Theory of Electric Birefringence in a Strong Field for a Long Flexible Polymer Chain: Tetrahedral Lattice Model

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Received April 27, 1998; Revised Manuscript Received August 13, 1998

ABSTRACT: The Kerr effect for a long polar polymer chain in a strong electric field is studied using the rotational-isomeric-state model on a tetrahedral lattice. A polymer chain containing only a longitudinal component of the dipole moment has been considered. In such chains the Kerr effect is the largest. The field dependence of conformational properties and of orientational characteristics has been calculated. The overall chain behavior in a strong electric field can be treated as a superposition of two effects: (1) an elongation of the "effective" rigid element of the chain (the rigid elements can be considered as the trans sequences in the chain between gauche isomers); (2) an orientation of the "effective" segment like that in the freely jointed chain.

1. Introduction

During the last several years the Kerr effect in a strong field has received considerable attention since this measurement allows the determination of both the dipole moment and the optical polarizability of the macromolecule.[1,2] In contrast, the measurement of the Kerr effect in a weak field can yield only a combination of the dipole moment and the optical polarizability. The Kerr effect for polymer chains containing a longitudinal component of the dipole moment is much larger than those without (for example, for poly(butyl isocyanate) in tetrachlormethane[1,2]).

In a weak field, a linear dependence of the electric birefringence on the square of the external field value is obtained. This corresponds to the well-known Kerr law.[1−5] In a strong field, a deviation from the linear dependence is observed. This nonlinear dependence was explained by Yoshioka,[3] V. Tsvetkov,[1] and others by using a simple model of a freely jointed chain (FJC). However, in a real flexible polymer chain subject 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.

The main purpose of this paper is to develop a theory of the Kerr effect in a strong field for a long flexible polymer chain containing only a longitudinal component of the dipole moment which takes into account conformational changes due to redistribution of rotational isomers. The case where the direction of the bond dipole moments alternates is more common, but the magnitude of the effect is then much smaller. This case will be discussed in a later paper.

The theory of the Kerr effect for the rotational-isomeric-state (RIS) model of a polymer chain was derived by Gotlib and Volkenshtein,[4] Nagai,[5] and others in a weak field only. However, this approach does not take into account the change in the conformational characteristics of the polymer chain with the increase of the field strength.

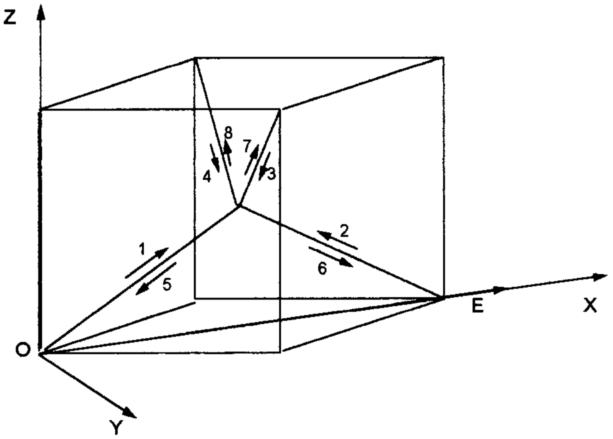

Figure 1. Elementary cell of the tetrahedral lattice. Possible orientations of the bond dipole moments (1−8). External field direction is shown by *E*.

A related nonlinear dielectric effect (NLDE) leading to dielectric saturation was studied by Khanarian[6] on a RIS polymer chain model. In the NLDE experiment a strong electric field is applied across the medium, and a weak-probe electric field is used to detect the anisotropy of the dielectric constant. The observed effect depends essentially on the fluctuation of the square of the chain dipole moment. In our case, it is the averaged quadrupole order parameter S for the monomer unit vector that determines the field dependence of the Kerr effect. Eventually, both the NLDE and the Kerr effect may be used to study the conformational properties of the polymer chain in a strong field.

2. Tetrahedral Lattice Model

In this work a long polar polymer chain with fixed valence angles is considered. The RIS chain model on a tetrahedral lattice is used to describe this chain.

The elementary cell of the tetrahedral lattice is shown in Figure 1. The chain is supposed to be sufficiently long for end effects to be negligible.

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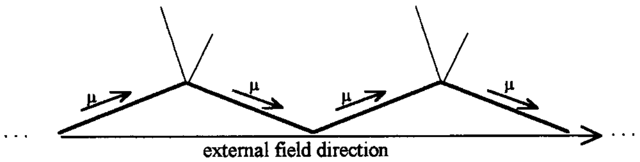

Figure 2. Distribution of dipole moments along the chain. μ—dipole moment of a bond.

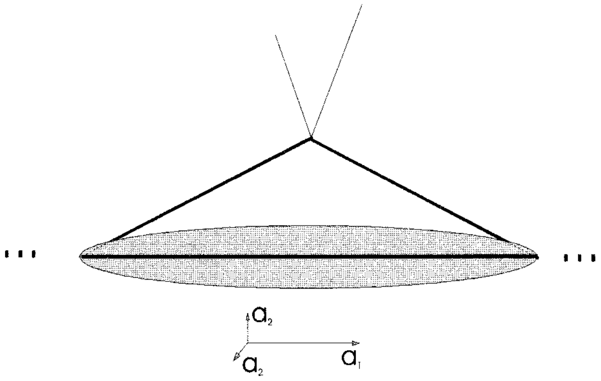

Figure 3. Optical polarizability tensor of a monomer unit of a chain.

