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Polarizability of Rigid Rod Macromolecules with Dipolar Side Chains. A Nonlinear Dielectric Effect Study

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ABSTRACT: This paper considers the contribution of dipolar side chains to the dielectric properties of rigid rod macromolecules. It is shown that the rotational potential of a side dipole greatly influences the anisotropy of the electric polarizability. Other possible reasons for the high anisotropy determined from the nonlinear dielectric effect (NDE) are discussed for helical polypeptides. The tensors of electrical as well as optical polarizability for poly(γ-benzyl L-glutamate) in dioxane are determined from the increments of the refraction index, the electric permittivity, the electrooptical Kerr effect, and the NDE. The results suggest that the motion of the side groups of a cooperative nature depends on the solvent and the polymer concentration. The calculated molecular anisotropy is of the opposite sign of the experimentally obtained effective anisotropy.

Toward the end of the 1960's the nonlinear dielectric effect (NDE) method was introduced for the study of the electric properties of macromolecules. The NDE consists of the change in electric permittivity of a medium subjected to an electric field of high intensity. As the first experimental data were being presented,[1,2] Kielich was developing the NDE theory for rigid macromolecules.[3,4] This theory made it possible to determine molecular electric parameters if the relation between the NDE and the intensity of the field including this effect is known. Particularly, depending on the measuring field frequency, either the dipole moment[2,5-7] or both the dipole moment and the anisotropy of the electric polarizability can be obtained.[6-8] Since the dipole moments can be obtained by many other experimental methods,[9-11] the NDE is unique in that it makes possible the determination of the electrical anisotropy. The optical effect can in turn be determined from the external field induced birefringence of a solution, as, e.g., in the electrooptical Kerr effect (EKE). Thus, measuring the two effects—the EKE and the NDE—allowed us to compare the anisotropies of the optical and the electrical polarizabilities.

The anisotropic part of the NDE, proportional to the electric polarizability, has so far been measured for three categories of macromolecules: synthetic polypeptides,[6-8] cellulose derivatives,[5] and polyisocyanates.[7,12] The first two cases offer easily observable results; in this study, however, we have not observed NDE in the cellulose derivatives. This can be interpreted as caused by the low dipole moment of those macromolecules which is insufficient to orient them significantly in the electric field and thus to induce an observable NDE. It is remarkable, however, that polypeptides and polyisocyanates of comparable dipole moments of the order of 10^{-27} Cm (10^2–10^3 D) and of similar helical structure in solutions have greatly different NDE and therefore different anisotropies of polarizability, the difference being 1 or 2 orders of magnitude.[7] As the polypeptides had polar side chain groups attached to the helical backbone while the groups in the polyisocyanates are of a nonpolar kind, one is inclined to assume that the dipole moments of side groups may play a decisive role in the magnitude of the effect.

This paper intends to show the influence of side groups on the anisotropy of electric polarizability, as proposed by Wada,[13] and discuss other competing explanations of the mechanisms of polarizability of helical polypeptides.

Theory

Model of Anisotropy. Let us consider a rigid, axially symmetrical macromolecule with regularly placed dipolar side chain groups. Following Wadas assumption[14] that dipoles can rotate independently along the axes perpendicular to the molecular axis (Figure 1), we obtain the contribution of a dipolar side group to the polarizability tensor[15]

$$\alpha^s_{11} = \frac{\mu_s^2}{kT}(\langle\cos^2\theta\rangle - \langle\cos\theta\rangle^2) \quad \text{(1a)}$$

$$\alpha^s_{33} = \alpha^s_{22} = \frac{\mu_s^2}{2kT}(\langle\sin^2\theta\rangle - \langle\sin\theta\rangle^2) \quad \text{(1b)}$$

where μ_s is the dipole moment component perpendicular to its rotation axis, since all the parallel components cancel out due to the symmetry of the helix. The averaging $\langle...(\theta)\rangle$ is carried out through all the possible orientations θ of the side group dipole in relation to the molecular axis

$$\langle...(\theta)\rangle = \int_{-\pi}^{+\pi}...(\theta)e^{-\beta U(\theta)}\,d\theta \Big/ \int_{-\pi}^{+\pi} e^{-\beta U(\theta)}\,d\theta \quad (2)$$

where $U(\theta)$ is the potential for dipole rotation and $\beta = 1/(kT)$.

