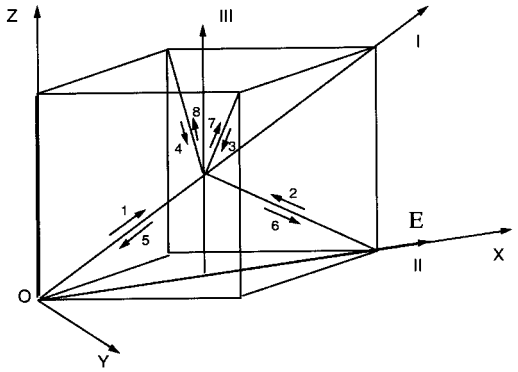

Figure 2. Elementary cell of the tetrahedral lattice. Possible orientations of bond dipole moments (1−8). Probable orientation of the lattice as a whole (I−III). External field direction is shown by *E*.

The aim of this paper is 2-fold: (1) to develop a theory of the Kerr effect in a strong electric field for a long flexible polymer chain possessing only transverse components of dipole moments and which takes into account conformational changes due to redistribution of rotational isomers; (2) to compare the Kerr effect for chains with longitudinal or transverse dipole moments.

2. Tetrahedral Lattice Model

To describe a long polar polymer chain of type B (Figure 1), we consider the same RIS chain model on a tetrahedral lattice (Figure 2) which has been used for type A chains.[3] The model takes into account conformational changes under an external field influence. Earlier, only the freely jointed chain model[2,10] was used for the theoretical description of the Kerr effect in a strong field. There are eight possible dipole moment orientations of a single bond on a tetrahedral lattice site (Figure 2). In our model, each backbone chain bond has a dipole moment μ. The energy U_i^{ext} of the ith backbone chain bond in an external field of dipole symmetry is written as

$$U_i^{\text{ext}} = -\mu E_0 \cos \phi_i \tag{1}$$

where ϕ_i is the angle between the dipole moment of magnitude μ of the ith backbone bond and the external field direction and E_0 is the magnitude of the external electric field.

The monomer unit, directed along the chain backbone, consists of two neighboring bonds (Figure 1). Its net dipole moment M is transverse to the monomer unit and has magnitude

$$M = \frac{2}{\sqrt{3}}\mu \tag{2}$$

It is assumed that the optical polarizability tensor of each chain bond is an axially symmetric and diagonal tensor (a_1,a_2,a_2) in the bond coordinate system. Then, after simple tensor transformations, it follows that the optical polarizability tensor of the monomer unit is diagonal in the monomer unit coordinate system and can be expressed as (A_{xx},A_{yy},A_{zz}). The problem of the tetrahedral lattice orientation as a whole in the strong external field is briefly discussed in Appendix 1: the lattice as a whole is oriented transverse to the external field direction along the axis O*X* (Figure 2). Let us consider the simplest case, when the optical polarizability tensor of a monomer unit $\hat{A}$ is diagonal and axially symmetric. Then we have the following tensor for the monomer unit: $(A_{xx},(A_{yy} + A_{zz})/2,(A_{yy} + A_{zz})/2)$ in its own coordinate system. The optical polarizability tensor of the monomer unit (Figure 3) may be written as (A_1,A_2,A_2) in its own coordinate system. Thus, the largest value A_{xx} is directed along the monomer unit (Figure 3). Let us illustrate these assumptions with the help of a chain of poly(vinylidene bromide) (Figure 4). The optical polarizability tensors of the bonds C−C, C−Br, and C−H are axially symmetric and they are diagonal tensors in their own bond coordinate systems:[1] $\hat{A}^{\text{X}} = \text{diag}(a_1^{\text{X}},a_2^{\text{X}},a_2^{\text{X}})$, where X = CC, CBr, or CH, respectively. The main value a_1^{X} of the optical polarizability tensor of each bond is directed along the bond in the bond coordinate systems. It is easy to show that the optical anisotropy ΔA of the poly(vinylidene bromide) monomer unit in its own coordinate system (Figure 4) may be expressed as follows:

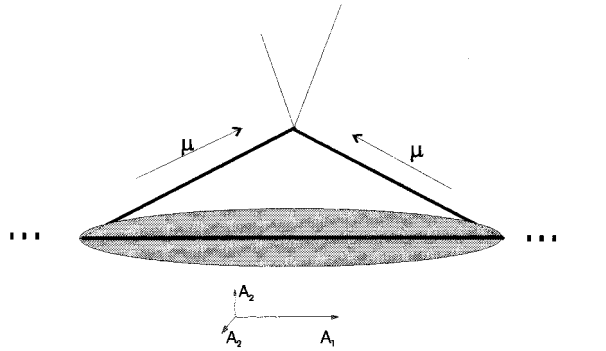

Figure 3. Optical polarizability tensor of a chain monomer unit.

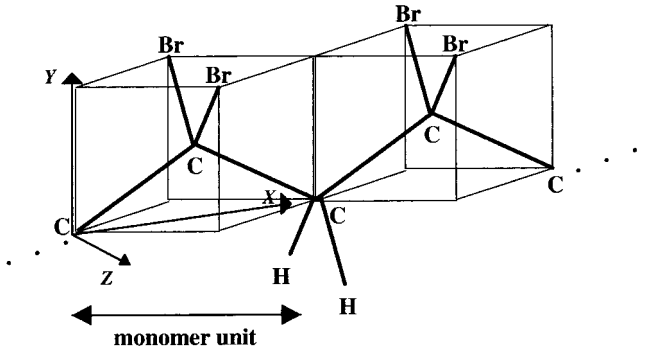

Figure 4. Optical polarizability tensor of a monomer unit of poly(vinylidene bromide).

$$\overline{\Delta A} = \Delta A^{\text{CC}} - \Delta A^{\text{CBr}} - \Delta A^{\text{CH}} \tag{3}$$

where $\Delta A^{\text{X}} = a_1^{\text{X}} - a_2^{\text{X}}$ is the optical anisotropy of bond X in each bond coordinate system and X is CC, CBr, or CH.

We consider a polymer chain with nonequivalent rotational isomers in the absence of a field. In this case the parameter x is a measure of the chain thermodynamic rigidity

$$x = \frac{E_{\text{g}}}{kT} \tag{4}$$

where E_{g} is the difference between the energy of trans and gauche isomers. In this work, it is assumed that both coiled (gauche) isomers are energetically equivalent.

