γ_3) was found; it is possible that this peak may correspond to isotactic material, although the evidence for this is weak. Finally, comparison of experimental and literature data for all the viscoelastic relaxations in PMMA suggests that the transitions all converge at ~200 °C and 10^9 Hz.

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References and Notes

(1) A preliminary report of this work was presented in *Phys. Rev. Lett.*, **35**, 951 (1975). The present paper is based in part on the doctoral thesis of J. Williams, McGill University, 1978.
(2) See, for example, D. W. McCall, *Acc. Chem. Res.*, 223 (1971).
(3) See, for example, V. J. McBrierty, *Polymer*, **15**, 503 (1974).
(4) See, for example, K. J. Laidler, *"Chemical Kinetics"*, McGraw-Hill, New York, N.Y., 1965.
(5) J. Heijboer, Doctoral Dissertation, University of Leiden, 1972.
(6) T. P. Das, *J. Chem. Phys.*, **27**, 763 (1957).
(7) J. G. Powles and H. S. Gutowsky, *J. Chem. Phys.*, **21**, 1695 (1953).
(8) E. O. Stejskal and H. S. Gutowsky, *J. Chem. Phys.*, **28**, 388 (1958).
(9) F. Apaydin and S. Clough, *J. Phys. C*, **1**, 932 (1968).
(10) R. B. Davidson and I. Miyagawa, *J. Chem. Phys.*, **52**, 1727 (1970).
(11) M. Bloom, *Pure Appl. Chem.*, **32**, 99 (1972).
(12) P. S. Allen, *J. Phys. C*, **7**, L 22 (1974).
(13) A. Huller and D. M. Kroll, *J. Chem. Phys.*, **63**, 4495 (1975).
(14) C. S. Johnson, Jr., and C. Mottley, *J. Phys. C*, **9**, 2789 (1976).
(15) A. Odajima, A. E. Woodward, and J. A. Sauer, *J. Polym. Sci.*, **55**, 181 (1961).
(16) C. D. Knutson and D. M. Spitzer, Jr., *J. Chem. Phys.*, **45**, 407 (1966).
(17) J. Haupt and W. Muller-Warmuth, *Z. Naturforsch., A*, **24**, 1066 (1969).
(18) R. Kosfeld and U. von Mylius, *Kolloid-Z.*, **250**, 1081 (1972).
(19) B. Lammel and R. Kosfeld, *Colloid Polym. Sci.* **253**, 881 (1975).
(20) S. Clough and J. R. Hill, *J. Phys. C*, **7**, L 20 (1974).
(21) S. Clough and B. J. Mulady, *Phys. Rev. Lett.*, **30**, 161 (1973).
(22) J. L. Carolan, S. Clough, N. D. McMillan, and B. Mulady, *J. Phys. C*, **5**, 631 (1972).
(23) S. Clough, J. R. Hill, and T. Hobson, *Phys. Rev. Lett.*, **33**, 1257 (1974).
(24) S. Clough, J. R. Hill, and F. Poldy, *J. Phys. C*, **5**, 1739 (1972).
(25) S. Clough, J. R. Hill, and F. Poldy, *J. Phys. C*, **5**, 518 (1972).
(26) A. Eisenberg and S. Reich, *J. Chem. Phys.*, **51**, 5706 (1969).
(27) S. Reich and A. Eisenberg, *J. Chem. Phys.*, **53**, 2847 (1970).
(28) Y. Tanabe, J. Hirose, K. Okano, and Y. Wada, *Polym. J.*, **1**, 107 (1970).
(29) J. A. Sauer, *J. Polym. Sci., Part C.* **32**, 69 (1971).
(30) P. D. Golub' and I. I. Perepechko, *Sov. Phys.-Acoust. (Engl. Transl.)*, **19**, 391 (1974).
(31) J. S. Higgins, G. Allen, and P. N. Brier, *Polymer*, **13**, 157 (1972).
(32) G. Allen, C. J. Wright, and J. S. Higgins, *Polymer*, **15**, 319 (1974).
(33) J. Jäckle, *Z. Phys.*, **257**, 212 (1972).
(34) O. Yano, K. Saiki, S. Tarucha, and Y. Wada, *J. Poly. Sci., Polym. Phys.*, **15**, 43 (1977).
(35) B. I. Halperin, *Ann. N.Y. Acad. Sci.*, **279**, 173 (1976).
(36) See, for example, R. O. Pohl and G. L. Salinger, Ann. *N.Y. Acad. Sci.*, **279**, 150 (1976).
(37) J. J. Gilman and H. C. Tong, *J. Appl. Phys.*, **42**, 3479 (1971).
(38) N. G. McCrum, B. E. Read, and G. Williams, "Anelastic and Dielectric Effects in Polymeric Solids", Wiley, New York, N.Y., 1967.
(39) D. W. McCall, *Natl. Bur. Stand. Spec. Publ.* **301**, 475 (1969).
(40) P. G. Bordoni, M. Nuovo, and L. Verdini, *Nuovo Cimento*, **20**, 667 (1961).
(41) T. Kajiyama and W. J. MacKnight, *Macromolecules*, **2**, 254 (1969).
(42) J. G. Powles, *J. Polym. Sci.* **22**, 79 (1956).
(43) K. M. Sinnott, *J. Polym. Sci.*, **42**, 3 (1960).
(44) S. Reich, private communication.
(45) R. Hayakawa et al., *Proc. Jap. Conf. Polym. Solid State*, 99 (1972).
(46) B. Golding, *"Polymers and Resins"*, Van Nostrand, Princeton, N.J., 1959.
(47) W. R. Krigbaum and J. V. Dawkins in "Encyclopaedia of Polymer Science and Technology", Vol. 8, Wiley, New York, N.Y., 1968, p 764.
(48) A. Nishioka, H. Watanabe, K. Abe, and Y. Sono, *J. Polym. Sci.*, **48**, 241 (1960).
(49) N. W. Johnston and P. W. Kopf, *Macromolecules*, **5**, 87 (1972).
(50) K. C. Ramey and J. Messick, *J. Polym. Sci., Part A-2*, **4**, 155 (1966).
(51) B. Cayrol, Doctoral Thesis, McGill University, 1972.
(52) These are presented in a number of sources and are summarized by R. Yeo, Doctoral Thesis, McGill University, 1976.
(53) G. S. Fielding-Russell and R. E. Wetton, "Plastics and Polymers", June 1970, p 179.
(54) S. Reich and A. Eisenberg, *Rev. Sci. Instrum.*, **41**, 1905 (1970).
(55) H. Schlein and M. Shen, *Rev. Sci. Instrum.*, **40**, 587 (1969).
(56) D. Y. Chung, *Rev. Sci. Instrum.*, **42**, 878 (1971).
(57) G. Brunton, D. Griller, L. R. C. Barclay, and K. U. Ingold, *J. Am. Chem. Soc.*, **98**, 6803 (1976).
(58) J. G. Powles, J. H. Strange, and D. J. H. Sandiford, *Polymer*, **4**, 401 (1963).
(59) T. M. Connor and A. Hartland, *Phys. Lett.*, **23**, 662 (1966).
(60) H. W. Starkweather, Jr., *J. Macromol. Sci., Phys.*, **2**, 781 (1968).
(61) G. D. Patterson, *J. Polym. Sci., Polym, Phys.*, **15**, 455 (1977).