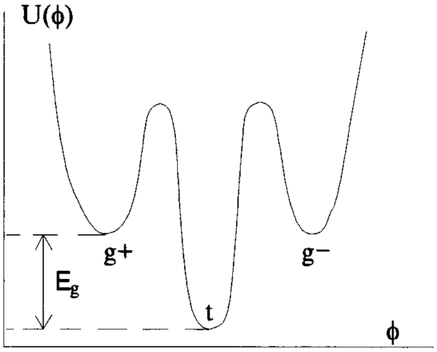

Figure 4. Internal rotation energy in the polymer chain.

A polymer chain of the A-type (according to the Stockmayer classification[7,8]) is considered (Figure 2). In this chain each bond has a dipole moment which is parallel to the bond. There are eight possible orientations of one bond dipole moment on a tetrahedral lattice site (Figure 1). A hypothetical monomer unit consisting of two neighboring bonds will be considered (Figure 5). Its dipole moment is assumed to be directed along the monomer unit.

It is assumed that the principal axis of the optical polarizability tensor of a monomer unit (which consists of two bonds) is directed along the monomer unit (Figure 3).

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

$$x = \frac{E_g}{kT} \tag{1}$$

where E_g is the difference between the energy of trans and gauche isomers (Figure 4). 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

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

and the fraction of gauche isomers is given by

$$P_0(g) = \frac{1 - P_0(t)}{2} = \frac{e^{-x}}{1 + 2e^{-x}} \tag{3}$$

3. Theory

3.1. Electric Birefringence and Order Parameter. If electrostrictive effects are neglected, the electric birefringence is given by the following expression:[1,4,5]

$$\frac{\Delta n}{c} = D\overline{\Delta A} \tag{4}$$

where Δn is the value of the electric birefringence (i.e., the difference between two main refractive indexes), c is the polymer concentration, $\overline{\Delta A}$ is the average anisotropy of the optical polarizability of a monomer unit in a laboratory coordinate system, and D is a factor independent of the external field. According to the assumptions which are made below, $D = [2\pi N_A(n^2 + 2)^2]/9\tilde{M}n$, n is the mean refractive index of the solution, $\tilde{M}$ is the molecular weight of the polymer chain, and N_A is Avogadro's number. The statistical averaging in eq 4 is carried out over all spatial orientations.

The components $\overline{A_{ik}}$ of the average optical polarizability tensor of a monomer unit are given by[1,4,5]

$$\overline{A_{ik}} = \sum_{\sigma,\tau} A_{\sigma\tau}\overline{(\sigma i)(\tau k)} \tag{5}$$

where $A_{\sigma\tau}$ is the component of the optical polarizability tensor of the monomer unit, Greek symbols denote coordinates in the molecular coordinate system (ξ,η,ζ), Latin symbols denote coordinates in the laboratory coordinate system (x,y,z), and σi is the cosine of the angle between two axes in different coordinate systems.

Let us consider the simplest case, when the optical polarizability tensor of a monomer unit $\hat{A}$ is diagonal and axially symmetric:

$$\hat{A} = \mathrm{diag}(A_1,A_2,A_2) \tag{6}$$

The symmetry axis coincides with the direction of the monomer unit in the molecular coordinate system. Let us emphasize that A_1 and A_2 are independent of the external field.

The lattice as a whole is oriented in the external field. This problem has been discussed earlier.[9−11] The most probable lattice orientation related to the external field direction is shown in Figure 1. If the fluctuations around this direction are neglected, the relative error in the free energy of a long polymer chain is of the order of $\sim(\ln N)/N$, where N is the number of bonds.

Using eqs 5 and 6, one obtains

$$\overline{A_{xx}} = (A_1 - A_2)\overline{(\xi x)^2} + A_2 \tag{7}$$

$$\overline{A_{yy}} = (A_1 - A_2)\overline{(\xi y)^2} + A_2 \tag{8}$$

$$\overline{A_{zz}} = (A_1 - A_2)\overline{(\xi z)^2} + A_2 \tag{9}$$

The condition $A_1 > A_2$ is used. In principle, this condition is not important for later considerations.

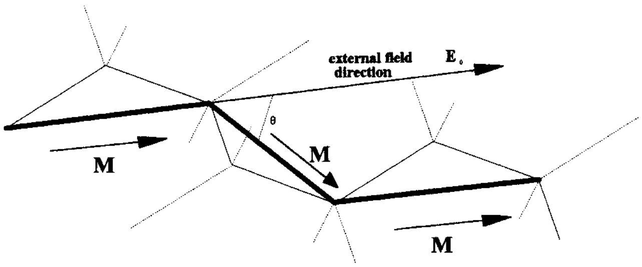

Figure 5. Monomer units of the polymer chain. *M*—dipole moment of a monomer unit.

The average anisotropy of the optical polarizability of a monomer unit may be given by

$$\overline{\Delta A} = A_{xx} - \frac{A_{yy} + A_{zz}}{2} \tag{10}$$

The average anisotropy of the optical polarizability of a polymer chain in the laboratory coordinate system can be obtained from eqs 5−10.

$$\overline{\Delta A} = (A_1 - A_2)\cdot\left(\frac{3}{2}\overline{(\xi x)^2} - \frac{1}{2}\right) = \Delta A\cdot S \tag{11}$$

where $\Delta A \equiv A_1 - A_2$ is the anisotropy of the optical polarizability of a monomer unit in the coordinate systems connected with this unit and S is the quadrupole order parameter for the monomer unit vector.