The fraction of trans isomers in the absence of the external field is given by

$$P_0(t) = \frac{1}{1 + 2e^{-x}} \tag{5}$$

and the fraction of gauche isomers is given by

$$P_0(g) = \frac{1 - P_0(t)}{2} = \frac{e^{-x}}{1 + 2e^{-x}} \tag{6}$$

3. Theory. Electric Birefringence and Order Parameter

In the case when electrostrictive effects are neglected and the optical polarizability tensor of a monomer unit $\hat{A}$ is diagonal and axially symmetric in its own coordinate system, the electric birefringence is given by the following expression:[1−3]

$$\frac{\Delta n}{c} = D \cdot \Delta A \cdot S \tag{7}$$

Here Δn is the value of the electric birefringence (i.e., the difference between two main refractive indexes), c is the concentration, $\Delta A \equiv A_1 - A_2$ is the anisotropy of the optical polarizability of a monomer unit in its own coordinate system, S is the quadrupole order parameter for a monomer unit vector, and D is a factor independent of an external field. According to the above assumptions, $D = 2\pi N_A(n^2 + 2)^2/9\tilde{M}n$, n is the mean refractive index of the solution, $\tilde{M}$ is the molecular weight of a polymer chain, and N_A is Avogadro's number.

The quadrupole order parameter S for a monomer unit vector is one of the main orientational characteristics of a polymer chain

$$S = \frac{3}{2}\left(\langle \cos^2 \theta \rangle - \frac{1}{3}\right) \tag{8}$$

where θ is the angle between the monomer unit vector and the direction of the chain orientation. This direction in a strong field is the most probable orientation of the lattice as a whole with respect to the external field (Appendix 1).

To calculate S for the lattice RIS model, the method developed for type A polymer chains[3] is used. This calculation procedure is based on the transition matrix method described in Appendix 1.

4. Results and Discussion

4.1. Field Dependence of the Electric Birefringence. The field dependence of the electric birefringence for type B polymer chains with different values of the initial thermodynamic rigidity parameter x were obtained over a wide range of external fields (Figure 5). In a weak field the value of the electric birefringence is proportional to the square of the external field (i.e., the usual Kerr law is valid). The electric birefringence achieves its limiting value with increasing field. When the chain contains the monomer units described above, the chain stretches transverse to the field direction. Then we have

$$\frac{\Delta n/c}{(\Delta n/c)_{max}} = S \tag{9}$$

where $(\Delta n/c)_{max}$ is the maximum value of $\Delta n/c$.

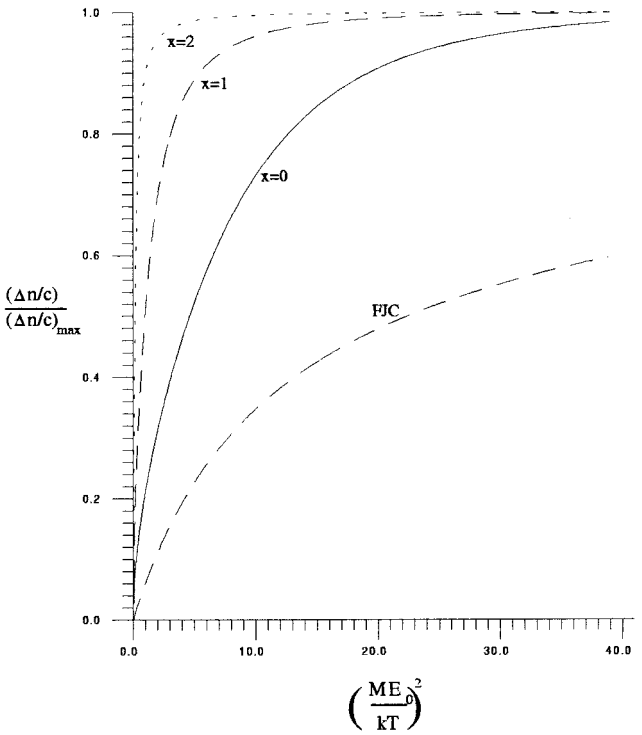

Figure 5. Field dependence of the electric birefringence at different values of thermodynamic chain rigidity x.

As the external field changes, the rate of growth of the electric birefringence increases with the chain rigidity x. The initial polymer chain rigidity strongly influences the Kerr effect (Figure 5).

4.2. Conformational Properties and Orientation in a Strong Field. Conformational properties of the polymer chain in an external field are described completely by the field dependence of different sequences of trans and gauche isomers. These sequences (i.e., fractions of trans and gauche isomers, dyads, and triads) were calculated for type B polymer chains (Figures 6 and 7) according to the procedure used by authors previously for type A chains.[3] It is interesting to compare the conformational properties for type A[3] and B polymer chains at the equal dipole moments μ of backbone chain bonds. Parts a−g of Figure 6 show that very good qualitative and quantitative agreement is observed for most conformational properties of type A and B polymer chains. However, for some fractions of rotational isomers, for example, for P(gg*), P(gtg*), and P(tgt) (Figure 7, parts a−c) a relatively strong difference is observed.

To explain this fact, let us study the orientation of the polymer chain as a whole in a strong external field at different types of dipole moment distribution along the chain. In a very strong external field the chains of both types become trans chains. The question is how the macromolecules of each type stretch forming the trans configuration. For type A chain only elongation along the external field direction is probable. Hence, in type A chain, long trans sequences and short kinks exist in the strong field (Figure 8). The shortest kinks are related to the tg*tgt sequences (Figure 8). For type B polymer chain, the elongation both along and opposite to the field direction is probable (Figure 9). Thus, in type B chains the short kinks and folds still exist between long trans sequences under the influence of the strong field. The shortest fold determined by the tg*gg*t pentad