Electric Birefringence of Dilute Suspensions of Poly(ethylene oxide) Crystals in Ethylbenzene

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ABSTRACT: Suspensions of poly(ethylene oxide) (PEO) crystals in ethylbenzene were subjected to electric pulses, including those of rapidly reversed polarity, and to alternating fields. The time and frequency dependence of the resulting birefringence shows that crystal orientation arises from a slowly induced dipole moment, as concluded by Picot et al. from the frequency dependence of the birefringence. The effect of the finite rate of polarization on the time and frequency dependence of the birefringence is discussed in terms of an electric-relaxation time, estimated to be a few milliseconds, and the birefringence-relaxation time. The field-strength dependence of the steady-state birefringence was represented by an equation; derived by Shah, that applies to a disk-shaped particle in which a dipole moment is induced perpendicular to its unique axis. Thereby it was found that $(\alpha_2 - \alpha_1)/L^3 \cong 2.4 \times 10^{-11}$ F/m, where $(\alpha_2 - \alpha_1)$ is the excess electric polarizability and L is the effective length of the square lamellar crystals. This relation agrees semiquantitatively with that obtained from a treatment by O'Konski and Krause of the excess polarizability of a conducting spheroid in a fluid. The suspensions studied were prepared by the self-seeding technique from ethylbenzene solutions of a PEO–PPO–PEO triblock copolymer (Pluronic F127), where PPO denotes atactic poly(propylene oxide). The size of the crystals, which were essentially monodisperse, was varied between 0.87 and 2.65 μm.

When a liquid suspension of polymer crystals is subjected to an electric field, the crystals orient and the suspension thereby becomes birefringent. Following some exploratory studies,[2-4] Picot et al.[5,6] investigated suspensions of single crystals prepared by the self-seeding technique[7-10] from solutions of a diblock copolymer of poly(ethylene oxide) (PEO) and polystyrene (PS) and also from solutions of PEO and polyethylene homopolymers. Because the birefringence was

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negative, they concluded that the lamellar crystals orient parallel to the electric field. The conclusion was confirmed by light-scattering data obtained on a suspension of crystals, prepared from the diblock copolymer, under an alternating electric field. It was also found that the crystals became highly oriented under a low field (ca. 400 V/cm) at low frequencies and that the orientation, under a field of constant amplitude, decreases rapidly with the frequency above 500 Hz and appears to vanish at a few kilohertz.

Measurements[5] of the frequency-dependent birefringence, made on a suspension of crystals whose relaxation time for birefringence decay was 0.5 s, showed that the alternating component of the birefringence essentially vanishes at 50 Hz and that the steady (time-independent) component approaches zero at about 1 kHz. From these results, it was concluded that crystal orientation does not result from a permanent dipole moment and that polarization possibly arises from electric charges in the crystals, the charge mobility being dependent on the conductivity of the material.

In the present study of suspensions of PEO crystals, measurements were made of the electric birefringence produced by rectangular pulses, pulses of rapidly reversed polarity, and alternating fields. Pulses of rapidly reversed polarity, which were not employed in the previous study,[5] are of special utility[11-14] for determining characteristics of the electric polarization.

Theoretical Background

Rotary Diffusion Coefficient. The crystals investigated were square lamellae about 10 nm thick having axial ratios between about 100 and 300. It was assumed that the rotary diffusion coefficients of a crystal of thickness h, each side being of length L, equal those of an oblate ellipsoid whose volume equals that of the crystal, i.e., $4\pi ab^2/3 = hL^2$, where a and b are the lengths of the unique (symmetry) and equivalent (transverse) semiaxes, respectively, of the ellipsoid. Upon equating the diagonal ($2^{1/2} L$) of the crystal to $2b$, it follows that $b = L2^{-1/2}$ and $a = (3/2\pi)h = 0.955(h/2)$. Thus, the length of the symmetry axis of the equivalent ellipsoid nearly equals the thickness of the crystal.