To arrive at a general formulation for the influence of side chain dipoles upon the molecular properties, let us replace the real shape of the rotational potential barrier by a rectangular well potential with depth ΔU and width 2ϵ, which is convenient for calculations. For this model, the mean polarizability $\bar{\alpha}^s$ and the anisotropy of polarizability $\Delta\alpha^s$ for one side group will be

$$\bar{\alpha}^s = \frac{1}{3}(\alpha^s_{11} + 2\alpha^s_{22}) = \frac{\mu_s^2}{3kT}\left[1 - \left(C\frac{\sin\epsilon}{\epsilon}\right)^2\right] \quad (3)$$

$$\Delta\alpha^s = \alpha^s_{11} - \alpha^s_{22} = \frac{\mu_s^2}{4kT}\left[1 + 3\cos 2\theta_0\left(C\frac{\sin 2\epsilon}{2\epsilon}\right) - (1 + 3\cos 2\theta_0)\left(C\frac{\sin\epsilon}{\epsilon}\right)^2\right] \quad (4)$$

where $C = [1 - \pi/\epsilon(e^{\Delta U/kT} - 1)]^{-1}$. It can be seen therefore that the anisotropy of polarizability is related not only to the depth and width of the well but, unlike the case of mean polarizability, also to the mean orientation θ_0 of the side group dipoles.

Two observations concerning the anisotropy are worth noting. First, it can be negative as well as positive, depending on θ_0. For example, when only small librations are allowed in a deep well, the sign reversal occurs at $\theta_0 = 33°44'$ or $146°16'$. Typical temperature plots of the anisotropies of polarizability for two priviliged dipole orientations—parallel and perpendicular to the molecular axis—are shown in Figure 2. Second, the anisotropy for hindered dipole rotation may not only be lower but also higher than that for free rotation, when $\Delta\alpha^s = \mu_s^2/4kT$.

The method of determination of the anisotropy of polarizability $\Delta\alpha^s$ requires, besides NDE, use of several ex-

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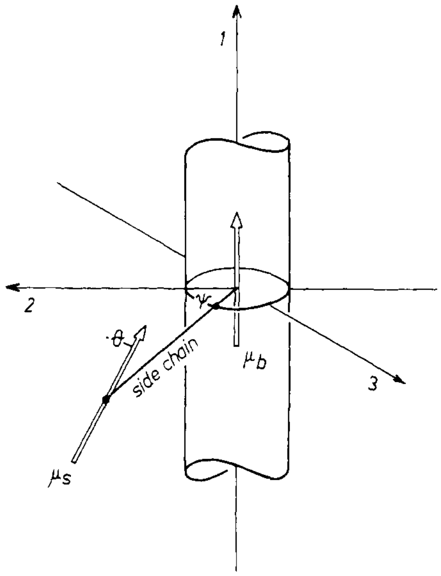

Figure 1. Model for the mer polarizability of a polypeptide with the dipole moment of the side group μ_s and that of the backbone μ_b. Adapted from ref 14.

perimental methods and will be discussed in detail later on.

Determination of Polarizability Tensor Components. Total electric polarizability α^e of a macromolecule n-mer

$$\alpha^e = \alpha^0 + \alpha^a + \alpha^s \tag{5}$$

is the sum of electronic polarizability α^0, atomic polarizability α^a, and orientational polarizability of the side chain dipole α^s. The experiments enable us to determine the mean value $\bar{a}$ and the anisotropy Δa, both related to the components $a_{11} = \bar{a} + 2\Delta a/3$ and $a_{22} = a_{33} = \bar{a} - \Delta a/3$, of the effective polarizability. Depending on the field frequency, by the effective polarizability we mean: a^0 is measured at optical frequencies, or $a^0 + a^a + a^s$ are measured at frequencies below the side dipoles' dispersion range, but above the dipole dispersion of the whole macromolecule. We arrive at the total effective mer polarizability based upon the theory of polarizability excess[16]

$$a_{11} = \alpha_{11}\gamma_{11} = \frac{v_0}{4\pi}(\epsilon_1 - 1) \tag{6}$$

where v_0 is the mer volume, and the internal field factor γ

$$\gamma_{11} = \lim_{E\to 0} \partial F_1/\partial E_1 = (1 + m_1 L_1)^{-1} \tag{7}$$

depends through m_1

$$m_1 = \frac{\epsilon_1}{\epsilon_s} - 1 = \frac{1}{\epsilon_s}\left(\frac{4\pi}{v_0}a_{11} + 1\right) - 1 \tag{8}$$

on the electric permittivity of the solvent ϵ_s, on the main permittivities of the macromolecule ϵ_1, and through the L factor[16] on its shape. Equations 6–8 permit the determination of molecular components α_{11} based on effective values of $\bar{a}$ and a, obtained from experimental data.