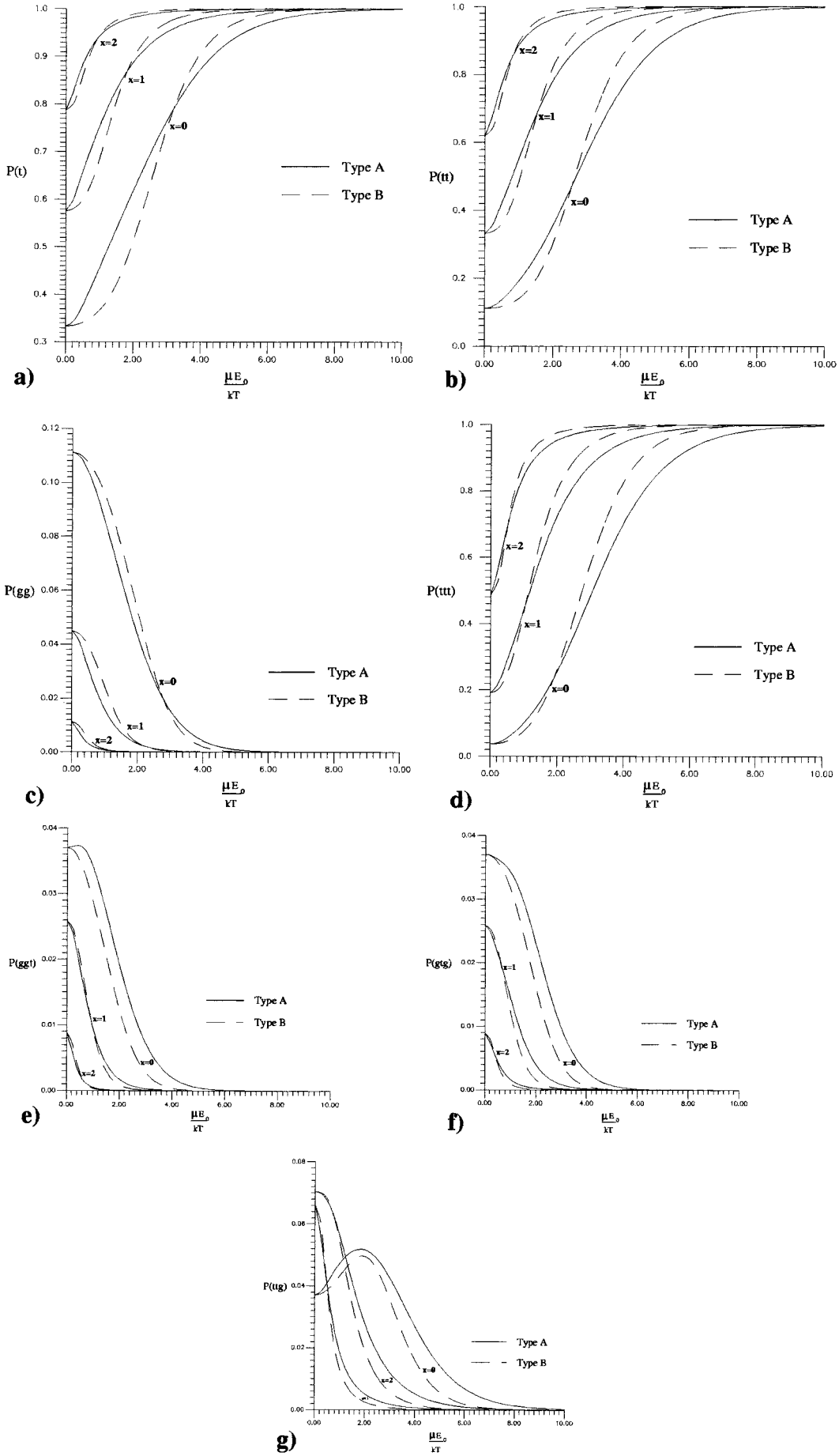

Figure 6. Field dependence of fractions of different sequences of isomers: (a) $P(t)$; (b) $P(tt)$; (c) $P(gg)$; (d) $P(ttt)$; (e) $P(ggt)$; (f) $P(gtg)$; (g) $P(ttg)$.

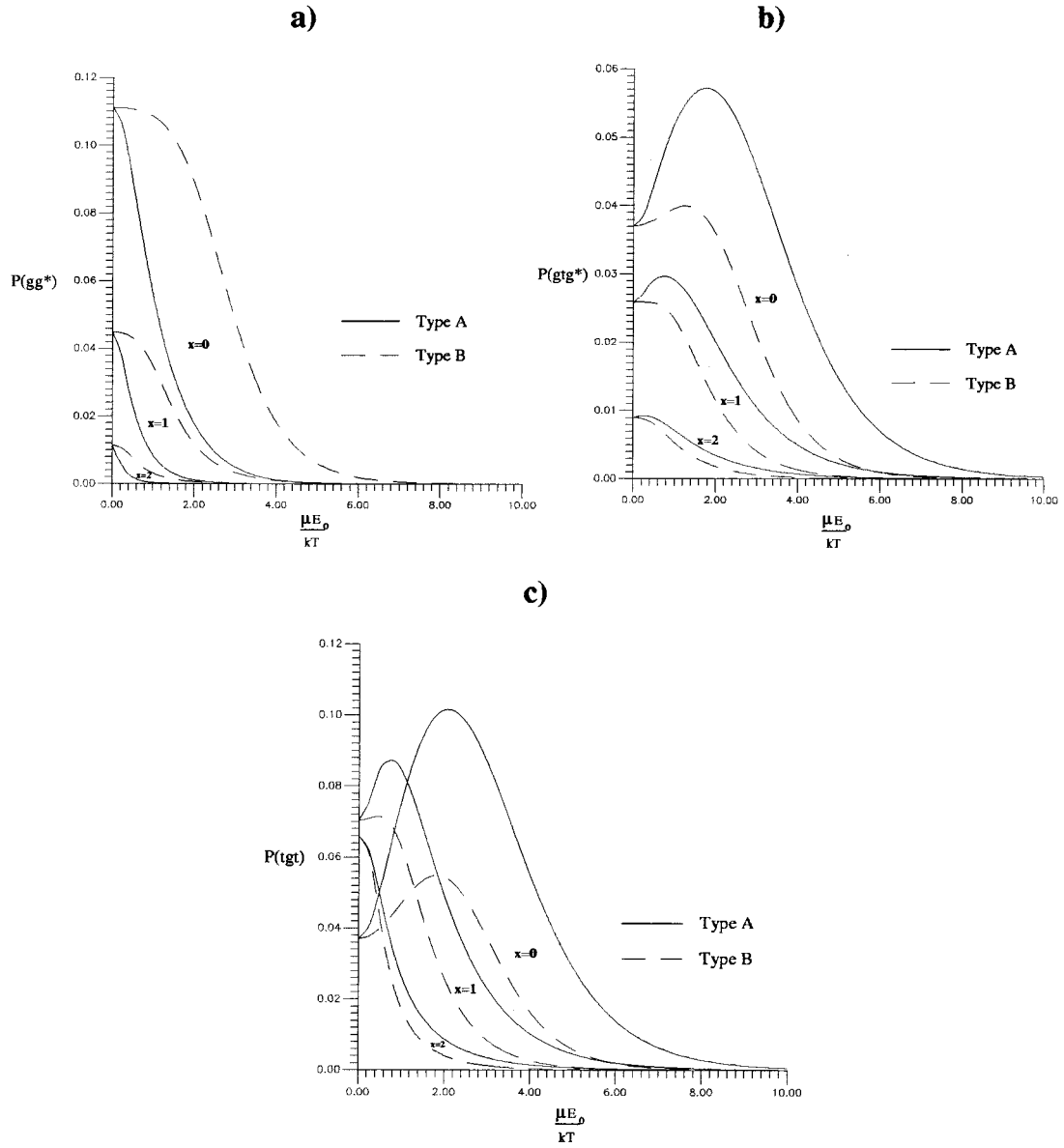

Figure 7. Field dependence of fractions of different sequences of isomers: (a) *P*(gg*); (b) *P*(gtg*); (c) *P*(tgt).

