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Nonlinear Dielectric Effect of Flexible Polar Polymers

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ABSTRACT: The nonlinear dielectric effect (NLDE) is the change of the dielectric constant of a medium when subject to a strong electric field. It is the result of a sensitive interplay between the fourth and second moments of the dipole moment, $\langle \mu^2 \rangle^2 \sigma$, where $\sigma = \langle \mu^4 \rangle / \langle \mu^2 \rangle^2 - 5/3$, μ is the dipole moment, and the angular brackets denote statistical averaging over all internal configurations in the absence of the external field. σ is a measure of the non-Gaussian behavior of a polymeric chain of x repeat units, since $\sigma \to 0$ as $x \to \infty$. We employ the rotational isomeric state models of Flory and co-workers to calculate the NLDE of the stereoregular polymers poly(oxyethylene glycol) and poly(oxyethylene dimethyl ether), the stereoirregular poly(vinyl chloride) and its oligomers 2,4-dichloropentane and 2,4,6-trichloroheptane, and the copolymer poly(styrene-*co*-*p*-bromostyrene). We examine the dependence of the NLDE on chain length, tacticity, and, in the case of the copolymer, composition. We find the NLDE to be sensitive to all these parameters and conclude that the NLDE is an important configurational property of a polar polymer.

The non-Gaussian behavior of short polymeric chains has been the subject of many theoretical studies.[1,2] These have shown that the deviation of the probability distribution function of the end-to-end distance from a Gaussian distribution is related to the even moments of the end-to-end distance. Mathematical methods have been devised to calculate these moments, but to date only the second moments of a polymer have been the subject of extensive experimental study. These include the mean square end-to-end distance $\langle r^2 \rangle$, mean square dipole moment $\langle \mu^2 \rangle$, and radius of gyration $\langle s^2 \rangle$.

One experimental approach to evaluating the higher moments of the end-to-end distance is by scattering radiation from a polymer. The theory for this is given by Flory.[1] In this paper we wish to discuss an experiment by which a higher moment of the dipole moment of a polymeric chain may be obtained, namely, the nonlinear dielectric effect (NLDE) or dielectric saturation.[3-5] In this experiment a strong electric field is applied across a medium to render it anisotropic, and a low-frequency weak probe electric field is used to detect the anisotropy of the dielectric constant. If a high-frequency probe electric field were used, then the experiment would observe the anisotropy of the refractive index squared, i.e., the Kerr effect.[4] The applied electric field will influence the molecule in two ways: first, it will orient the total dipole moment and second, it will perturb the equilibrium conformations of the molecule in favor of those conformations with the larger dipole moment. Thus the orienting effect of the field will cause a decrease while the perturbation of the conformations will cause an increase in the dielectric constant, the net result depending on a sensitive interplay between the two effects. For a flexible polar molecule the observed effect depends essentially on $\langle \mu^2 \rangle^2 \sigma$, where

$$\sigma = \frac{\langle \mu^4 \rangle}{\langle \mu^2 \rangle^2} - \frac{5}{3} \tag{1}$$

μ is the dipole moment, and the angular brackets denote statistical averaging over all internal configurations of the flexible molecule in the absence of a strong electric field. σ tends towards zero as $1/x$ as x tends to infinity, where x is the number of repeat units in the polymeric chain. However, $\langle \mu^2 \rangle^2$ increases as x^2 and so the product $\langle \mu^2 \rangle^2 \sigma$ increases linearly with x for large values of x. The factor σ differs significantly from zero only when the chain is relatively short, say 50 bonds or less, and is therefore a measure of the non-Gaussian behavior of the chain.

Recently, we presented calculations of the NLDE of the α,ω-dibromoalkanes[6] using the rotational isomeric state scheme (RIS) with nearest-neighbor interactions. Matrix multiplication methods of Flory[1] were used to calculate the fourth and second moments of the dipole moment and we found good agreement with the experimental results. We also found the NLDE calculation to be sensitive to the details of the RIS model used, so that it could be used with other configurationally sensitive quantities to characterize a polymer.