When the axial ratio of an oblate ellipsoid exceeds about 15 or 20, the diffusion coefficient for rotation about either the unique axis or an equivalent axis is given by[15,16] $\theta = 3kT/32\eta b^3$, where k is the Boltzmann constant, T is the absolute temperature, and η is the viscosity of the liquid surrounding the ellipsoid. Substitution of $b = L/2^{1/2}$ gives:

$$\theta = 6(2^{1/2})kT/32\eta L^3 \tag{1}$$

Origin of Electric Birefringence. A solution or suspension of mobile particles becomes birefringent under an electric field whenever the electric and optical polarizabilities of the particles are unsymmetric. Electric polarization can result from various processes,[12-14] including the transport of mobile counterions associated with polyelectrolytes in solution. From a study of dilute aqueous solutions of tobacco mosaic virus (TMV), O'Konski and Haltner[11] found that polarization from ion transport exceeds by 50-fold that from electronic and atomic displacements, in satisfactory agreement with the theory developed subsequently.[17] The relaxation time of the polarization process (ca. 5×10^{-7} s) is several orders of magnitude greater than that characteristic of distortion polarization. When the conductivity of the medium is low, polarization can possibly result from transport of charged species other than counterions and can have an electric relaxation time in the millisecond range, as shown subsequently.

Transient Response to Electric Pulses of Low Intensity. The reversing pulse technique,[13,14] introduced by O'Konski and Haltner,[11] consists of first applying suddenly a constant electric field to a solution and monitoring the transient birefringence. After a steady state is reached, the polarity of the field is reversed suddenly and the transient, which often develops in the birefringence, is determined.

In a theoretical analysis of the reversing pulse technique, Tinoco and Yamaoka[18] considered that polarization can result from permanent, fast-induced, and slow-induced moments, that the particles are rigid, noninteracting, and cylindrically symmetric, and that the potential energy of a particle in the field is small compared to kT. The equations given below, obtained from their general expressions, are applicable to monodisperse particles whose rotary diffusion can be characterized by a single coefficient. The transient birefringence under fields of high intensity has been treated by Yoshioka and collaborators.[19,20]

Consider that particles are oriented under an electric field. When the field is then removed suddenly, the birefringence, Δn, decays according to

$$\Delta n/\Delta n_0 = e^{-6\theta t} = e^{-t/\tau_o} \tag{2}$$

where Δn_0 (not necessarily an equilibrium, or steady-state, value) is the birefringence when the field is removed, and τ_o is the birefringence relaxation time. Because $\tau_o = 1/6\theta$,[21,22] it follows from eq 1 that τ_o for square lamellar crystals is given by

$$\tau_o = 4(2^{1/2})\eta L^3/9kT \tag{3}$$

If particle orientation results solely from a dipole moment induced slowly along either the unique or equivalent axis, the birefringence that develops upon applying a constant field at zero time is given by[18]

$$\frac{\Delta n}{\Delta n_0} = 1 - \frac{1}{(\tau_o - \tau_e)}(\tau_o e^{-t/\tau_o} - \tau_e e^{-t/\tau_e}) \tag{4}$$

provided $\tau_o \neq \tau_e$, where τ_e is the relaxation time (electric) for the polarization process, and Δn_0 is here the steady-state (equilibrium) birefringence. According to this equation, the initial slope of the birefringence–time curve is zero. As discussed elsewhere,[13,18,19] a zero initial slope also occurs when polarization results from a pure permanent moment. In contrast, *the initial slope is finite whenever a fast induced moment* (i.e., when $\tau_e \simeq 0$) contributes to the total polarization.

If the polarity of the field is suddenly reversed after steady state has been reached, the birefringence is unaffected provided $\tau_e \ll \tau_o$. Otherwise a transient develops, represented by[18]

$$\Delta n/\Delta n_0 = 1 - [\tau_e/(\tau_o - \tau_e)](e^{-t/\tau_o} - e^{-t/\tau_e}) \tag{5}$$

where t is now the time after reversal of the polarity. A minimum occurs at

$$t_m = [\tau_e/(\tau_e/\tau_o - 1)] \ln(\tau_e/\tau_o) \tag{6}$$

and there the birefringence is given by

$$\frac{\Delta n_m}{\Delta n_0} = 1 - \left(\frac{\tau_e}{\tau_o}\right)^{1/(1 - \tau_e/\tau_o)} \tag{7}$$

Steady-State Response to Alternating Fields of Constant Amplitude. The birefringence produced by a field of low intensity that varies sinusoidally is given by[11,23,24]

$$\Delta n = \Delta n_{st} + \Delta n_{alt} \cos(2\omega t - \delta) \tag{8}$$

where Δn_{st} is the steady or average (time-independent) component of the birefringence, Δn_{alt} is the amplitude of the alternating (time-dependent) component whose angular frequency, 2ω, is twice that of the imposed field, and δ is the phase angle. At low frequencies, Δn_{alt} equals Δn_{st}.

When polarization results only from an induced moment and $\tau_e \ll \tau_o$, Δn_{st} is frequency independent as long as $\omega \ll 1/\tau_e$, but Δn_{alt} goes to zero with increasing frequency. The maxima and minima values of the alternating component of the birefringence, Δn_M, approach each other according to[11,23,24]

$$\Delta n_M = \Delta n_{st}[1 \pm (1 + 4\omega^2\tau_o{}^2)^{-1/2}] \quad (9)$$

When $\omega \ll \tau_o$, the birefringence is a constant, Δn_{st}, independent of frequency. Hence, the average orientation of the particles is independent of time and frequency. This behavior signifies that the polarization remains in phase with the field and thus its amplitude depends only on that of the field.

On the other hand, whenever τ_e is not small compared to $1/\omega$, the polarization lags the field, and its amplitude decreases with increasing frequency. Thus, the average orientation of the particles, though independent of time, becomes frequency dependent. With increasing frequency, the birefringence decreases toward an anticipated low plateau associated with polarization from electronic and atomic displacements.