Thus, the quadrupole order parameter S for the monomer unit vector determines the field dependence of the electric birefringence:

$$\frac{\Delta n}{c} = D\cdot\Delta A\cdot S \tag{12}$$

The electric birefringence achieves its limiting value as the field increases. Then we have

$$\frac{\Delta n/c}{(\Delta n/c)_{\max}} = S \tag{13}$$

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

The quadrupole order parameter for a monomer unit vector (Figure 5) is one of the main orientational characteristics of a polymer chain:

$$S = \frac{3}{2}\left(\langle\cos^2\theta\rangle - \frac{1}{3}\right) \tag{14}$$

where θ is the angle between the direction of the external field and the monomer unit vector (Figure 5).

To calculate S for the lattice RIS model, the equation suggested by Gotlib and Medvedev[9] can be used for the average variables, such as $\langle\pi_i\pi_j\rangle$. Here, $\pi(\beta)$ is a function of an orientation of the ith bond on the lattice and β is the parameter characterizing the bond orientation, $\beta = 1, ..., f$ (f is the total number of possible orientations on the lattice):

$$\langle\pi_i\pi_j\rangle = \sum_{\beta,\gamma=1}^{f} \pi(\beta)\cdot\pi(\gamma)\cdot\left\{\left[\frac{\hat{G}}{\lambda_1}\right]^{|i-j|}\right\}_{\beta\gamma} u_\beta v_\gamma \tag{15}$$

$\hat{G}$ is the transition matrix, μ_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 matrix $\hat{G}$ ($\mathbf{v}\hat{G} = \lambda_1\mathbf{v}$, $\hat{G}\mathbf{u} = \lambda_1\mathbf{u}$).

In our case $\langle\cos^2\theta\rangle$ can be calculated according to eq 15 if $i = j$ and $\pi(\beta) = \cos\theta_\beta$; θ_β is the angle corresponding to the monomer unit in the β orientation:

$$\langle\cos^2\theta\rangle = \sum_{\beta,\gamma=1}^{12} \cos\{\theta(\beta)\}\cdot\cos\{\theta(\gamma)\}\cdot\left\{\left[\frac{\hat{G}}{\lambda_1}\right]^{|i-j|}\right\}_{\beta\gamma} u_\beta v_\gamma \tag{16}$$

3.2. Transition Matrix. The statistical properties of a chain at a given lattice orientation are completely determined by the elements of the transition matrix $\hat{G}$.[12] The elements $\hat{G}_{\alpha\beta}$ of this matrix are as follows:

$$\hat{G}_{\alpha\beta} = G^*_{\alpha\beta}\exp\left\{-\frac{U(\alpha,\beta)}{kT}\right\} \tag{17}$$

The total energy of a polymer chain consists of the energy of the chain in the external field and the energy of the internal rotation, determined by the parameter of initial rigidity x of the chain or by E_g. Thus, for $U(\alpha,\beta)$ we have $U(\alpha,\beta) = U^{\text{ext}}(\alpha,\beta) + U^{\text{int}}(\alpha,\beta)$. α and β are possible orientations of the chain bond which depend on the orientation of the previous bond (see eq 19), and G^* is a constant matrix describing the allowed orientations of the bond dipole moment on the lattice, $G^*_{\alpha\beta} = 0$ or 1. This factor is also related to the internal energy.

In our model, each chain bond has a dipole moment μ. The energy U_i^{ext} of the ith chain bond in the external field of dipole symmetry is written as

$$U_i^{\text{ext}} = -\mu E_0 \cos\phi_i \tag{18}$$

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

The energy of a polymer chain $U(\Omega_1,\Omega_2,...,\Omega_N)$ in the external field may be expressed as a sum of the energies of three neighboring bonds in the simple case of independent internal rotations:

$$U(\Omega_1,\Omega_2,...,\Omega_N) = U(\Omega_1,\Omega_2,\Omega_3) + U(\Omega_2,\Omega_3,\Omega_4) + \\ ... + U(\Omega_{N-2},\Omega_{N-1},\Omega_N) \tag{19}$$

where Ω_i determines the orientation of the ith bond, $U(\Omega_{i-1},\Omega_i,\Omega_{i+1})$ is the energy of three neighboring bonds, and N is the number of chain bonds.

When real polymer chains are placed in a strong external field, the conformational rearrangements may involve long-range correlations along the chain. However, the field dependence on the electric birefringence is determined by the quadrupole order parameter S for the monomer unit vector (see eqs 12−14). S depends on the correlations of the third order and is independent of the correlations of higher order.

For a polymer chain on a 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. Taking into account the symmetry of the system, in the case of equivalent trans and gauche rotational isomers, the dimensions of the "reduced" matrix $\hat{\hat{G}}$ are 8×8.[10,11]

To reduce the dimensions of the transition matrix 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. Hence, the dipole moment of a monomer unit M is equal to

$$M = 2\sqrt{\frac{2}{3}} \cdot \mu \tag{20}$$

With the help of the method proposed by Darinskii and Neelov[13] and Medvedev and Gotlib[14] (in which other structural units are also taken into consideration) the dimension of the transition matrix for nonequivalent rotational isomers may also be reduced. Since the monomer unit vector has 12 possible orientations, the dimensions of the "reduced" matrix $\hat{\hat{G}}$ for monomer units are 12 × 12.