In this paper we present calculations of the NLDE for a number of commonly studied polymers: poly(oxyethylene glycol), $H(OC_2H_4)_xOH$ (POEG), poly(oxyethylene dimethyl ether), $CH_3(OC_2H_4)_xOCH_3$ (POEDE), the stereoirregular poly(vinyl) chloride), $CH_3(CHClCH_2)_xH$ (PVC) and its oligomers 2,4-dichloropentane (DCP) and 2,4,6-trichloroheptane (TCH), and the copolymer poly(styrene-*co*-*p*-bromostyrene), $CH_3(CHRCH_2)_xH$ ($R = C_6H_4Br$, C_6H_5) (PPBS–PS). We examine the dependence of the NLDE on chain length, tacticity, and, in the case of the copolymer, composition. We employ the same RIS models as used by us[7-9] recently to calculate the Kerr effect and

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dipole moments of these polymers, which were in good agreement with the experimental results.

Theory

The NLDE is the change of the dielectric constant $\Delta\epsilon$ of a medium when it is subject to a strong electric field E. A measure of this effect is the Piekara factor $\Delta\epsilon/E^2$, which is related to the dipole moment and polarizability of a polymer by[3]

$$ {}_{\mathrm{m}}S = \frac{V_{\mathrm{m}}}{3}\left[\frac{3}{\epsilon_0 + 2}\right]^4 \frac{\Delta\epsilon}{E^2} = 4\pi N_{\mathrm{A}}\left[\frac{\langle \mathrm{tr}\ (\hat{\alpha}^0\hat{\alpha}^0)\rangle}{15kT} + \frac{2\langle \mu^{\mathrm{T}}\hat{\alpha}^0\mu\rangle}{15k^2T^2} + \frac{\langle\mu^2\rangle^2\sigma}{30k^3T^3}\right] $$

$$ \hat{\alpha}^0 = \alpha^0 - \alpha^0\mathbf{I} \qquad (2) $$

${}_{\mathrm{m}}S$ denotes the molar nonlinear dielectric constant, $\hat{\alpha}^0$ and α^0 are the static anisotropic and average polarizabilities, respectively, μ and μ^{T} are the dipole moment and its transpose, respectively, and $\mathbf{I}$ is the identity matrix. Further, ϵ_0, V_{m}, N_{A}, k, and T denote the dielectric constant in the absence of a strong electric field, the molar volume, Avogardo's number, Boltzmann's constant, and temperature, respectively. In eq 2 we have assumed that hyperpolarizability contributions are negligible and that the Lorentz internal field approximation is applicable. The expression for σ is given by eq 1 and it is a measure of the non-Gaussian behavior of the chain, since σ tends to zero as the number of repeat units x of the polymer becomes very large.

The configurational averages $\langle g(\tau)\rangle$ over all internal degrees of freedom τ are assumed to be evaluated in the absence of the external electric field E and excluded volume interactions. In that case Flory[2] has shown that

$$ \langle g(\tau)\rangle = Z^{-1}\mathbf{J}^*G_1{}^n\mathbf{J} \qquad (3) $$

Z is the partition function, $G_1{}^n$ denotes a serial product of generator matrices for each bond in the chain (1 to n), and $\mathbf{J}^*$ and $\mathbf{J}$ are row and column vectors. Flory's book[1] gives the generator matrices which are applicable for each configurational average given in eq 1 and 2.

In order to carry out the calculations we require a RIS model for the bond rotational probabilities, dipole moments and polarizabilities for the repeat units, and valence and torsional bond angles. The details for the derivation of these parameters for the four polymers considered in this paper are presented elsewhere.[7-9] Here, we only summarize the parameters used in this study.

POEG and POEDE

The RIS model of Flory, Mark, and their co-workers[10-12] was used with the energetic parameters $E_{\sigma'} = 1300$, $E_\omega = 250$, and $E_\sigma = -400$, all values being expressed in cal mol^{-1}. The dipole moment of the repeat unit was $10^{18}\ \mu = 1.32$ SC cm (SC = statcoulomb) and the polarizability was calculated according to approximation b of ref 7. In the case of POEG the terminal dipole moments and rotational probabilities were treated as in ref 7. The bond angles along the backbone were 110° and the rotational states corresponded to t(0°) and g$^\pm$(±120°).