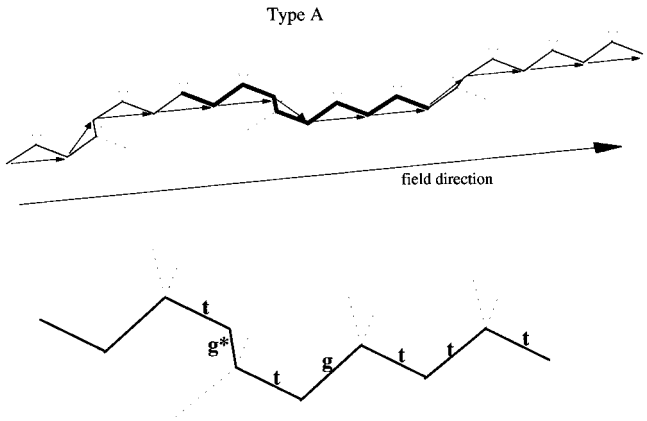

Figure 8. Orientation of type A chain as a whole in a strong field. Shortest kink in the chain.

(Figure 9). Thus, for type A polymer chains only tg*tgt pentads including gauche isomers are more advantageous in the strong field. For type B polymer chains both tg*tgt and tg*gg*t pentads are advantageous in the strong field. Therefore, *P*(gtg*) and *P*(tgt) are more probable for type A chains, and *P*(gg*) are more probable for type B chains.

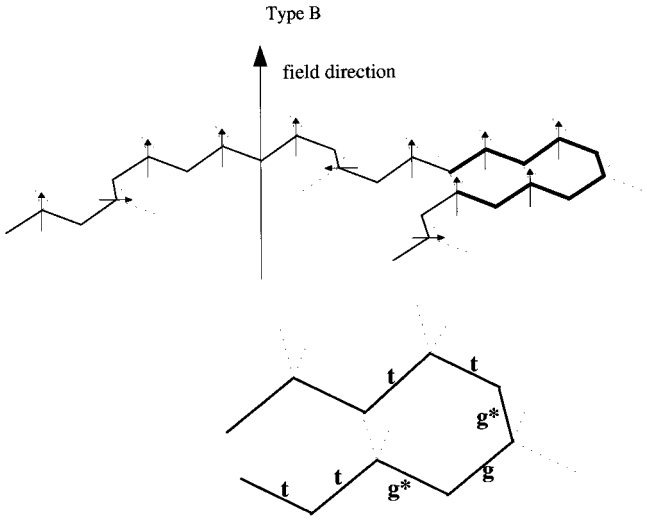

Figure 9. Orientation of type B chain as a whole in a strong field. Shortest fold in the chain.

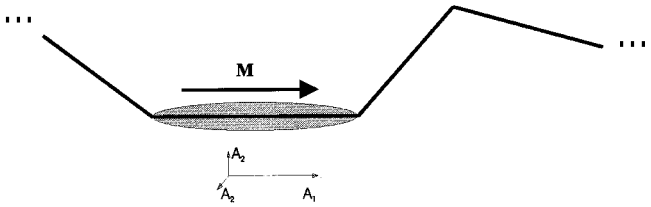

Figure 10. FJC model. *M* is a dipole moment of the FJC segment. (A_1,A_2,A_2) is an optical polarizability tensor of the FJC segment.

Consequently, a scrupulous conformational analysis shows that in the strong field type B chain has a greater number different probable conformations at each field magnitude as compared to type A chain. In other words, the orientation of type B chain is stronger.

4.3. "Effective" Freely Jointed Chain. Let us use again[3] the "effective" FJC to consider the field dependence of the electric birefringence. When the Kerr effect obtained for the RIS lattice model of a very flexible polymer chain (i.e., the parameter of thermodynamic rigidity x is equal to zero) is compared with that obtained for the "corresponding" FJC model, a considerable difference is observed in a strong field (Figure 5). In the "corresponding" FJC model the values of the dipole moment of the monomer unit and the optical polarizability tensor per unit length are equal to the corresponding characteristics of the RIS model. This used FJC model is shown in Figure 10. The difference in the strong field may be explained by the conformational rearrangements in the polymer chain under the influence of this field. Thus, for types A and B chains both the orientation of segments and the conformational changes in the polymer chain in the strong electric field influence the Kerr effect. To estimate the contribution of the effects of each type, the "effective" FJC with the adjusted segment length can be used. As shown earlier,[3] the "effective" FJC describes correctly the Kerr effect for a long flexible polymer chain, taking into account field-induced conformational rearrangements. At each magnitude of the external field the length of the FJC segment is recalculated to equalize the values of the birefringence for the RIS lattice model and for the "effective" FJC model. Parts a−c of Figure 11 show the field dependence of the "effective" segment length for polymer chains with different values of the parameter of thermodynamical rigidity x.

The length of the effective segment calculated from the birefringence of the chain on the lattice is approximately equal to the average length of the trans sequence $\langle l_t \rangle$ at different values of the parameter x. The procedure of $\langle l_t \rangle$ calculation was described by the authors previously.[3]

The difference between the effective segment length and the average length of the regular trans sequence is observed only in a very strong field and in a highly oriented system in which the quadrupole order parameter S exceeds 0.9. This value is unattainable in the real experiment.