Taking into account eqs 1, 17, and 18, we obtained the following transition matrix $\hat{\hat{G}}$ for nonequivalent isomers:

$$\hat{\hat{G}} = \begin{vmatrix}
t^2\sigma^4 & tg\sigma^3 & tg\sigma^3 & 0 & g^2\sigma & g^2\sigma & 0 & tg\sigma^3 & g^2\sigma^2 & 0 & tg\sigma^3 & g^2\sigma^2 \\
tg\sigma^3 & t^2\sigma^2 & tg\sigma^2 & 0 & tg & g^2 & 0 & g^2\sigma^2 & g^2\sigma & 0 & g^2\sigma^2 & tg\sigma \\
tg\sigma^3 & tg\sigma^2 & t^2\sigma^2 & 0 & g^2 & tg & 0 & g^2\sigma^2 & tg\sigma & 0 & g^2\sigma^2 & g^2\sigma \\
0 & g^2\frac{1}{\sigma} & g^2\frac{1}{\sigma} & t^2\frac{1}{\sigma^4} & tg\frac{1}{\sigma^3} & tg\frac{1}{\sigma^3} & tg\frac{1}{\sigma^3} & 0 & g^2\frac{1}{\sigma^2} & tg\frac{1}{\sigma^3} & 0 & g^2\frac{1}{\sigma^2} \\
0 & tg & g^2 & tg\frac{1}{\sigma^3} & t^2\frac{1}{\sigma^2} & tg\frac{1}{\sigma^2} & g^2\frac{1}{\sigma^2} & 0 & g^2\frac{1}{\sigma} & g^2\frac{1}{\sigma^2} & 0 & tg\frac{1}{\sigma} \\
0 & g^2 & tg & tg\frac{1}{\sigma^3} & tg\frac{1}{\sigma^2} & t^2\frac{1}{\sigma^2} & g^2\frac{1}{\sigma^2} & 0 & tg\frac{1}{\sigma} & g^2\frac{1}{\sigma^2} & 0 & g^2\frac{1}{\sigma} \\
g^2\sigma & 0 & g^2 & tg\frac{1}{\sigma^3} & 0 & g^2\frac{1}{\sigma^2} & t^2\frac{1}{\sigma^2} & tg & tg\frac{1}{\sigma} & tg\frac{1}{\sigma^2} & g^2 & 0 \\
tg\sigma^3 & 0 & g^2\sigma^2 & g^2\frac{1}{\sigma} & 0 & g^2 & tg & t^2\sigma^2 & tg\sigma & g^2 & tg\sigma^2 & 0 \\
g^2\sigma^2 & 0 & tg\sigma & g^2\frac{1}{\sigma^2} & 0 & tg\frac{1}{\sigma} & tg\frac{1}{\sigma} & tg\sigma & t^2 & g^2\frac{1}{\sigma} & g^2\sigma & 0 \\
g^2\sigma & g^2 & 0 & tg\frac{1}{\sigma^3} & g^2\frac{1}{\sigma^2} & 0 & tg\frac{1}{\sigma^2} & g^2 & 0 & t^2\frac{1}{\sigma^2} & tg & tg\frac{1}{\sigma} \\
tg\sigma^3 & g^2\sigma^2 & 0 & g^2\frac{1}{\sigma} & g^2 & 0 & g^2 & tg\sigma^2 & 0 & tg & t^2\sigma^2 & tg\sigma \\
g^2\sigma^2 & tg\sigma & 0 & g^2\frac{1}{\sigma^2} & tg\frac{1}{\sigma} & 0 & g^2\frac{1}{\sigma} & g^2\sigma & 0 & tg\frac{1}{\sigma} & tg\sigma & t^2
\end{vmatrix} \tag{21}$$

In this matrix $t = P_0(t)$, $g = P_0(g)$, and $\sigma = \exp(ME_0/4kT)$.

Each monomer unit is determined by two bonds (Figure 5) and has 12 possible orientations in space. The relationship between the number of monomer units and the pairs of corresponding chain bonds (Figures 1) are as follows:

$$\begin{gathered}1 \rightarrow 1-6,\ 2 \rightarrow 1-7,\ 3 \rightarrow 1-8,\ 4 \rightarrow 2-5, \\ 5 \rightarrow 2-7,\ 6 \rightarrow 2-8,\ 7 \rightarrow 3-5,\ 8 \rightarrow 3-6, \\ 9 \rightarrow 3-8,\ 10 \rightarrow 4-5,\ 11 \rightarrow 4-6,\ 12 \rightarrow 4-7\end{gathered} \tag{22}$$

The partition function Z of a polymer chain is determined by the set of eigenvalues $\lambda_i (i = 1, ..., 12)$ of the matrix $\hat{\hat{G}}$:[12]

$$Z = \sum_{i=1}^{12} \lambda_i^N \tag{23}$$

For a long chain

$$Z \cong \lambda_i^N \tag{24}$$

where λ_1 is the largest eigenvalue.

Consequently, using the known values of λ_1, $\mathbf{u}$, and $\mathbf{v}$, we can calculate all statistical and conformational characteristics which are of interest. Following this procedure, analytical results were obtained for a thermodynamically flexible polymer chain (i.e., for the chain with equivalent rotational isomers, $x = 0$. In the case of a chain with thermodynamical rigidity, $x \neq 0$, exact analytical calculations become impossible and numerical computations were made.

3.3 Conformational Properties. According to eq 12, the field dependence of the electric birefringence for a polymer chain is determined by the order parameter S. The orientational effects and conformational reorganizations occur in the polymer chain under the influence of the external field. Both effects are interconnected and conformational rearrangements influence the order parameter.[10,11] Therefore, it is important to study the conformational properties of the polymer chain (i.e., the field effect on the fractions of trans isomers $P(t)$ and of gauche isomers $P(g)$ as well as on their different sequences: dyads, triads, and pentads). To obtain $P(t)$ and $P(g)$, one must calculate the distribution functions of the third order $\omega(\Omega_\alpha,\Omega_\beta,\Omega_\gamma)$ where Ω_α is the orientation parameter of the chain bond, $\alpha = 1, ..., 8$. Distribution functions of the higher order can be computed according to the "superposition" principle[12] as

$$\omega(\Omega_\alpha,\Omega_\beta,\Omega_\gamma) = \frac{\omega(\Omega_\alpha,\Omega_\beta)\ \omega(\Omega_\beta,\Omega_\gamma)}{\omega(\Omega_\beta)} \tag{25}$$

These functions are used to determine fractions of dyads, triads, and pentads, which were also obtained. The distribution functions of the third order can be recalculated from the distribution functions of the second order for the monomer unit vector $\omega_M(\Omega_\alpha,\Omega_\beta)$:[12]

$$\omega_M(\Omega_\alpha,\Omega_\beta) = u_\alpha v_\beta \hat{\hat{G}}_{\alpha\beta}/\lambda_1 \tag{26}$$

where Ω_α is the αth conformation of the monomer unit vector, $\alpha = 1, ..., 12$.