PVC and Its Oligomers

The RIS model of Williams, Pickles, and Flory,[13,14] as modified by us,[8] was used with the energetic parameters $E_\eta = -850$, $E_\tau = 500$, $E_\omega = 2000$, $E_{\omega'} = 2500$, and $E_{\omega''} = 3000$, all values being expressed in cal mol^{-1}. The dipole moment was directed along the C–Cl bond, with a value of $10^{18}\mu = 2.05$ SC cm, and the polarizability was derived according to ref 8. The bond angles along the backbone were 112° and the rotational states corresponded to t(0°) and g$^\pm$(±120°). The stereoirregular chains were generated by a Monte Carlo technique, corresponding to a probability of racemic dyad replication of $p_{\mathrm{r}} = 0.5$, i.e., atactic chain.

Table I

${}_{\mathrm{m}}S/x$ ($\times10^{-9}$ cm^7 SC^{-2} mol^{-1}) and σ of Poly(oxyethylene dimethyl ether) and Poly(oxyethylene glycol) at $T = 298$ K

	$CH_3(OC_2H_4)_xOCH_3$		$H(OC_2H_4)_xOH$	
x	${}_{\mathrm{m}}S/x$	$10^3\sigma$	${}_{\mathrm{m}}S/x$	$10^3\sigma$
1	−16.4	−381		
2	−7.70	−199	−38.5	−276
3	−2.87	−75	−28.9	−216
4	−0.335	−7	−19.7	−162
5	0.78	20	−13.9	−122
10	2.83	51	−4.28	−38
20	3.87	43	0.32	3
40	4.51	27	2.73	13
80	4.71	15	3.81	11
160	4.81	8	4.36	7
320	4.86	4	4.66	4

PPBS–PS Copolymer

The two-state RIS model of Yoon et al.[15] was used with the energetic parameters $E_\eta = -397$, $E_\omega = E_{\omega'} = 1987$, and $E_{\omega''} = 2186$, all values being expressed in cal mol^{-1}. The dipole moment of the repeat units was $10^{18}\mu = 1.89$ SC cm for R = C_6H_4Br and $10^{18}\mu = 0.32$ SC cm for R = C_6H_5. The polarizability tensor of the repeat units was calculated according to ref 9. The bond angles along the backbone were 112° and the rotational angles corresponded to t(0°) and g$^\pm$(±120°). Stereoirregular atactic chains of tacticity $p_{\mathrm{r}} = 0.5$ and variable composition of polystyrene in the copolymer PPBS–PS were generated by a Monte Carlo technique. Results were also obtained for isotactic chains.

In order to calculate statistically significant results of $\langle g(\tau)\rangle$ for stereoirregular chains, it is necessary to generate many chains and take their average. Our goal was to calculate ${}_{\mathrm{m}}S$ values with standard deviations of 1–10%. In order to accomplish this for a polymer chain of x repeat units, we found it necessary to generate 2000–4000 chains for $x = 6$, 1000–2000 chains for $x = 11$, 500–1000 chains for $x = 21$, 300 chains for $x = 41$, 150 chains for $x = 81$, and 60 chains for $x = 201$. The expression for ${}_{\mathrm{m}}S$ becomes linearly dependent on x for large values of x. It is therefore convenient to calculate ${}_{\mathrm{m}}S/x$ for polymeric chains and these values are given in Tables I–III.

Results and Discussion

Prior to discussion of the results of the calculations, it is worthwhile to consider the magnitude of the NLDE effects which can be measured with existing instruments. Parry Jones[5] has described an improved NLDE apparatus that is capable of measuring accurately very small NLDE values, such as found in the nonpolar liquid carbon tetrachloride.[16] For that case $10^9\Delta\epsilon/E^2 = 0.174$ cm^4 SC^{-2}, $V_{\mathrm{m}} = 97.2$ cm^3 mol^{-1}, $\epsilon_0 = 2.227$, and so from eq 2, $10^9{}_{\mathrm{m}}S = 1.43$ cm^7 SC^{-2} mol^{-1}. Our calculations on these flexible polar polymers and copolymers show that ${}_{\mathrm{m}}S/x$ have a range of values -10^2 to $+10$ ($\times10^{-9}$ cm^7 SC^{-2} mol^{-1}), and so they should be easily measured. It is also predicted that for most of these polymers ${}_{\mathrm{m}}S/x$ has a negative value.