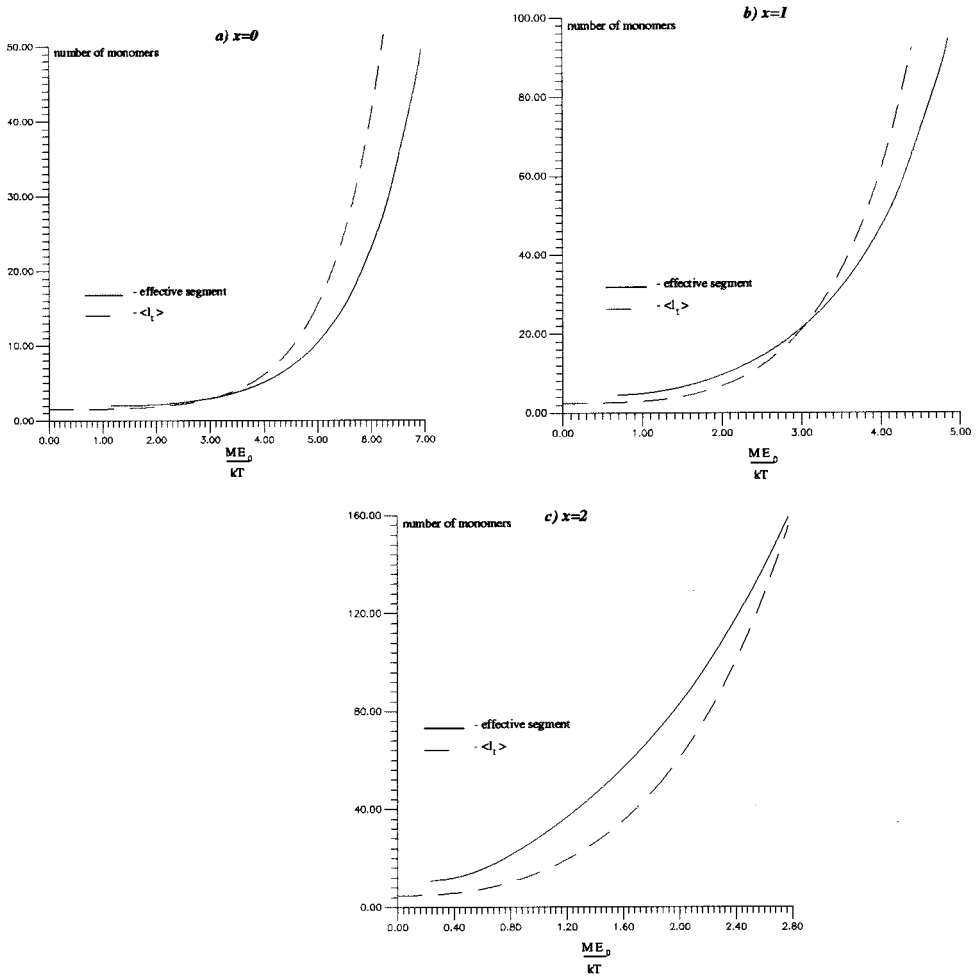

Figure 11. Field dependence of the effective segment length and of the average length of a trans sequence $\langle l_t \rangle$ at different values of initial thermodynamic rigidity: (a) $x = 0$; (b) $x = 1$; (c) $x = 2$.

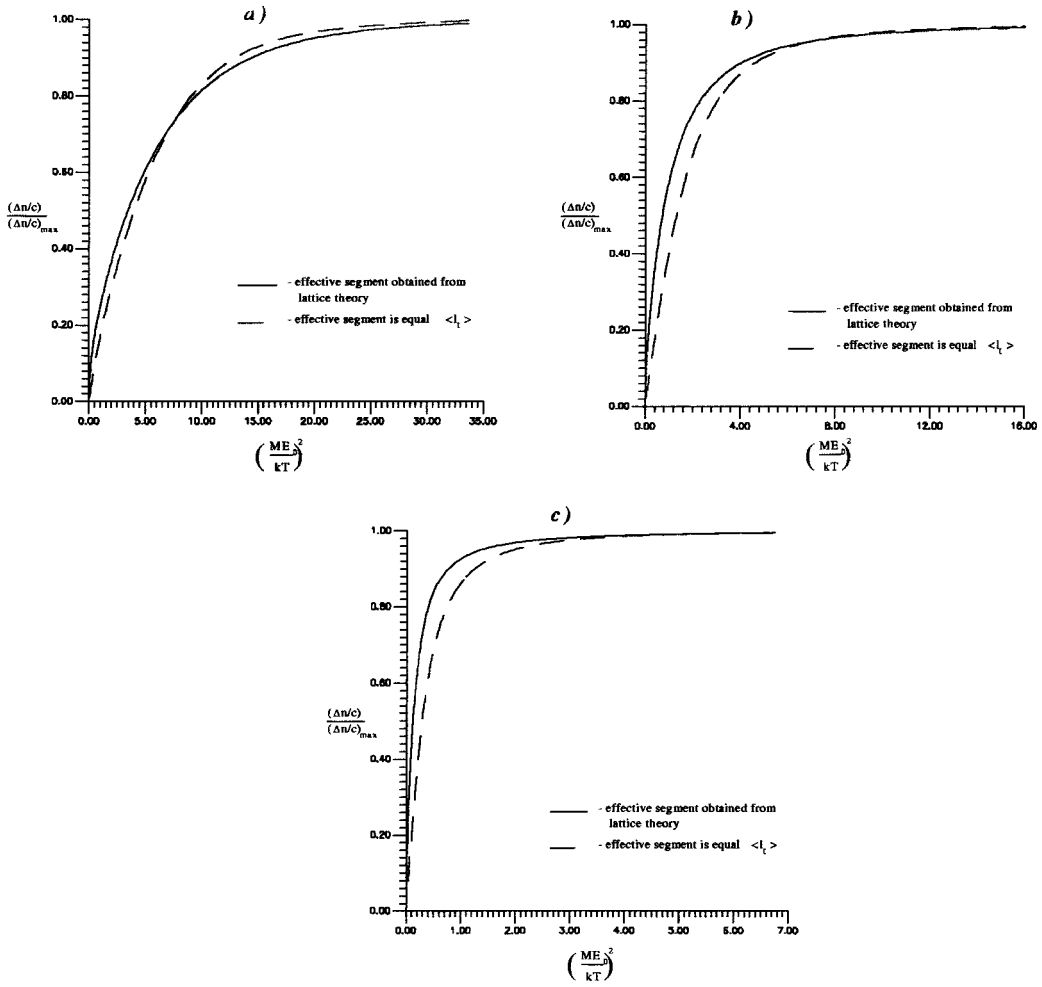

Figure 12. Field dependence of the electric birefringence for the FJC model with different effective segment lengths at different values of initial thermodynamic rigidity: (a) $x = 0$; (b) $x = 1$; (c) $x = 2$.