Such a dispersion has been found to begin at about 10 kHz for several types of particles,[11,24] including TMV, and at a significantly lower frequency for suspensions of polymer crystals.[5] While a quantitative treatment has not been given, it has been pointed out[17] that the behavior is possibly quite complex and that the use of a single relaxation time τ_e may be inadequate to account for the dependence of the polarization on time, and thus on frequency.

Dependence of Birefringence on Field Strength. At low fields, the steady-state birefringence is proportional to the square of the field strength E, in conformity with Kerr's law.[12,14] An analysis of deviations from this law, which begin when E becomes sufficient to orient the particles substantially, provides information on the polarizability of the particles.

The analysis by O'Konski et al.[25] has been applied by Shah[26] to a disk-shaped particle having a permanent dipole moment parallel to the unique axis and an induced moment acting in the plane of the disk. He computed the normalized birefringence $\Delta n/\Delta n_s$, where Δn_s is the birefringence (saturation) at infinite field strength, as a function of the dimensionless parameters $\mu EB_1/kT$ and $(\alpha_2 - \alpha_1)E^2/2kT$ where μ is the permanent moment, B_1 is an internal field function, and α_2 and α_1 ($\alpha_2 > \alpha_1$) are the excess polarizabilities of the particle in the solvent in directions perpendicular and parallel, respectively, to the unique axis. A curve representing the behavior when $\mu = 0$, which is of present interest, is presented elsewhere[26] and also in Figure 12, discussed subsequently. When $\Delta n/\Delta n_s > 0.6$ and $\mu = 0$, Shah's equation reduces to

$$\Delta n/\Delta n_s = 1 - 3kT/(\alpha_2 - \alpha_1)E^2 \quad (10)$$

Experimental Section

Materials. The BASF Wyandotte Corporation kindly furnished triblock copolymers of poly(ethylene oxide) and poly(propylene oxide), whose trade name is Pluronics. The materials investigated were Pluronic F127 and the "reverse" Pluronic 25R8 whose block sequences are PEO–PPO–PEO and PPO–PEO–PPO, respectively. ^{1}H- and ^{13}C-NMR spectra showed that the PPO chains are atactic and that the ethylene oxide contents of F127 and 25R8 are 76.8 and 84.8 mol %, respectively, in excellent agreement with 76 and 84 mol % given in the BASF Wyandotte literature. According to this literature, the molecular weights of F127 and 25R8 are about 12 500 and 9000, respectively. It follows from these data that the molecular weight of the inner PPO block in F127 is about 3560 and of each outer PEO block it is 4470. For Pluronic 25R8, the molecular weight of the inner PEO block is approximately 7280 and of each outer PPO block it is 860. Also, the molecular weight distribution, obtained by gel-permeation chromatography on F127 and other Pluronics, has been reported[27] to be rather narrow ($M_w/M_n \approx 1.2$).

Solutions of the Pluronics were prepared in ethylbenzene (Eastman Kodak white-label grade) whose electric conductivity was about 10^{-11} ohm^{-1} cm^{-1}. The conductivity of a 5% solution of F127 in which crystals had formed was found to be about 1×10^{-9} ohm^{-1} cm^{-1}.

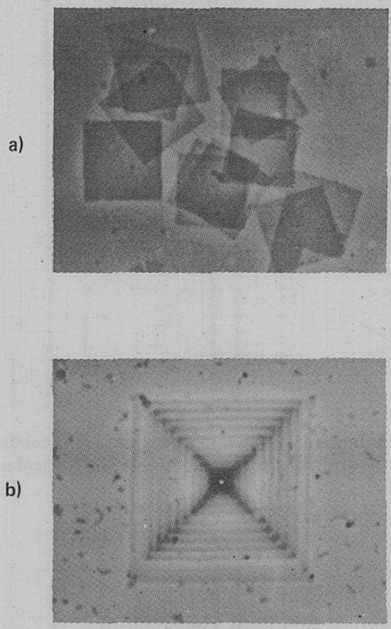

Figure 1. Crystals grown from a 1% solution of the triblock copolymer PPO–PEO–PPO (Pluronic 25R8) in ethylbenzene. The crystals are severalfold larger than those in the suspensions whose electric birefringence was studied. The crystal in (b), which has a spiral growth, is twofold larger than those in (a). Photomicrographs of crystals from PEO–PPO–PEO (Pluronic F127) were similar.

Characteristics and Preparation of Crystals. Studies[27–30] have been made of the degree of crystallinity and the melting points and heats of fusion of crystals in undiluted diblock and triblock copolymers of PEO and PPO. Whereas the derived melting point[31] of large perfect crystals of a PEO homopolymer is 76 °C, the crystals in various PEO–PPO–PEO Pluronics melt between 52 and 63 °C.[27] However, the melting point of such crystals is no more than 4 °C below that of crystals of a PEO homopolymer whose molecular weight equals that for the PEO segments in the block copolymer. (Lamellar crystals have also been found[32] to develop from concentrated solutions of a PEO–PPO–PEO Pluronic in a solvent better for the PPO than for the PEO segments.) Thus, the melting point of single crystals grown from a dilute solution of a PEO–PPO–PEO copolymer should be rather close to that for the crystals of the corresponding PEO homopolymer. In contrast, the melting points of crystals in undiluted PPO–PEO–PPO copolymers have been found[28] to depend significantly on the length of the noncrystallizable PPO segments, being as much as 15 °C below that of crystals from the corresponding PEO homopolymers.