The effective mean polarizability $\bar{a}^e$ is determined from the increment of electric permittivity measured for dilute solutions at suitably high frequency when the overall dipole moment of the macromolecule does not contribute to the electric permittivity. Given those conditions we have

$$\epsilon - 1 = 4\pi(N_s a_s^e + N\bar{a}^e) \tag{9a}$$

$$\epsilon_s - 1 = 4\pi N_{s0} a^e \tag{9b}$$

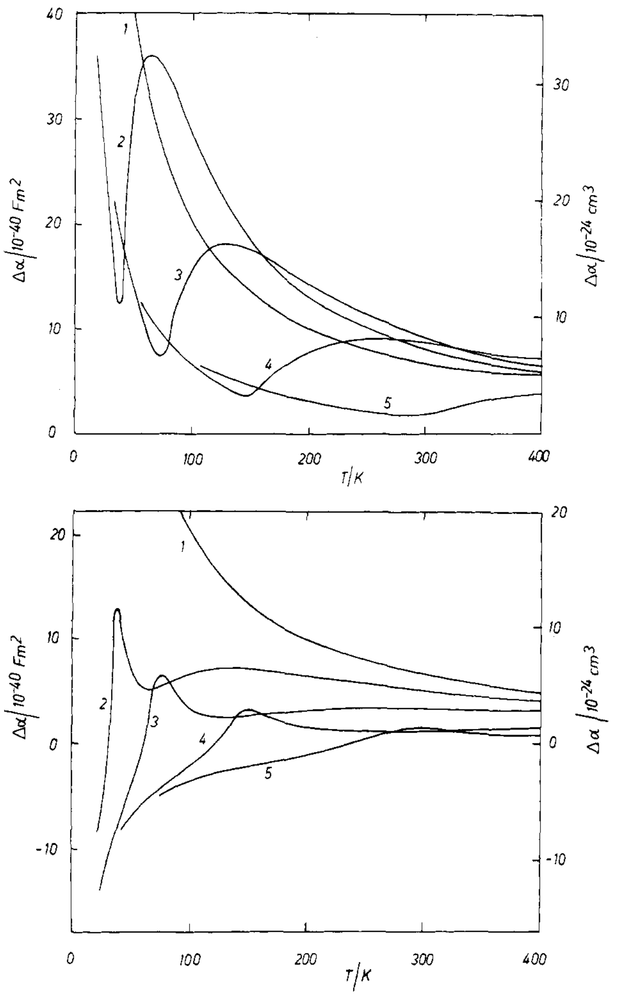

Figure 2. Plots of anisotropy of polarizability $\Delta\alpha^s$ vs. temperature T for $\theta_0 = \pm\pi/2$ (a, top) or $\pm\pi/2 + \pi/2$ (b, bottom). The calculations are $\mu_s = 3.3 \times 10^{-30}$ Cm, $\epsilon = \pi/6$, $\Delta U = 0$ (1), 1.25 kJ mol^{-1} (2), 2.50 kJ mol^{-1} (3), 5.0 kJ mol^{-1} (4), and 10.0 kJ mol^{-1} (5).

where the values with the "s" index refer to the solvent, N_s and N_{s0} being the number of solvent molecules per volume unit of the solution and that of the pure solvent, respectively, while

$$N = N_A W d/M$$

is the mer concentration in the same units. From equation 9 we obtain

$$\frac{\epsilon - \epsilon_s}{N} + \eta\frac{\epsilon_s - 1}{N_{s0}} = 4\pi\bar{a}^e \tag{10}$$

where

$$\eta = \frac{N_{s0} - N_s}{N} = \frac{M}{M_s}\left(1 - \frac{1}{d}\,\frac{d - d_s}{W}\right) \tag{11}$$

d is the solution density, and W is the weight fraction of the polymer. Equations 10 and 11 are equivalent to the formula given by Wada,[9,17] noting, however, the wrong sign of the expression with $\epsilon_s - 1$ of the original eq 7 of ref 9. Similarly to $\bar{a}^e$, the effective mean optical polarizability $\bar{a}^0$ can be determined from the increment of refractive index

$$2n_s\frac{n - n_s}{N} + \eta\frac{n_s^2 - 1}{N_{s0}} = 4\pi\bar{a}^0 \tag{12}$$