The electric birefringence curves for the FJC model with effective segment length calculated from the RIS model was compared to the curves where effective segment length was taken to be equal to the average length of the trans sequence. These curves show much better agreement for all magnitudes of the external field and for the parameter x (Figure 12, parts a−c) than those found from the direct comparison of the field dependence for two different effective segment lengths. Good agreement is also observed in a very strong field. Hence, one can use with a good precision the average length of a trans sequence as the effective segment length.

4.4. Comparison between Type B and Type A Chains. As shown in the previous sections, for both cases of the dipole moment distribution the initial chain rigidity, the orientation of the segments, and the conformational changes strongly influence the Kerr effect.

The question is how to estimate the influence of the type of dipole moment distribution along the chain backbone on the field dependence of the electric birefringence. To answer this question let us compare quantitatively the field dependence of the electric birefringence for the polymer chains of types A and B.

For the polymer chains of types A and B two most interesting relationships between backbone bond dipole moments are considered.

(1) The chains of different types have equal dipole moments of the monomer unit. In this case, taking into account the geometry of the system (Figure 1), we have for the backbone bond dipole moments

$$\sqrt{2}\mu^{A} = \mu^{B} \tag{10a}$$

where μ^{A} and μ^{B} are the dipole moments of the bond for type A and B chains, respectively.

(2) The backbone bonds have equal dipole moments:

$$\mu^{A} = \mu^{B} \tag{10b}$$

The field dependence of the electric birefringence for the different types of the chains is shown in parts a and b of Figure 13 for relationships between dipole moments, eqs 10a and 10b, respectively. When the different types of the chains have equal dipole moments of the monomer unit (eq 10a) values of the electric birefringence for type B chain are higher than those for type A chain at the same magnitude of the external field (Figure 13a). If the dipole moments of the bonds are equal (eq 10b), the values of the electric birefringence for type B chain are also higher (Figure 13b). However, in the last case the difference between values of the electric birefringence for the chains of both types becomes smaller.

Let us also compare the field dependence of the effective segment for type B chain with those for type A chain at different values of the rigidity parameter x. The field dependence of the effective segment differs for both types of chains, although they have the same

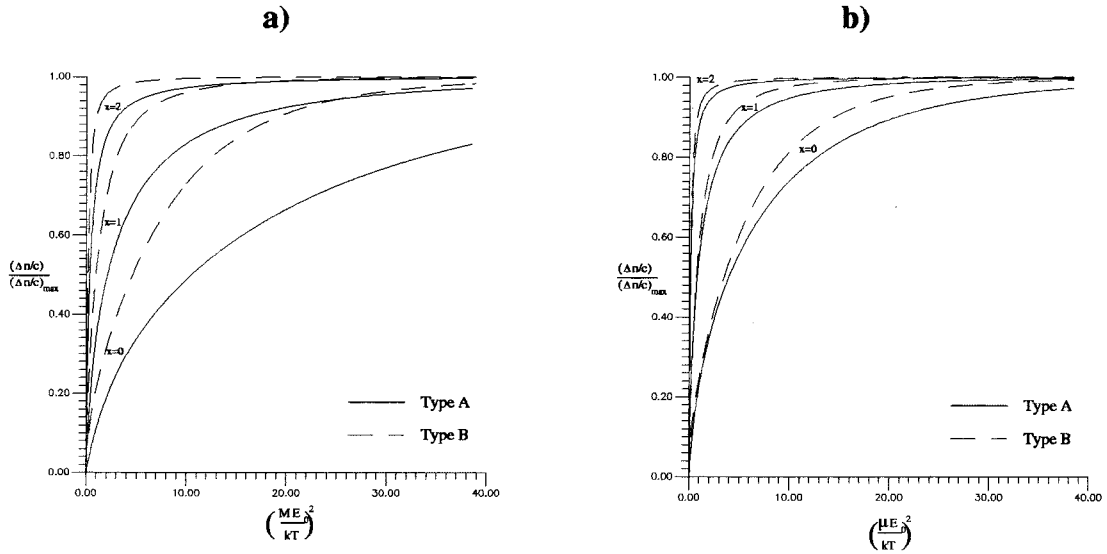

Figure 13. Field dependence of the electric birefringence for polymer chains of types A and B. (a) Chains of different types have equal dipole moment of the monomer units, $\sqrt{2}\mu^A = \mu^B$. (b) Chains of different types have equal dipole moments of the bonds $\mu^A = \mu^B$.

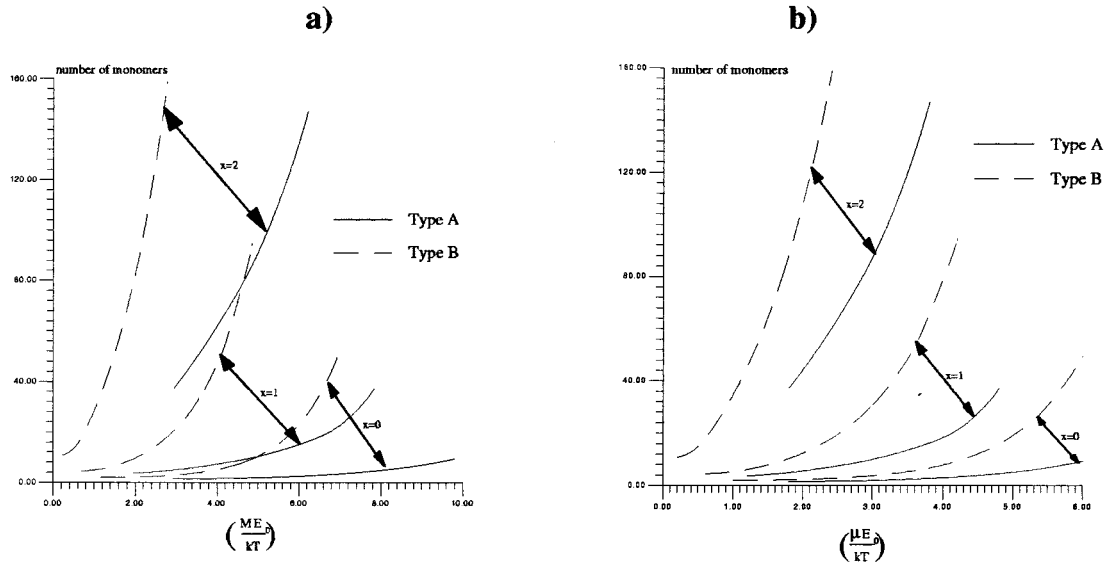

Figure 14. Field dependence of the effective segment length for the chains of types A and B at different values of initial thermodynamic rigidity x and (a) at equal dipole moments of the monomer units and (b) at equal dipole moments of the bonds.

qualitative behavior at the field growth. The effective segment for type B chain is longer than that for type A chain (Figure 14, parts a and b) for both types of the relationships between chain dipole moments (eqs 10a and 10b). At equal dipole moments of the bonds, the difference between the effective segment length for the chains of both types also decreases.