To prepare suspensions of single crystals by the self-seeding technique,[7–10] a dilute solution of a Pluronic in ethylbenzene, usually either 0.4 or 1.0 g/dL, was first heated to 60 °C to ensure complete dissolution. Crystallization was then allowed to occur near ambient temperature. The suspension was next placed in a constant-temperature bath at T_s ($\approx$35 °C). The crystals appeared to dissolve completely as the temperature approached T_s, but submicroscopic fragments (or nuclei) remained. When the solution was thereafter removed from the bath, the nuclei grew simultaneously, yielding crystals of uniform size. The number and size of the resulting crystals depend on the concentration of nuclei, controlled primarily by the magnitude of T_s. When crystals several microns or more in size were desired for microscopy, a T_s a few degrees above 35 °C was selected to obtain a reduced concentration of nuclei. To prepare smaller crystals for the birefringence studies, a T_s a few degrees below 35 °C was chosen. As crystal size depends on factors other than T_s, as discussed by Blundell and Keller,[33,34] a precise relation between crystal size and T_s could not be established because all aspects of the procedure were not standardized. The extent of crystallization was not determined.

Crystal morphology was examined primarily by phase-contrast and polarized light microscopy with a Zeiss Photomicroscope III. Crystals were rinsed with solvent and placed between cover slides. The solvent was then allowed to evaporate slowly. Figure 1a shows typical square crystals, observed by phase contrast, grown from a 1% solution of Pluronic 25R8. It was found, as expected, that crystal size depends on T_s. Crystal thickness can be assumed to be about 10 nm, which is close to values reported for certain of the single crystals from the

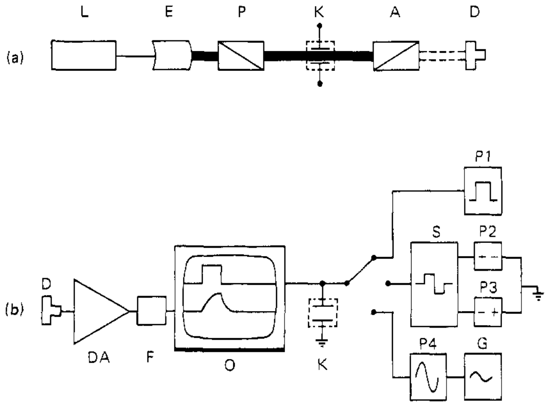

Figure 2. Block diagram of the apparatus used to measure the electric birefringence: (a) and (b) show respectively the optical and electrical components.

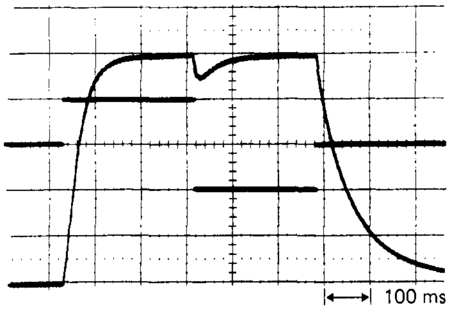

Figure 3. Time dependence of the light intensity resulting from the application of 625 V/cm whose polarity was thereafter reversed. The field-free decay curve gives a birefringence–relaxation time of 164 ms ($L = 1.15$ μm) for the crystals, which were grown from a 1% solution of the triblock copolymer PEO–PPO–PEO (Pluronic F127) in ethylbenzene.

PS–PEO diblock copolymers studied by Lotz et al.[9] (The thicknesses of crystals formed in undiluted block copolymers of PEO and PPO have also been reported.[28–30]) Spiral growths on the crystals were sometimes observed (Figure 1b), especially when the polymer concentration was 1 g/dL. Such growths frequently began in the center, rarely elsewhere; they are more likely to develop when the polymer concentration is high.[34]

No differences were noted in the crystallizability and in the crystals and suspensions obtained from Pluronics F127 and 25R8. The dispersed crystals are seemingly fragile, and fragments were observed under the microscope, especially after a suspension had been subjected to an electric field. The fragmentation of crystals has been proposed[6] to account for the observed reduction in the intensity of light scattered by a suspension *after each application of an electric field*.

Birefringence Apparatus. The components are shown schematically in Figure 2. The light source (L) was a 2 mW helium–neon laser (Oriel Corp.) whose wavelength is 632.8 nm. The diameter of the light beam was increased severalfold with an Oriel Beam-Expander (E) and then polarized at 45° to the electric field by a Nicol prism (P). The beam then passed through a 1-cm square spectrophotometer cell (K) and between copper electrodes held 0.80 cm apart in the cell by Teflon spacers. A Nicol prism analyzer (A) was crossed with the polarizer; in the absence of a birefringent sample or scattered light, no light reached the photodiode, D (Pin-10 United Detector Technology, Inc.). The output from the photodiode passed through an amplifier (DA), which served as a low-voltage power supply and a preamplifier, into a low-pass filter (F) and was displayed on a Tektronix 7844 Dual-Beam Oscilloscope (O). (The amplifier and the filter, which reduced the high-frequency noise, are part of the 7A22 differential amplifier in the Tektronix Oscilloscope.) The voltage applied to the cell K and the resulting birefringence signal were recorded on Polaroid film.

A rectangular electric pulse was generated by P1, which could supply a pulse of preselected duration at any voltage between 150 and 8000 V. A reversing pulse was obtained from a specially designed switch (S) and two power supplies: a Hewlett-Packard 6515A Power Supply (P2) and a Kepco (BOP 1000M) Bipolar Operational Power Supply/Amplifier (P3). A sinusoidal voltage was supplied by a function generator G (Hewlett-Packard, 3310B) and amplifier (P4), which was contained in P3.