Equation 22 uniquely determines relations between distribution functions of the second order $\omega_M(\Omega_\alpha,\Omega_\beta)$ for monomer units and distribution functions of the fourth order $\omega_B(\Omega_\alpha,\Omega_\beta,\Omega_\gamma,\Omega_\zeta)$ for chain bonds. Then, the distribution function $\omega_B(\Omega_\alpha,\Omega_\beta,\Omega_\gamma)$ of the third order[12] is given by

$$\omega_B(\Omega_\alpha,\Omega_\beta,\Omega_\gamma) = \sum_{\zeta=1}^{8} \omega_B(\Omega_\alpha,\Omega_\beta,\Omega_\gamma,\Omega_\zeta) \tag{27}$$

The fraction of trans isomers is written as

$$P(t) = \sum_{\substack{\alpha,\beta=1 \\ \alpha\neq\beta}}^{8} \omega_B(\Omega_\alpha,\Omega_\beta,\Omega_\alpha) \tag{28}$$

The following relationship between fractions of trans and gauche isomers is valid:

$$P(g) = \frac{1 - P(t)}{2} \tag{29}$$

In the case of independent internal rotations when the fraction of trans isomers is known, one can calculate the average length of a trans sequence $\langle l_t \rangle$[11]

$$\langle l_t \rangle = \frac{\sum_{n=1}^{\infty} n\cdot[P^n(t)]\cdot[1 - P(t)]}{\sum_{n=1}^{\infty} [P^n(t)]\cdot[1 - P(t)]} \tag{30}$$

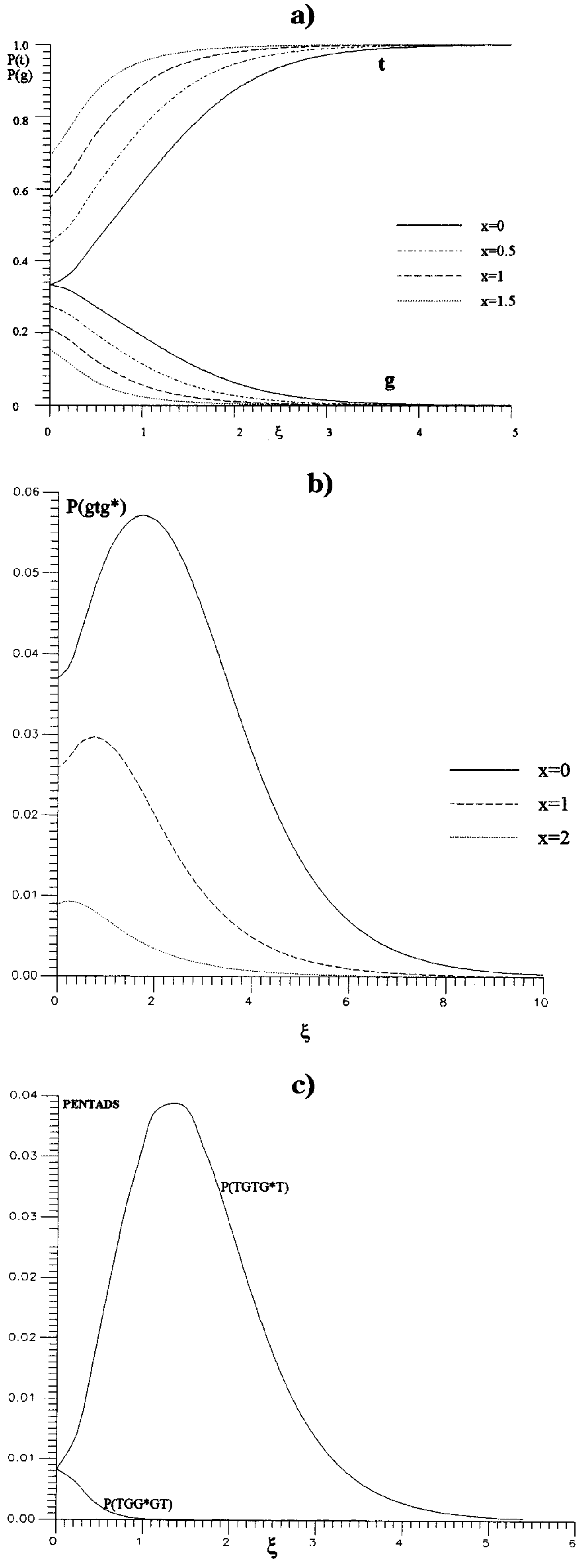

Figure 6. (a) Field dependence of the fractions of trans *P*(*t*) and gauche *P*(*g*) isomers. $\xi = (\mu E_0/2kT)$. (b) Field dependence of the fractions of triads gtg* at different values of the parameter *x*. $\xi = (\mu E_0/2kT)$. (c) Fractions of some pentads vs the quadrupole order parameter (normalized to the maximum value) for the chain bond vector. $x = 0$. $\xi = (\mu E_0/2kT)$.