Experimentally, one may deduce the value of σ from ${}_{\mathrm{m}}S$ by knowing the values of $\langle\mu^2\rangle$, $\langle\mu^{\mathrm{T}}\hat{\alpha}^0\mu\rangle$, and $\langle \mathrm{tr}\ (\hat{\alpha}^0\hat{\alpha}^0)\rangle$. The latter two may be deduced from Kerr effect and light scattering experiments and after taking into account the dispersion between static and optical polarizabilities. $\langle\mu^2\rangle$

Table II

A. ${}_{\mathrm{m}}S/x$ ($\times 10^{-9}$ cm^7 SC^{-2} mol^{-1}) and σ of 2,4-Dichloropentane (Meso (m) and Racemic (r) Isomers), 2,4,6-Trichloroheptane (mm, mr, and rr Isomers), and Atactic (p_r = 0.5) Poly(vinyl chloride) Chains at T = 298 K

$CH_3(CHClCH_2)_xH$

x	${}_{\mathrm{m}}S/x$	$10^3\sigma$
2 (m)	−35.7	−616
2 (r)	−38.2	−661
3 (mm)	−10.6	−377
3 (mr)	−37.1	−338
3 (rr)	−145	−607
6[a]	−108	−288
11[a]	−113	−181
21[a]	−116	−101
41[a]	−144	−65
81[a]	−160	−37
201[a]	−138	−13

B. ${}_{\mathrm{m}}S/x$ ($\times 10^{-9}$ cm^7 SC^{-2} mol^{-1}) and σ of PVC (x = 201) vs. Probability of Racemic Dyad Replication p_r at T = 298 K

p_r	${}_{\mathrm{m}}S/x$	$10^3\sigma$
0.0[b]	−68.1	−11
0.2	−70.8	−14
0.4	−87.2	−12
0.6	−234	−15
0.8	−133	−3
1.0[c]	1.71×10^5	485

[a] Atactic, p_r = 0.5. [b] Isotactic. [c] Syndiotactic.

Table III

A. ${}_{\mathrm{m}}S/x$ ($\times 10^{-9}$ cm^7 SC^{-2} mol^{-1}) and σ of Atactic (p_r = 0.5) Poly(p-bromostyrene) Chains at T = 298 K

$CH_3(CHC_6H_5BrCH_2)_xH$

x	${}_{\mathrm{m}}S/x$	$10^3\sigma$
6	−41.9	−274
11	−37.3	−140
21	−31.6	−67
81	−29.5	−18
201	−22.6	−6

B. ${}_{\mathrm{m}}S/x$ ($\times 10^{-9}$ cm^7 SC^{-2} mol^{-1}) and σ of Isotactic and Atactic Chains of Poly(styrene-*co*-p-bromostyrene), x = 201, at T = 298 K[a]

	% poly(p-bromostyrene)					
	100		80		60	
p_r	${}_{\mathrm{m}}S/x$	$10^3\sigma$	${}_{\mathrm{m}}S/x$	$10^3\sigma$	${}_{\mathrm{m}}S/x$	$10^3\sigma$
0.0	−131	−17	−58.3	−10	−19.7	−8
0.5	−22.6	−6	−16.4	−6	−8.40	−5

[a] The percentages refer to the fraction of styrene repeat units which have a bromine in the para position.

may be readily obtained from a dielectric polarization experiment. Often one may neglect the relatively small contributions of the first two terms of eq 2, and then a knowledge of $\langle \mu^2 \rangle$ and x suffices to deduce σ from ${}_{\mathrm{m}}S$. Therefore σ is an experimentally derived quantitiy which is a measure of the non-Gaussian behavior of a polymeric chain. It would also be useful experimentally to study the temperature dependence of the NLDE since it may be possible to separate the relative contributions of the three terms in eq 2.