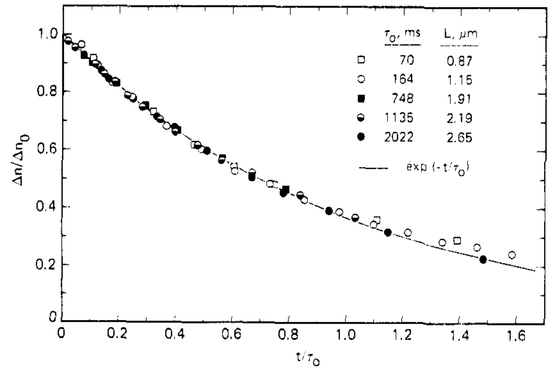

Figure 4. Birefringence relaxation data shown by a plot of $\Delta n/\Delta n_0$ vs. t/τ_0, where Δn_0 is the birefringence when the field was removed at $t = 0$ and τ_0 is the birefringence–relaxation time. The suspensions of crystals were grown from ethylbenzene solutions of PEO–PPO–PEO and were subjected to a field of 625 V/cm. The initial concentration of polymer was 0.4%, except the suspension whose $\tau_0 = 164$ ms; it was prepared from a 1% solution. The tabulated values of L were derived from τ_0 using eq 3.

The intensity I of the transmitted light is given by (cf. ref 13, Section 3.2): $I = k' \sin^2 \delta/2 \simeq k\delta^2$ where k' and k are constants and δ is the optical retardation. The retardation, expressed in radians, is related to the birefringence by: $\delta = 2\pi l \Delta n/\lambda$ where l is the path length through the solution and λ is the wavelength of the light under vacuum. The birefringence was always small and thus δ was taken to be proportional to $I^{1/2}$. The absolute value of δ, and thus of Δn, was not determined. Also, corrections were not made for the contribution of scattered or stray light to the intensity of the transmitted light.

The method selected for monitoring the birefringence precludes the determination of $\Delta n/\Delta n_0$, during field-free decay for example, when its value becomes less than about 0.2. Because $\Delta n/\Delta n_0 = (I/I_0)^{1/2}$, where I and I_0 are the intensities of the transmitted light that correspond to Δn and Δn_0, respectively, it follows that $I = 0.04 I_0$ when $\Delta n/\Delta n_0 = 0.2$. This and smaller values of I could not be obtained accurately from an oscillograph trace.

Results and Discussion

Figure 3 shows results from a reversing-pulse experiment made on a suspension of crystals grown from a 1% solution of Pluronic F127 (PEO–PPO–PEO triblock copolymer). The horizontal line-segments indicate that the voltage was changed stepwise from 0 to 500 V (625 V/cm), then from 500 to −500 V, and finally from −500 to 0 V. The curve represents the intensity of light transmitted through the crossed Nicol prisms. We shall now examine the three distinct portions of such response curves, obtained on several suspensions, beginning with the field-free decay of the birefringence.

Field-Free Decay of Birefringence and the Size of Crystals. Values of the light intensity, I, were obtained from the curve in Figure 3 and also from curves for four suspensions prepared from 0.4% solutions of F127. Because $\Delta n \propto I^{1/2}$, it follows from eq 2 that a plot of log $I^{1/2}$ vs. t should give a straight line whose slope equals $-1/2.303\tau_0$, provided the crystals are monodisperse. Values of τ_0 obtained by this graphical method were used in preparing the plot of normalized birefringence $\Delta n/\Delta n_0$ $[=(I/I_0)^{1/2}]$ against t/τ_0 shown in Figure 4. The curve in this figure is a simple exponential; it represents the data closely, except those on two suspensions when $\Delta n/\Delta n_0 < 0.35$. (Data at such values of $\Delta n/\Delta n_0$ were obtained on three of the five suspensions.)

The lengths of the crystals were derived from τ_0 using eq 3. As indicated in Figure 4, the values of τ_0 range from 0.070

to 2.02 s; the derived values of L range from 0.87 to 2.65 μm. These values are possibly somewhat large because no account was taken of the reduction in the rotary diffusion coefficient effected by the sheath of PPO chains containing partially immobilized solvent attached to each crystal. Also, as discussed in the text above eq 1, eq 3 is based on the assumption that τ_o for a square lamellar crystal equals that for a highly oblate ellipsoid whose volume equals that of the crystal.

If the particles in a suspension are in fact monodisperse, the decay curve not only should be a simple exponential but also should be independent of field strength. But if the particles are polydisperse, the rate of birefringence decay should increase with the strength of the applied field, as shown earlier.[25] For one suspension (not among those considered in Figure 4), decay curves following the application of six fields between 300 and 900 V/cm were found to conform closely to a simple exponential law, giving relaxation times between 704 and 770 ms, the average being 745 ms. (The relaxation time did not vary systematically with the field strength.) At fields of 1020 and 1210 V/cm, the decay curves clearly deviated from a simple exponential and gave mean relaxation times of 570 and 430 ms, respectively. This latter behavior possibly resulted because large crystals were fragmented under the high fields.[6]

The above findings suggest that the crystals in certain suspensions were essentially monodisperse whereas those in other suspensions were somewhat polydisperse. To obtain an indication of the size distribution, the decay curve for the suspension for which τ_o = 164 ms (Figure 4), and which deviates from a simple exponential expression at $\Delta n/\Delta n_0 < 0.35$, was analyzed by the "peeling" method.[13,35] The resulting equation

$$\Delta n/\Delta n_0 = 0.83e^{-t/206} + 0.17e^{-t/47} \qquad (11)$$

represents the data to within several percent over the entire range of $\Delta n/\Delta n_0$. The mean relaxation time $\bar{\tau}_o$ (=0.83 × 206 + 0.17 × 47) is 179 ms, which is somewhat larger than 164 ms obtained from the data at $\Delta n/\Delta n_0 < 0.35$. Equation 11 suggests that the birefringence relaxation times are 47 and 206 ms for certain crystals; their respective sizes (eq 3) are 0.76 and 1.23 μm. However, in light of eq 11, it appears that few small crystals exist; most crystals should be about 1.15 μm, the value derived from the birefringence decay when $\Delta n/\Delta n_0 > 0.35$ (cf. Figure 4). It is therefore concluded that the crystals, even when clearly polydisperse, have a narrow size distribution.