For dilute solutions, eq 10–12 can be easily transformed into a particularly simple Dale–Gladstone formula[18] for optical frequencies and its equivalent for lower ones

$$\frac{\mathrm{d}n}{\mathrm{d}c} = \bar{v}(\bar{n} - n_{\mathrm{s}}) \qquad \frac{\mathrm{d}\epsilon}{\mathrm{d}c} = \bar{v}(\bar{\epsilon} - \epsilon_{\mathrm{s}}) \qquad (13)$$

which permits the calculation of the mean index of refraction $\bar{n}$ and the mean electric permittivity $\bar{\epsilon}$ of the polymer, c being its weight/volume concentration and $\bar{v}$ its partial specific volume.

The effective anisotropy of optical polarizability Δa^0 and that of the electric polarizability Δa^{e} are determined from the increments of the Kerr constant defined here as $\Delta n E^{-2}$ and the NDE constant, defined as $\Delta\epsilon E^{-2}$. Δn and $\Delta\epsilon$ are respectively the anisotropy of the refractive index and the change of the electric permittivity, both caused by a strong electric field of intensity E. For the case where the dipole moment of a macromolecule is mainly responsible for its orientation in the strong field but does not contribute to the orientation in the measuring field, we obtain in agreement with ref 3, 11, and 19 the following

$$\frac{(\Delta\epsilon - \Delta\epsilon_{\mathrm{s}})E^{-2}}{N} + \eta\frac{\Delta\epsilon_{\mathrm{s}}E^{-2}}{N_{\mathrm{s0}}} = \frac{8\pi}{3}\Delta a^{\mathrm{e}}\Phi(p)E^{-2} \qquad (14)$$

$$\frac{(\Delta n - \Delta n_{\mathrm{s}})E^{-2}}{N} + \eta\frac{\Delta n_{\mathrm{s}}E^{-2}}{N_{\mathrm{s0}}} = \frac{2\pi}{n_{\mathrm{s}}}\Delta a^0\Phi(p)E^{-2} \qquad (15)$$

where Φ is the orientation function introduced by O'Konski.[19]

$$\Phi(p) = 1 - 3\,(\coth p - 1/p)/p \qquad p = \mu E/(kT) \qquad (16)$$

It follows from eq 14–16 that by measuring the Kerr constant or the NDE constant as a function of the electric field intensity, one can determine, e.g., by the best fitting procedure, the dipole moment and simultaneously the anisotropy of the effective polarizabilities of the macromolecule.[6,7,19] Since the mean effective polarizabilities can in turn be determined from the refractive index, the electric permittivity, and the density data, it is completely possible to determine the tensors of effective as well as of molecular polarizabilities of rodlike macromolecules.

Experimental Section

Materials. Nonfractionated ethylcellulose (BDH, Prod. No. 28330) and poly(γ-benzyl L-glutamate) (PBLG) of mol wt 125 000 (Shwartz-Mann, lot Y 3633) were dried and used without further purification. Solvents were purified using standard methods. As the experimental results depend on the momentary state of molecular association in the solution [e.g., 20] only fresh samples were measured. Moreover, the strong electric field applied could change the state of association,[8,21] affecting the results obtained. In order to get the correct result, one must apply fields of proper duration, considerably longer than the rotational relaxation time but much shorter than the solution restructuring time under the influence of the field. The latter depends on the type of association, the solvent, and the strength of the electric field.[8] These limitations made some measurements impossible, e.g., of a solution of PBLG 75 000 in chlorobenzene or PMLG 300 000 in dioxane.

Measurements. To measure the NDE we used an apparatus of the type described in ref 22, working at ca. 2 × 10^6 Hz. High-field pulses of duration of 10^{-3} s were applied. The additional change in the electric permittivity, due to Joule heating, can be neglected in these conditions only for liquids of electric conductivity lower than ca. $10^{-7}\ \Omega^{-1}\ \mathrm{m}^{-1}$. For this reason we could perform the measurements, using solvents of low electric permittivity favoring molecular association.