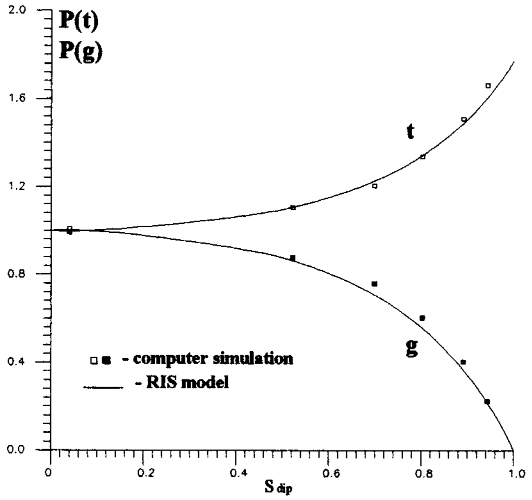

Figure 7. Fractions of trans *P*(*t*) and gauche *P*(*g*) isomers normalized to the initial value vs the chain dipole order parameter S_{dip}, $S_{\mathrm{dip}} = \langle\cos\theta\rangle$. Comparison with computer simulation results.[16] $x = 1$.

where $P^n(t)$ is the probability of the sequence of n trans isomers, $(1 - P(t))$ is the probability that the $(n+1)$th isomer is a gauche isomer.

Equation 30 gives

$$\langle l_t\rangle = \frac{1}{1 - P(t)} \tag{31}$$

4. Results and Discussion

4.1. Conformational Changes in a Strong Field.

The results obtained for the conformational properties of a polymer chain in an electric field are illustrated in Figures 6a, 6b, 6c, and 7.

With the growth of the external field the fraction of trans isomers in a polymer chain increases to unity. Consequently, the fraction of gauche isomers decreases to zero (Figure 6a).

The field effect on the different sequences of trans and gauche isomers (dyads, triads, and pentads) which govern the local dynamical properties of the chain[13,15] were also calculated for different values of the rigidity parameter *x*. For example, the field dependence of the gtg* triad probability is shown in Figure 6b. The shortest kinks determined by pentads tgtg*t are formed from these triads. The same results have been obtained earlier.[13] A nonmonotonic field dependence of the pentad tgtg*t (Figure 6c) is obtained.

The fractions of trans and gauche isomers, calculated in this work as functions of the order parameter *S*, are in good agreement with computer simulation results obtained by using a Brownian dynamics method[15] for a more realistic nonlattice model of a polymer chain (Figure 7). In the computer simulations, the chain has a fixed tetrahedral valence angle; the chain is finite and the space is continuous. It turns out that the discrete lattice effect is not very important if one considers conformational characteristics as a function of the dipole order parameter S_{dip}, characterizing the degree of the elongation of the chain in an external field:

$$S_{\mathrm{dip}} = \langle\cos\theta\rangle \tag{32}$$

In a strong external field the polymer chain has a long trans sequences and short kinks. The shortest kink[15] is determined by the pentad tgtg*t. The average length

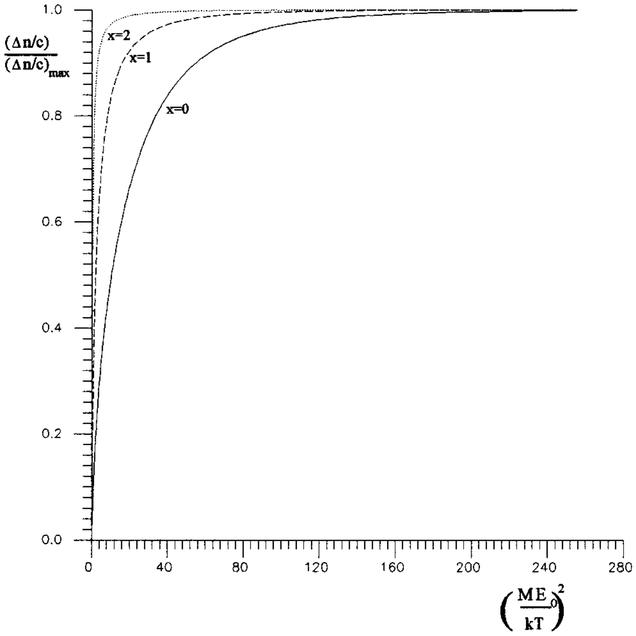

Figure 8. Influence of thermodynamic chain rigidity x on the field dependence of the electric birefringence.

of the trans sequences increases with increasing field. It is natural to propose that the average length of a trans sequence may be considered as an effective segment of the RIS model of a polymer chain on a tetrahedral lattice. This assumption will be proved below.

4.2. Field Dependence of the Electric Birefringence. The field dependence of the electric birefringence for polymer chains with different values of the initial thermodynamic rigidity parameters x were obtained over a wide range of external fields (Figure 8). 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).

As the field increases, the electric birefringence achieves a constant limiting value.

The growth rate of the electric birefringence with the field increases with increasing initial chain rigidity x. The initial polymer chain rigidity strongly influences the Kerr effect (Figure 8).

The Kerr effect depends on the degree of the chain elongation in the external field, characterized by the S_{dip}, which is closely related to the conformational properties according to the results shown in Figure 7. Hence, conformational properties directly influence the Kerr effect.

4.3. "Effective" Freely Jointed Chain. It is interesting to compare first the field dependence of the Kerr effect obtained for the RIS lattice model of a very flexible polymer chain when the parameter of thermodynamical rigidity x is equal to zero with that for the corresponding FJC model (Figure 9). Let us assume that values of the dipole moment and the optical polarizability tensor per unit length of a polymer chain in the RIS model are equal to the corresponding characteristics of the FJC.