Behavior on Reversal of Field. In the reversing-pulse experiments, the birefringence attained essentially a steady state before the polarity of the field was reversed. Studies on various suspensions showed that a transient developed in the birefringence, upon field reversal, when τ_o was less than several hundred milliseconds, i.e., $L \lesssim 1.5$ μm. The transient had a minimum, illustrated in Figure 3, whose depth decreased with an increase in crystal size. Although a minimum, or in some instances a maximum, is expected if a permanent dipole moment contributes to the total polarization,[18] the observed transient cannot be ascribed to a permanent moment.

Consider a dilute solution of cylindrically symmetric particles whose polarization results from both fast-induced and permanent moments. According to theory[18] applicable when the applied field is of low intensity, the magnitude of the birefringence at the extremum, Δn_{m}, in the transient is given by

$$\frac{\Delta n_{\mathrm{m}}}{\Delta n_0} = 1 - \frac{2P/Q}{3^{1/2}(P/Q + 1)} \qquad (12)$$

The ratio P/Q equals $(p_3 - p_1)/q$, where p_3 and p_1 are related to the components of the permanent dipole along the unique and the two equivalent axes, respectively, of a particle and q depends on the principal values of the electrical polarizability tensor. The extremum occurs at a time, measured from the instant of field reversal, given by

$$t_{\mathrm{m}} = (3\tau_o/2)\ln 3 = 1.648\tau_o \qquad (13)$$

If the polymer crystals do in fact possess a permanent moment, its magnitude should increase with crystal size. Thus, according to eq 12, a transient should always result upon reversal of the field regardless of how q depends on crystal size. As no transient was observed when $L \gtrsim 1.5$ μm, such crystals cannot have a permanent moment of significant magnitude. (When the crystals were large, the reversal transient occasionally exhibited a very small maximum, for obscure reasons.)

To account for the dependence of $\Delta n_{\mathrm{m}}/\Delta n_0$ on crystal size, consider that polarization is a slow process and, for illustration, that the electric relaxation time τ_{e} is proportional to the length of a crystal. As $\tau_o \propto L^3$ (cf. eq 3), it follows that $\tau_{\mathrm{e}}/\tau_o = (k/L)^2$, where k is a constant. Substitution in eq 7 gives

$$\Delta n_{\mathrm{m}}/\Delta n_0 = 1 - (k/L)^{2/[1-(k/L)^2]} \qquad (14)$$

According to this equation, Δn_{m} approaches Δn_0 as L becomes large, as was observed. Actually, regardless of how τ_{e} depends on L, this behavior should always occur provided τ_{e}/τ_o decreases with an increase in L and eq 7 is applicable.

The curve in Figure 3 has a minimum at t_{m} = 15 ms and $\Delta n_{\mathrm{m}}/\Delta n_0 = (0.903)^{1/2} = 0.95$. Substitution in the equation below, obtained from eq 6 and 7,

$$\tau_{\mathrm{e}} = -t_{\mathrm{m}}/\ln(1 - \Delta n_{\mathrm{m}}/\Delta n_0) \qquad (15)$$

gives τ_{e} = 5.01 ms. Substitution of t_{m} and τ_{e} in eq 6 gives τ_o = 84 ms which corresponds to L = 0.92 μm. But the field-free decay of the birefringence gives τ_o = 164 ms, or L = 1.15 μm (cf. Figure 4). This substantial disagreement, which cannot be ascribed to minor errors in t_{m} and $\Delta n_{\mathrm{m}}/\Delta n_0$, possibly arises in part because eq 6, 7, and 15 are not strictly applicable; their derivation rests on the assumption, among others, that the potential energy of a particle in an electric field is small compared to kT. (As mentioned below, the present measurements were not made using a low field.) More likely, the disagreement arises because the crystals were somewhat polydisperse.

The minimum develops in the transient because the particles disorient somewhat under Brownian motion during the finite time required for the electric polarization to reverse its direction after the polarity of the applied field has been reversed; i.e., the polarization lags the field. Because small crystals will disorient more rapidly than large ones, the former will have a strong effect on the magnitude of the minimum. According to eq 11, the suspension studied contained some crystals for which τ_o = 47 ms (L = 0.76 μm). This value of τ_o is substantially smaller than 84 ms, derived from t_{m} and $\Delta n_{\mathrm{m}}/\Delta n_0$, which in turn is substantially smaller than 164 ms obtained from the field-free decay of the birefringence. It is therefore reasonable to consider that t_{m} and $\Delta n_{\mathrm{m}}/\Delta n_0$ were determined in substantial measure by the smaller crystals.

As discussed above, the minimum in the transient gives τ_{e} = 5.01 ms, τ_o = 84 ms, and L = 0.92 μm. Substitution of these values in the relation $\tau_{\mathrm{e}}/\tau_o = (k/L)^2$ gives k = 0.225 μm. Upon adopting this relation and the assumptions underlying eq 14, it follows that $\Delta n_{\mathrm{m}}/\Delta n_0$ should increase from 0.87 when L = 0.50 μm to 0.99 when L = 1.8 μm. These illustrative calculations support the observation that $\Delta n_{\mathrm{m}} \simeq \Delta n_0$ when $L \gtrsim 1.5$ μm.