The measurability of low NDE's was tested for chlorobenzene, 1,2-dimethoxyethane, and di-n-buthyl ether, obtaining -6×10^{-19}, -5×10^{-18} and $-4 \times 10^{-18}\ \mathrm{V}^{-2}\ \mathrm{m}^2$, respectively. The standard error varied from 30 to 5% for a field intensity of 20–90 kV cm^{-1}. The high error for lower fields made it impossible to determine the molecular dipole moment correctly. In order to calculate the electric anisotropy Δa^{e}, the dipole moment was taken from more precise Kerr effect measurements.

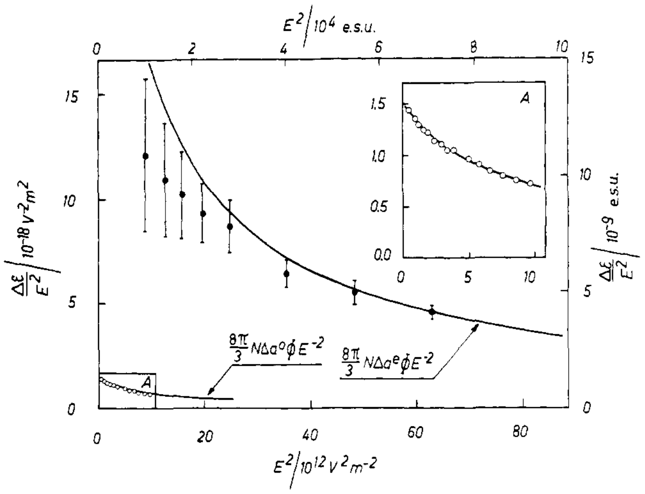

Figure 3. NDE constant $\Delta\epsilon E^{-2}$ measured (●) and calculated (○) from EKE data for PBLG in dioxane, $c = 9.5 \times 10^{-4}\ \mathrm{g\ cm}^{-3}$. The solid lines are calculated by fitting eq 15 to all the points or by fitting eq 14 to the point of the smallest experimental error.

The Kerr effect was measured in a setup as follows: 550 nm light source, polarizer, Kerr cell, analyzer, photomultiplier. The standard error varied from 5 to 2% for applied pulsed fields of intensity of 5–40 kV cm^{-1}. The EKE as well as the NDE were measured at 25 °C.

The electric permittivity was measured at 25.0 °C, using a DM01 dipolmeter, Wissenschaftlish-Technische Werkstatten, working at the frequency of 2 × 10^6 Hz. The experimental error was lower than 0.01% when applied to the MFL 1D measuring cell. The refractive index increment of PBLG was assumed to be $\mathrm{d}n/\mathrm{d}c = 0.121\ \mathrm{g}^{-1}\ \mathrm{cm}^3$, the mean of the published values.[23–25] The density increment was calculated taking the PBLG density as 1.25 g cm^{-3}[26] and assuming that the solution density is a linear function of the polymer volume fraction.

Results and Discussion

In the solutions of ethylcellulose in carbon tetrachloride (concentration 1 × 10^{-2} g cm^{-3}), the NDE is practically unnoticeable, $|\Delta\epsilon E^{-2}| < 3 \times 10^{-18}\ \mathrm{V}^{-2}\ \mathrm{m}^2$. Considerable effects observed by Block and Hayes,[5] who used a different experimental technique, may be assumed to be artifacts.

In solutions of PBLG in 1,4-dioxane, the NDE is easily measurable, even at concentrations of the order of 10^{-3} g cm^{-3}. For such concentrations, due to strong association processes the relaxation time of molecular entities is long enough for their dipoles not to catch up with the measuring field.[15] In those conditions eq 14 applies, and since the solvent does not contribute visibly to the NDE, the constant $\Delta\epsilon E^{-2}$ is directly proportional to the electrical anisotropy Δa^{e}. Figure 3 represents a typical series of experimental NDE results. For comparison, a hypothetical NDE constant calculated with the assumption that macromolecules possess the electronic polarizability only, whose anisotropy Δa^0 has been determined from the Kerr constant, is also shown. It is remarkably evident that the total anisotropy of PBLG molecules is more than ten times greater than the optical anisotropy. For small molecules, the difference is not as drastic and amounts to from several to nearly 100%.[27]

Anomalously high effective polarizability along the axis of helical polypeptides has been noticed previously,[6–8,28] and this has been attributed to: (i) high hyperpolarizability of intramolecular hydrogen bonds situated along the axis; (ii) considerable contribution of helical spring vibrational modes of the helix polarizabiliy; and (iii) motions of side group dipoles, discussed in this paper. The first expla-

Table I
Increments of PBLG in 1,4-Dioxane at 25 °C[a]

dn/dc	1.21×10^{-4} m^3 kg^{-1}
$d\epsilon/dc$	60×10^{-4} m^3 kg^{-1}
$d\Delta n E^{-2}/dc$	0.85×10^{-18} m^5 kg^{-1} V^{-2}
$d\Delta\epsilon E^{-2}/dc$	37×10^{-18} m^5 kg^{-1} V^{-2}

[a] Data on electric field induced effects refer to $E \rightarrow 0$.