5. Conclusions

Type A and B chains are oriented differently in an external field. Type A chain stretches along the external field direction with the formation of long trans sequences. Type B chain is oriented transverse to the external field with "hairpins" formation.

Thus, the type of dipole moments distribution along the chain influences the conformational properties and chain orientation in the external field, i.e., the field dependence of the electric birefringence.

The field dependence of the electric birefringence obtained for type B chain is higher than that for type A chain at equal dipole moments of the monomer units.

Let us attempt to explain the difference in the field dependence of the electric birefringence. In case B the polymer chain has a greater number of possible configurations in the strong field, because long trans sequences in the chain may be oriented both along the external field direction and in the opposite direction. Moreover, the effective segment for type B chains is longer than that for type A chain because the trans sequence for type B chain is longer than that for type A chain. This fact may lead to increasing the electric birefringence for type B chains.

If type A and B polymer chains have equal dipole moments of the chain bonds, the observed difference in the field dependence of the electric birefringence decreases. In this case the dipole moments of type B chain monomer units is smaller than those of type A chain monomer units. It leads to more close values of the electric birefringence for both chains.

Thus, the orientation of type B chain in the external field is stronger than that of type A chain.

However, the Kerr effects for type A and B chains have similar features. As the external field changes, the rate of growth of the electric birefringence increases with the initial chain rigidity x, order parameter, and fractions of trans isomers. Consequently, the initial polymer chain rigidity, the segments orientation, and the conformational changes strongly influence the Kerr effect at any type of dipole moments distribution. For type A and B polymers the chain orientation on the lattice may be interpreted as the orientation of the "effective" FJC with the rigid segment length depending on the field. In a good approximation the effective segment is equal to the average length of the trans sequence. Although the chains of different types have different orientations in the strong field, some conformational properties of the chains (field dependence of fractions of trans and gauche isomers and fractions of some of their sequences) for the chains of both types are similar.

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Appendix 1. Transition Matrix

A tetrahedral lattice as a whole may be arbitrarily oriented with respect to an external field. The elements $\hat{G}_{\alpha\beta}$ of the transition matrix $\hat{G}$ completely determine all statistical properties of a chain at a given lattice orientation:[11]

$$\hat{G}_{\alpha\beta} = G^*_{\alpha\beta} \exp\{-U(\alpha,\beta)/kT\} \tag{11}$$

The total energy of a polymer chain consists of the energy in the external field U^{ext} and the energy of the internal rotation U^{int}. The latter factor is determined by E^g or by the parameter of initial rigidity x. Thus, we have

$$U(\alpha,\beta) = U^{ext}(\alpha,\beta) + U^{int}(\alpha,\beta) \tag{12}$$

where α and β are the possible orientations of the chain bond which depend on the orientation of the previous bond and the matrix G^* is a constant matrix describing the allowed orientations of the bond dipole moment on the lattice, $G^*_{\alpha\beta} = 0$ or 1.

For a polymer chain on the tetrahedral lattice, the transition matrix $\hat{G}$ generally has dimensions $8^2 \times 8^2$ because each chain bond has eight possible orientations in space (Figure 2). Taking into account the symmetry of the system, in the case of equivalent trans and gauche rotational isomers, the dimensions of the "reduced" matrix $\tilde{G}$ are 8×8.[12,13] To reduce the dimensions of the transition matrix $\hat{G}$ to 12×12 in the case of nonequivalent rotational isomers, let us consider a pair of chain bonds, i.e., a monomer unit (Figure 5), as a new element of the polymer chain. The monomer unit vector has 12 possible orientations. With the help of the method proposed by Darinskii and Neelov[14] and Medvedev and Gotlib[15] (in which other structural units are also taken into consideration) the "reduced" matrix $\tilde{G}$ was obtained as follows:

$$\tilde{G} = \begin{bmatrix}
t^2\sigma^2 & tg\sigma & tg\sigma & 0 & g^2\sigma & g^2\sigma & 0 & tg\sigma & g^2 & 0 & tg\sigma & g^2 \\
tg\sigma & t^2 & tg & 0 & tg & g^2 & 0 & g^2 & g^2\frac{1}{\sigma} & 0 & g^2 & tg\frac{1}{\sigma} \\
tg\sigma & tg & t^2 & 0 & g^2 & tg & 0 & g^2 & tg\frac{1}{\sigma} & 0 & g^2 & g^2\frac{1}{\sigma} \\
0 & g^2\sigma & g^2\sigma & t^2\sigma^2 & tg\sigma & tg\sigma & tg\sigma & 0 & g^2 & tg\sigma & 0 & g^2 \\
0 & tg & g^2 & tg\sigma & t^2 & tg & g^2 & 0 & g^2\frac{1}{\sigma} & g^2 & 0 & tg\frac{1}{\sigma} \\
0 & g^2 & tg & tg\sigma & tg & t^2 & g^2 & 0 & tg\frac{1}{\sigma} & g^2 & 0 & g^2\frac{1}{\sigma} \\
g^2\sigma & 0 & g^2 & tg\sigma & 0 & g^2 & t^2 & tg & tg\frac{1}{\sigma} & tg & g^2 & 0 \\
tg\sigma & 0 & g^2 & g^2\sigma & 0 & g^2 & tg & t^2 & tg\frac{1}{\sigma} & g^2 & tg & 0 \\
g^2 & 0 & tg\frac{1}{\sigma} & g^2 & 0 & tg\frac{1}{\sigma} & tg\frac{1}{\sigma} & tg\frac{1}{\sigma} & t^2\frac{1}{\sigma^2} & g^2\frac{1}{\sigma} & g^2\frac{1}{\sigma} & 0 \\
g^2\sigma & g^2 & 0 & tg\sigma & g^2 & 0 & tg & g^2 & 0 & t^2 & tg & tg\frac{1}{\sigma} \\
tg\sigma & g^2 & 0 & g^2\sigma & g^2 & 0 & g^2 & tg & 0 & tg & t^2 & tg\frac{1}{\sigma} \\
g^2 & tg\frac{1}{\sigma} & 0 & g^2 & tg\frac{1}{\sigma} & 0 & tg\frac{1}{\sigma} & tg\frac{1}{\sigma} & 0 & tg\frac{1}{\sigma} & tg\frac{1}{\sigma} & t^2\frac{1}{\sigma^2}
\end{bmatrix} \tag{13}$$

In this matrix $t = P_0(t)$, $g = P_0(g)$, and $\sigma = \exp(ME_0/2kT)$.