As expected, in a weak electric field (i.e., in the case when the Kerr law is valid and conformational rearrangements are not important) both models give approximately equal results. These results can be explained by the fact that the length of the FJC segment is close to that of the Kuhn segment length A of the RIS chain. In our previous paper[16] it has been shown that the A value for a polymer chain on a tetrahedral lattice in the absence of the field (i.e., for a Gaussian chain) may be expressed as $A = \sqrt{6}[(^2/_3 - P(g))/P(g)]$.

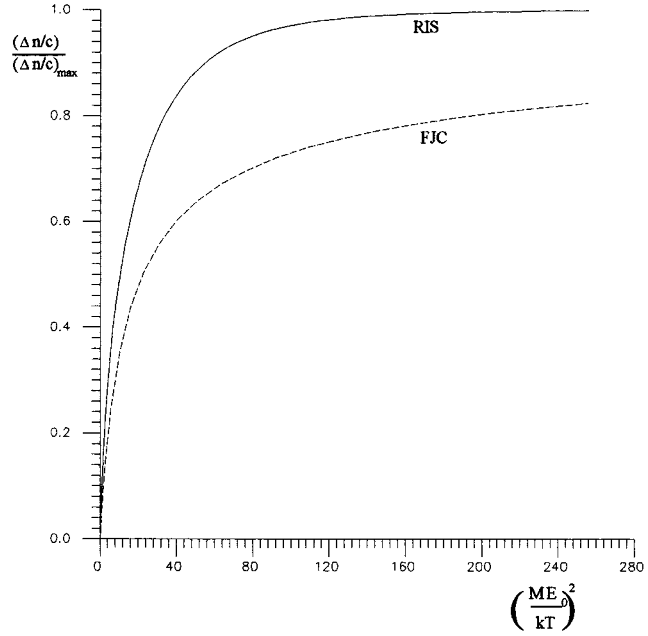

Figure 9. Theoretical dependence of the electric birefringence for the chain on the tetrahedral lattice compared with that for a freely jointed chain (FJC). $x = 0$. The dipole moment of the monomer unit M in the RIS model is equal to the dipole moment of the FJC segment.

However, a considerable difference between the two curves is observed in a strong field. It may be explained by the conformational rearrangements in the polymer chain under the influence of this field.

Thus, both the orientation of the segments and the conformational changes in the polymer chain in a strong electric field influence the Kerr effect. In the classic FJC model, only orientational effects are taken into account. The question of how to estimate the contribution of the effects of each type using the RIS model arises.

We can use the "effective" FJC with the adjusted segment length in order to describe correctly the Kerr effect for a long flexible polymer chain, taking into account field-induced conformational rearrangements. At each value of the external field the length of the FJC segment is recalculated to equalize the values of birefringence for the RIS lattice model and for the effective FJC model. Figures 10a, 10b, and 10c display the field dependence of the effective segment length for polymer chains with different values of the parameter of thermodynamical rigidity x. The next step is to explain the physical meaning of the obtained field dependence for the effective segments.

Figures 10a, 10b, and 10c show that in a strong field and at different values of the parameter x a good agreement between the length of the effective segment calculated from the birefringence of the chain on the lattice and the average length of the trans sequence is observed.

These differences between the effective segment length calculated with the help of the RIS model and the value of average length of the regular trans sequence are observed only in a very strong field in which the quadrupole order parameter S exceeds 0.9. It corresponds to a highly oriented system which is unattainable in the real experiment. At these values of the