Table II
Bulk Properties and Mer Polarizabilities of PBLG in Dioxane

property	component	
	longitudinal	transverse
electric permittivity, ϵ	10.2	9.5
refractive index, n	1.573	1.562
total polarizability, 10^{-40} Fm^2		
effective, a^e	238	217
molecular, α^e	238	574
optical polarizability, 10^{-40} Fm^2		
effective, a^o	37.9	37.0
molecular, α^o	37.9	40.9
side dipole + atomic polarizability, 10^{-40} Fm^2		
effective, $a^s + a^a$	200	180
molecular, $\alpha^s + \alpha^a$	200	533

nation requires a strong electric field induced proton shift in the CO···NH bonds into the biionic form of a higher dipole moment, in that way giving rise to the NDE. NDE theories for classical and quantum proton transfer, supplied by Piekara,[29] Weidemann and Zundel,[30] and Danielewicz-Ferchmin,[31] have, however, not been applied to polypeptides. The second mechanism has not been discussed quantitatively, but it is easy to notice that, as a practical matter, neither of the first two mechanisms contribute to polarizability measured perpendicularly to the helix axis. It makes the data from the first two mechanisms different from those of the third mechanism of the dipole motions and from the experimental data.

The experimental increments necessary to determine the main polarizabilities are shown in Table I and the calculated values in Table II. In calculations we assumed the n-mer volume to be $v_0 = 291 \times 10^{-24}$ cm^3, resulting from the PBLG density. Another value, as for example 350×10^{-24} cm^3, resulting from hydrodynamical data, will slightly change the polarizability obtained, without influencing any conclusions. From Table II it is seen that the effective transverse polarizability of PBLG differs markedly from the molecular one, due to the difference between the applied field and the internal one. As a consequence, the total molecular anisotropy, $\Delta\alpha^e = -336 \times 10^{-40}$ Fm^2, even has the opposite sign to that of the effective anisotropy, $\Delta a^e = +20.6 \times 10^{-40}$ Fm^2, as it is at optical frequencies, where $\Delta\alpha^0 = -3.0 \times 10^{-40}$ Fm^2 and $\Delta a^0 = +0.86 \times 10^{-40}$ Fm^2. The local field effect changing the sign of anisotropy has also been observed for poly(ϵ-(carbobenzyloxy)-L-lysine) where, as for PBLG, the molecules of the negative intrinsic anisotropy contribute positively to the Kerr effect in many solvents.[32] In view of these data, there is no reason to speak about the high longitudinal effective polarizability, but the PBLG molecule should be considered rather as the one with the high transverse molecular polarizability. It may be caused by the motions of dipolar side groups if the mean orientation of the dipoles is nearly parallel or antiparallel to the molecular axis. Indeed, in order to explain the overall PBLG dipole moment in various solvents, one assumes that the dipoles of the helical backbone and those of the side groups are nearly antiparallel.[9,33] Also, the negative molecular anisotropy at optical frequencies, where the dipole motions are of no significance, appears understandable as the optical polarizability of an n-mer is greatest along the side group elongated perpendicularly to the helix axis.[32,34]

A model of dipolar side group polarizability does not directly provide quantitative conformity with the molecular values obtained. The dipolar polarizability α^s practically equals that of $\alpha^s + \alpha^a$ given in Table II since the difference, being of the order of α^0, is small. Therefore, the mean side group polarizability, $\bar{\alpha}^s = 4.2 \times 10^{-38}$ Fm^2, and its anisotropy $\Delta\alpha^s = -3.3 \times 10^{-38}$ Fm^2, are several times greater than those possible for the model. Thus motions of dipoles cannot be independent, and the observed polarizabilities are strongly enhanced due to the cooperative nature of the motions.[15] The longitudinal and transverse polarizabilities are 5 and 25 times greater than those for freely rotating dipoles. This suggests the angular-dependent interaction of the side ester group with the nonsymmetrical surroundings.