The relationships between the number of monomer units and the pairs of corresponding chain bonds are given in Table 1.

Table 1. Relationship between the Number of the Monomer Units and the Pairs of Corresponding Chain Bonds

no. of monomer unit orientation	nos. of corresponding bonds according to Figure 2
1	1−6
2	1−7
2	1−8
4	2−5
5	2−7
6	2−8
7	3−5
8	3−6
9	3−8
10	4−5
11	4−6
12	4−7

The partition function Z for a long chain at the known orientation of the lattice as a whole is determined as[11]

$$Z \cong \lambda_1^N \tag{14}$$

where λ_1 is the largest eigenvalue of the matrix $\tilde{G}$.

In the case of long polymer chains the boundary effects are negligible and the quantities which have been investigated in the present paper are not influenced by the chain ends. Nevertheless, the present theory can be modified for the chains with finite length as well. As shown by Birshtein and Ptitsyn,[11] in order to calculate the partition function for short polymer chains not only maximum eigenvalue but all ones of the transition matrix $\tilde{G}$ should be taken into account. Considering only maximum eigenvalues in the calculation of partition function leads to the error of the order of $(\lambda_1/\lambda_2)^N$, where $\lambda_2$is the maximum eigenvalue next after λ_2. It is easy to

show that when the number of monomer units is larger than several Kuhn segments this error is small and can be neglected.

To calculate $\langle \cos^2 \theta \rangle$, determining the quadrupole order parameter S for the lattice RIS model, the equation introduced by Gotlib and Medvedev[16] can be used:

$$\langle \cos^2 \theta \rangle = \sum_{\beta,\gamma=1}^{12} \cos\{\theta(\beta)\} \cos\{\theta(\gamma)\} u_\beta v_\gamma \quad (15)$$

where u_β and v_γ are the βth and the γth components of the right **u** and left **v** eigenvectors, respectively, corresponding to the maximum eigenvalue λ_1 of the matrix $\tilde{G}$ ($\mathbf{v}\tilde{G} = \lambda_1\mathbf{v}$, $\tilde{G}\mathbf{u} = \lambda_1\mathbf{u}$), $\theta(\beta)$ is the angle between external field direction and the monomer unit in the β orientation, and β is the parameter characterizing the bond orientation, $\beta = 1, ..., 12$.

Consequently, using the known values of **u** and **v** we can calculate all statistical and conformational characteristics[12,13] which are of interest, including the quadrupole order parameter S for the monomer unit vector, which determines the field dependence of the electric birefringence. According to this procedure, analytical results were obtained for a thermodynamically flexible polymer chain (i.e., for a chain with equivalent rotational isomers, $x = 0$). In the case of a chain with thermodynamic rigidity, $x \neq 0$, exact analytical calculations become impossible and numerical computations were made.

As was shown by the authors previously[13,15] for the tetrahedral lattice only orientations I, II, and III (Figure 2), which correspond to the symmetry axes of the system, must be considered as the most probable orientations of the lattice as a whole. For these discrete orientations of the lattice with respect to the external field, the statistical weight matrix $\tilde{G}$ was investigated, and its maximum eigenvalue λ_1 was calculated as a function of the external field. Comparing for the orientations I, II, and III λ_1, which determines the partition function Z (eq 14), it is possible to show that, for the type B chain, orientation III is the most probable orientation of the lattice as a whole in the strong field.

References and Notes

(1) Volkenshtein, M. V. *Configurational Statistics of Polymer Chains*; Wiley-Interscience Publishers: New York, 1963.
(2) Tsvetkov, V. N. *Rigid-chain polymers. Hydrodynamic and optical properties in solution*; Consultants Bureau: New York, 1989.
(3) Lyulin, S. V.; Neelov, I. M.; Gotlib, Yu. Ya. *Macromolecules* **1998**, *31*, 9354−9361.
(4) Lezov, A. V.; Rotinyan, T. A.; Rjumtsev, E. I. *Opt. Spectrosc.* **1994**, *76*, 1008−1012.
(5) Stockmayer, W. H. *Pure Appl. Chem.* **1967**, *15*, 539−554.
(6) Gotlib, Yu. Ya.; Darinskii, A. A.; Svetlov, Yu. E. *Physical kinetics of macromolecules* (*in Russian only*); Khimiya: Leningrad, Russia, 1986.
(7) Lezov A. V.; Rotinyan, T. A.; Rjumtsev, E. I. Unpublished results.
(8) Tsvetkov, V. N.; Lezov, A. V.; Tsvetkov, N. V.; Andreeva, L. N. *Eur. Polym. J.* **1990**, *26*, 575−581.
(9) Tsvetkov, V. N.; Kolomiets, I. P.; Lezov, A. V.; Andreeva, L. N.; Bilibin, A. Yu.; Skorokhodov, S. S. *Eur. Polym. J.* **1986**, *22*, 543−547.
(10) Yoshioka, K. *J. Chem. Phys.* **1987**, *86*, 491−496.
(11) Birshtein, T. M.; Ptitsyn, O. B. *Conformations of Macromolecules*; Interscience Publishers: New York, 1966.
(12) Lyulin, S. V.; Gotlib, Yu. Ya. *Polym. Sci. Ser A* **1996**, *38*, 252−257.
(13) Gotlib, Yu. Ya.; Lyulin, S. V. *Macromol. Theory Simul.* **1996**, *5*, 449−465.
(14) Darinskii, A. A.; Neelov, I. M. *Polym. Sci. USSR Ser. A* **1978**, *20*, 2381−2387.
(15) Medvedev, G. A.; Gotlib, Yu. Ya. *Macromol. Theory Simul.* **1994**, *3*, 121−134.
(16) Gotlib, Yu. Ya.; Medvedev, G. A. *Polym. Sci. USSR Ser A* **1990**, *32*, 2426−2431.

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