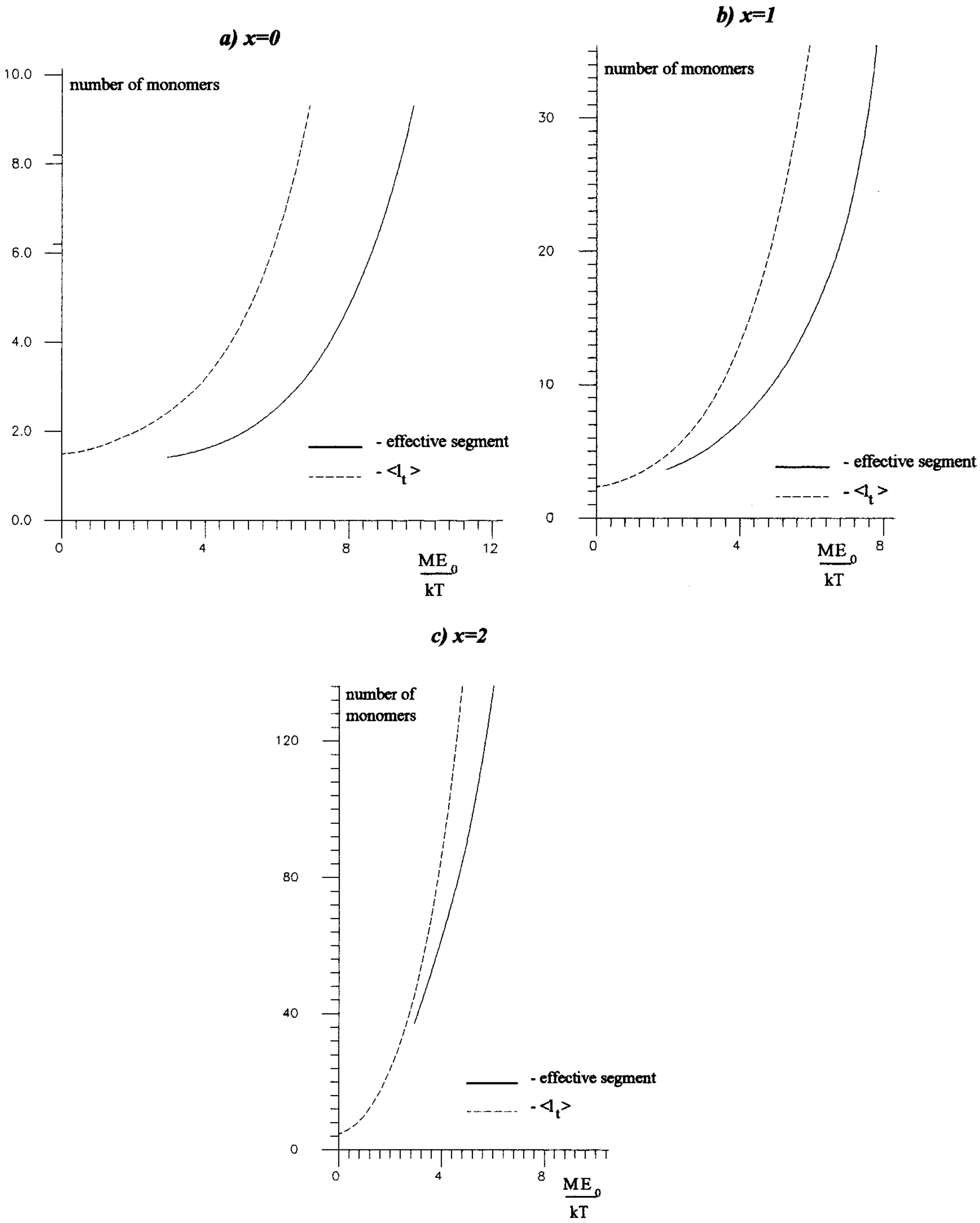

Figure 10. Segment length for an effective FJC from the birefringence for the tetrahedral lattice at different values of initial thermodynamic rigidity. (a) $x = 0$; (b) $x = 1$; (c) $x = 2$.

parameter S the electric birefringence achieves a limiting value. This difference may be partially explained, taking into account the fact that in a polymer chain under the influence of a strong external field both long regular trans sequences and short regions between trans sequences appear. The presence of these short regions decreases the average length of the effective segment.

One can also compare the electric birefringence curves for the FJC model with the effective segment length calculated from the RIS model to those where the effective segment length was taken to be equal to the average length of the trans sequence. These curves show a much better agreement for all values of the external field and the parameter x (Figure 11 shows an example for $x = 1$) than those found from the direct comparison of the field dependence for the two different effective segment lengths. Good agreement is also observed in a very strong field because in this case both the electric birefringence and the quadrupole order parameter achieve the same limiting value.

The results of the lattice theory with the experimental data for the Kerr effect could be directly compared if the experimental results for a long flexible polymer chain containing a longitudinal component of the permanent dipole moment were available (e.g., polyphosphazenes, polybutylisocyanates, etc.). At present, for such polymers there are experimental data only for a weak field.[1]

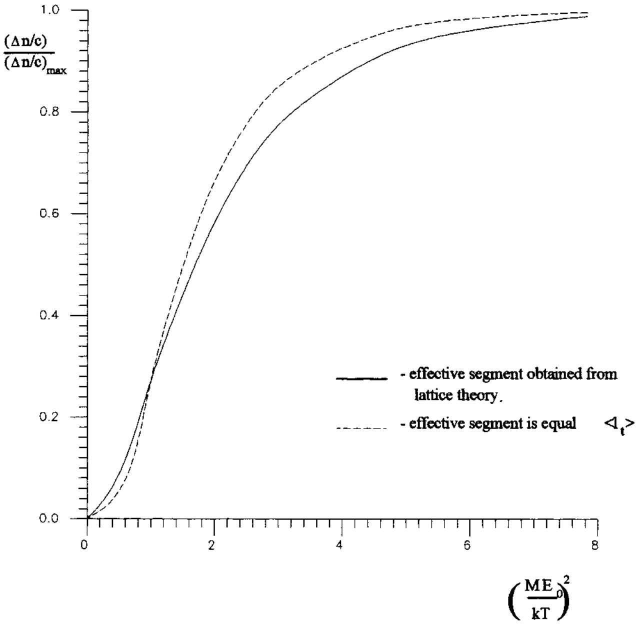

Figure 11. Field dependence of the electric birefringence for the FJC model with different effective segment lengths. $x = 1$.

5. Conclusions

The theory of the Kerr effect for an RIS model of a polymer chain on a tetrahedral lattice is developed. The field dependence of the electric birefringence is studied. The initial thermodynamic rigidity of a polymer chain strongly affects this dependence. An increase in the chain rigidity results in an increase of the electric birefringence at a given electric field. To consider the Kerr effect for a long flexible polymer chain in a strong external field, conformational rearrangements must be taken into account.

The orientation of the chain on the lattice may be interpreted as an orientation of "effective" FJC with the length of the rigid segment depending on the field. In a good approximation this effective element is shown to be equal to the average length of the trans sequence of a polymer chain on the lattice.

Acknowledgment. We are grateful to Prof. E. I. Rjumtsev and Dr. A. V. Lezov for many helpful discussions. This work was carried out with the financial support of RFBR Grants 96-03-33833 and 96-15-97401, ISSEP Grant a97-597 (S.V.L.), and St.-Petersburg Government Grant M97-2.2K-643 (S.V.L.). I.M.N. is grateful to the Academy of Finland for financial support during the final stage of the study.

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MA980680E