Independent information of the side group dipole orientation is, unfortunately, impossible to obtain from the overall dipole moment of PBLG in dioxane. For the solutions examined, one determines the moment of the aggregates, depending upon their structure, about which not much is known. However, the polarizability can be discussed satisfactorily, as it is not influenced by the unknown directions of molecular axes oriented side by side within the associates of high molecular weight PBLG.[33,35]

The microwave absorption found by Davies et al. in PBLG solutions[28] can also be attributed to cooperative side group motions. The absorption intensity corresponds to a free rotation of dipoles of 9.0×10^{-30} Cm for PBLG of mol wt 110 000 in dioxane, as compared with 15.0×10^{-30} Cm from our dielectric data for the sample of similar molecular weight, both markedly higher than the moment of a single group of 6.0×10^{-30} Cm. A considerably effective dipole moment of the side groups is the cause of the high electric permittivity, $\bar{\epsilon} = 10$, of PBLG in dioxane. Samulski and Samulski have similarly interpreted their value of $\bar{\epsilon} = 8$ found by nondielectric methods in dioxane–dichloromethane mixtures.[36] On the contrary, practically complete immobilization of dipoles in solid PBLG results in the electric permittivity falling to ca 2.5, close to $\bar{n}^2$. The state of the side groups highly depends on the solvent; e.g., in benzene we found $d\epsilon/dc = 2.1$ g^{-1} cm^3 equivalent to $\bar{\epsilon} = 4.8$, while in dioxane–nitrobenzene mixtures a value as high as $\bar{\epsilon} = 19 \pm 8$ has been found.[36] This suggests complexing of the side groups by aromatic molecules of benzene (nonpolar) or nitrobenzene (polar), resulting in a decrease or an increase of the effective dipole moment, respectively. The common orientation of the solvent molecules and the side groups of PBLG was strongly suggested by their identical relaxation times found by Adachi et al.[37]

Apart from interactions with the solvent, the association processes have significant influence on the side group behavior. The number of molecular contacts increases with the polymer concentration making entanglements and interactions of neighboring molecules easier, which rises the potential barrier[37] and brings down the number of possible side dipole orientations. This also bears upon the polarizability tensor components, as shown in Figure 4. For helical polypeptides, the concept of hindered but cooperative librations of the side group dipoles around the mean orientation is not in disagreement with the results obtained by methods sensitive to the mean orientation of other side group fragments, e.g., the phenyl ring. The side

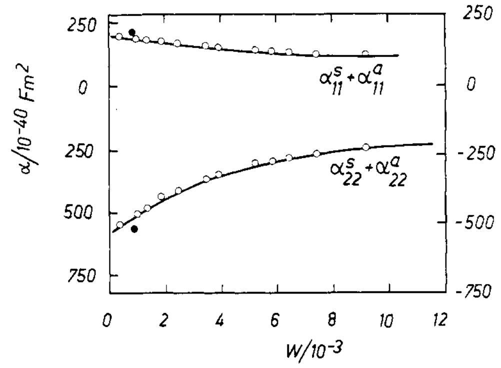

Figure 4. Components $\alpha^s{}_{11} + \alpha^s{}_{11}$ of the side dipole + atomic polarizability vs. weight fraction W of PBLG in dioxane. Calculated for NDE data of this work (●) and those of ref 7 (○) [dielectric data from ref 15].

chain of PBLG has been found to be highly oriented, not only in films but also in dilute solution.[26,38]

Conclusions

The NDE is unique as a method to determine the anisotropy of polarizability of rigid macromolecules. In conjunction with other methods, the NDE method makes it possible to determine the polarizability tensor of rigid macromolecules. As in helical polypeptides, the side groups contribute considerably to molecular anisotropy; the NDE can provide information on the behavior of these groups, which depends on the internal structure and the structure of the surroundings.

Some observations indicate the cooperative nature of the side group motions, which apart from the noted increase in mean electric polarizability and its anisotropy may result, as in small molecules,[39,40] in a hyperpolarizability increase as compared to noninteracting dipole systems. However, because of inadequate sensitivity of the experimental setup, we have not applied the NDE to determine those values in systems where the orientational phenomena are eliminated, as in gels or the liquid crystal phase of polypeptides.

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