We discuss briefly the results of the calculations for the individual polymers. In Table I, for POEDE, ${}_{\mathrm{m}}S/x$ has a large negative value for x = 1 and 2. However, it attains a small positive value for $x > 5$. The σ values also decrease rapidly toward zero with increasing x, indicating that this polymer is very flexible but change sign and become slightly positive for $x > 5$. σ reaches a maximum value near x = 20 and then decreases monotonically toward zero. Fujiwara and Flory[17] found for a hypothetical syndiotactic chain that $\langle r^4 \rangle / \langle r^2 \rangle^2 - 5/3$, where r is the end-to-end distance, reached a maximum value before decreasing toward zero for large values of x and ascribed this to choosing nearly tetrahedral angles for the backbone bond angles and 0° and ±120° for the trans and gauche states of the bond rotational angles. Slight deviations from this geometry resulted in the elimination of the maximum in σ and a more rapid convergence of σ to zero. Since POEDE and also POEG are readily available in several different molecular weights, it would be interesting to obtain experimental values of ${}_{\mathrm{m}}S/x$ and thereby test the validity of these calculations. POEG differs from POEDE only by the presence of dipole moments at each end of the polymer, resulting in larger negative ${}_{\mathrm{m}}S/x$ values for the shorter chains and a less rapid convergence of σ toward zero with increasing values of x.

The calculations of Table IIA predict that ${}_{\mathrm{m}}S/x$ values of the two isomers of DCP (meso and racemic) have nearly the same value, while the values of the three isomers of TCH are considerably different from each other. Measurement of the NLDE of the three separate isomers of TCH would provide a stringent test of the method of calculation presented here. ${}_{\mathrm{m}}S/x$ is remarkably constant for atactic chains of PVC as a function of the number of repeat units, although σ decreases rapidly toward zero. The calculations of Table IIB also show that ${}_{\mathrm{m}}S/x$ is not very sensitive to tacticity in the mainly isotactic regime but becomes increasingly so in the atactic and syndiotactic regime.

The results of Table IIIA for poly(p-bromostyrene) show that ${}_{\mathrm{m}}S/x$ values are about 3–4 times smaller than for PVC. Also the σ values decrease more rapidly as a function of x, indicating that this chain is more flexible than PVC. In Table IIIB we show the change in ${}_{\mathrm{m}}S/x$ values with increasing fraction of polystyrene in the copolymer PPBS–PS. With increasing polystyrene content, the polymer becomes less polar and so the ${}_{\mathrm{m}}S/x$ values decrease. The calculations also predict that the ${}_{\mathrm{m}}S/x$ values are considerably larger for an isotactic chain than for an atactic chain. These calculations may be readily tested experimentally. It is possible to obtain commercially monodisperse atactic low molecular weight polystyrene which then can be readily brominated randomly in the para position.[9] In this manner one can obtain the copolymer PPBS–PS of any desired composition and also the homopolymer poly(p-bromostyrene). Also, one may use isotactic polystyrene as starting material and brominate randomly to obtain isotactic copolymers of any desired composition.[18]

Conclusions

The NLDE is important for the study of polymers and their model compounds for several reasons. First, ${}_{\mathrm{m}}S/x$ is sensitive to the details of the RIS model of a polymer and therefore it may be used together with other configurationally sensitive quantities, such as the mean square end-to-end distance $\langle r^2 \rangle$, dipole moment $\langle \mu^2 \rangle$, anisotropy $\langle \gamma^2 \rangle$, and molar Kerr constant ${}_{\mathrm{m}}K$, to characterize a polymer. Second, the parameter σ is a measure of the non-Gaussian behavior of a chain molecule; i.e., it is a measure of the stiffness of the chain. Measurement of ${}_{\mathrm{m}}S/x$ vs. x would enable us to measure the relative stiffness of different polymers. Measurements have already been reported for the NLDE of the stiff polymers PBLG[19,20] and polyisocyanates[20] for different molecular weights. However, those results may not be interpreted by eq 3. Instead a helical wormlike chain model[21] would be more appropriate.

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Photochemistry of Polyundecanamides. 1. Mechanisms of Photooxidation at Short and Long Wavelengths

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ABSTRACT: An experimental and analytical study of the photooxidation of polyundecanamide films carried out at long wavelengths (λ >300 nm) and 60 °C or at short wavelengths (254 nm) and 30 °C is reported. Mechanisms are proposed that account for the behavior of the different intermediate photoproducts observed in each case. The hydroperoxides formed are shown to be thermally unstable above 60 °C and when photolyzed at short wavelength. At long wavelengths, they can accumulate until a fairly high photostationary concentration (1.5×10^{-2} mol·kg^{-1}) is reached. Photochemical decomposition of hydroperoxides into imide groups and *N*-1-hydroxypolyundecanamide is observed. The imide groups are either hydrolyzed or photolyzed into acidic and amide groups. At short wavelengths, products of a direct photoscission of the C–N bond (i.e., aldehydes and amides) are also observed. At long wavelengths, only amines can be detected.

The behavior of aliphatic polyamides, especially nylon-type polymers, on exposure to UV irradiation has attracted much attention (see, for example, ref 1 and 2). Most of the reported research in this field concerns either vacuum photolysis and photooxidation of the polymer at wavelengths shorter than 290 nm or autoxidation and photooxidation of model compounds.

It has been shown by means of ESR spectrometry that a primary process of photodissociation leading to the formation of two macroradicals is occurring when light is absorbed by the NHCO chromophore.

$$-CONH- \xrightarrow[\lambda < 290\ \text{nm}]{h\nu} -CO\cdot + \cdot NH- \qquad \text{(I)}$$

In secondary steps, these macroradicals abstract a hydrogen atom from the polymer matrix:

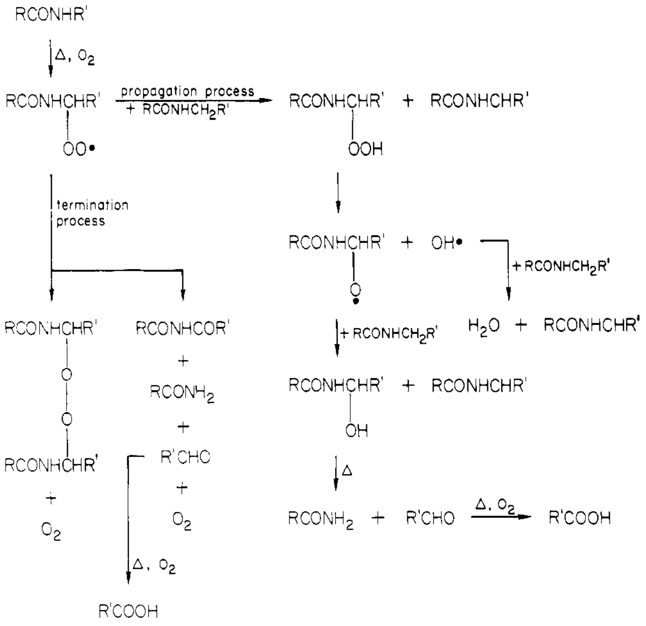
$$-CO\cdot + -CONH- \rightarrow -CHO + -CONH\dot{C}H- \qquad \text{(II)}$$

$$-NH\cdot + -CONH- \rightarrow -NH_2 + -CONH\dot{C}H- \qquad \text{(III)}$$

Aldehydic and amine groups have indeed been observed.

The same primary process is observed at wavelengths shorter than 290 nm in the presence of oxygen.[3] However, oxygen traps the two macroradicals, forming peroxy radicals and hydroperoxides.

Scheme I
Autoxidation of *N*-Alkyl Amides



Autoxidation of model compounds of *N*-alkyl amides $RCH_2CONHCH_2R'$ has been studied by Sagar et al.[4,5] at temperatures lower than 100 °C. *N*-Acyl amides, *N*-formyl

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