It is worth noting again that the minimum in the transient cannot be ascribed to the combined effect of permanent and fast-induced moments acting in the same direction. Substitution of t_{m} = 15 ms in eq 13 gives τ_o = 9.1 ms which is an order of magnitude smaller than 84 ms, obtained by consid-

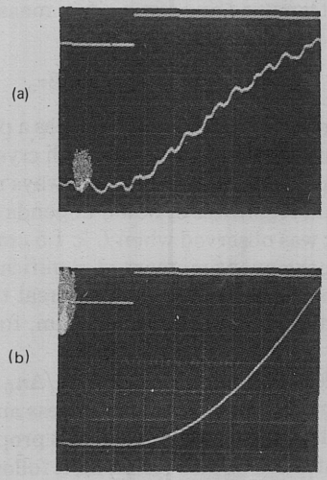

Figure 5. The initial portion of the light-intensity curve obtained on: (a) a suspension of small crystals; and (b) the same suspension after the crystals had grown significantly. The noise on the curve in (a) resulted because the output signal was amplified highly.

ering that the finite rate of polarization gives rise to the observed transient.

The preceding discussion of the response to a reversing pulse and the discussions hereafter of certain topics are based largely on concepts and equations that strictly apply only when the field strength is low. Our data were not obtained by using low fields, as evidenced by the relatively low fields required to effect saturation, considered subsequently. Matsumoto et al.[20] have computed the effect of field strength on the response to rectangular and reversing pulses when polarization results from various combinations of fast-induced and permanent moments. Their published curves show that the effect of field strength, while significant, is not major. It is thus believed that phenomena resulting from a slow induced moment will likewise not depend strongly on field strength and that the equations used in this paper to interpret the experimental data lead to conclusions of semiquantitative validity.

Deductions from the Rise Curve. Suppose that polarization results only from a slow-induced moment and that eq 4 represents the response to an electric pulse. As can be shown from eq 4, the rise curve has a zero slope initially and an inflection at

$$t_i = [\tau_e/(\tau_e/\tau_o - 1)] \ln (\tau_e/\tau_o) \qquad (16)$$

Because $\tau_o \propto L^3$, it follows from this expression that t_i increases with crystal size, except in the unlikely event that τ_e decreases significantly with an increase in crystal size.

The rise curve in Figure 3, which represents the intensity of transmitted light, has an inflection, though barely discernable, but its initial slope is obscure because the scale is compressed. Figure 5 shows on an expanded scale the initial portion of the rise curve for a suspension of small crystals and also for the same suspension after the crystals had grown significantly. For the suspension of large crystals (Figure 5b), the initial slope is clearly zero; the inflection point is off scale on the right. Although noise (owing to the high amplification) obscures the details of the curve for the suspension of small crystals (Figure 5a), the curve presumably has a zero slope initially and an inflection after a few milliseconds. Examination of curves obtained on a number of suspensions showed that t_i does in fact increase with crystal size. As the dependence of t_i on L was not obtained quantitatively, no attempt was made to evaluate the dependence of τ_e on L using eq 16.

The deductions from the rise curve are consistent with those

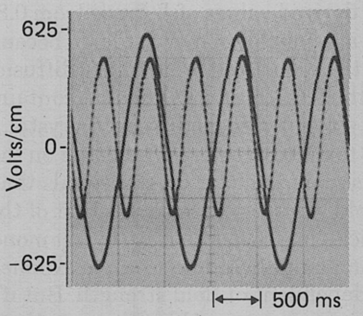

Figure 6. Variation of light intensity (partially broken trace) obtained by applying a sinusoidal voltage (±625 V/cm) at 1 Hz to a suspension of crystals for which τ_o = 220 ms (L = 1.27 μm). The crystals were grown from a 1% solution of PPO–PEO–PPO (Pluronic 25R8) in ethylbenzene.

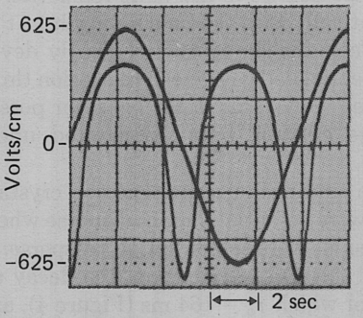

Figure 7. Distorted light-intensity curve obtained by applying a sinusoidal voltage (±625 V/cm) at 0.1 Hz to a suspension of crystals for which τ_o = 164 ms; cf. Figure 4.

from the reversing pulse experiments and hence constitute added evidence that particle orientation results from a slow-induced moment. If considered by itself, the zero initial slope of the rise curve indicates that polarization results from either a pure permanent moment[18,19] or a slow-induced moment (cf. eq 4). But polarization cannot arise from a pure permanent moment because the reversing-pulse experiment would then give $\Delta n_m/\Delta n_0 = -0.155$, according to eq 12, which clearly was not observed.

Response to Alternating Fields. The birefringence produced by a sinusoidal field will vary nonsinusoidally when the particles oscillate substantially under a field whose intensity goes beyond the range in which Kerr's law applies. Thus, when the amplitude of the field is high, the response curve should be distorted most highly at low frequencies.

Figures 6 and 7 show the response to a field whose extrema are ±625 V/cm. The curves in Figure 6 were obtained at 1 Hz on a suspension for which $\tau_o \approx 220$ ms ($L \simeq 1.3\,\mu$m), prepared from a 1% solution of Pluronic 25R8. The distortion in the response signal, though present, is small. In contrast, the highly distorted signal in Figure 7 was obtained at 0.1 Hz on the suspension for which τ_o = 164 ms (cf. Figures 3 and 4). Distortion thus appears to increase with a reduction in frequency. Results not presented here showed that the distortion at a particular frequency increases with the crystal size, as expected.

Measurements were made at frequencies between 0.5 and 1500 Hz on the suspension for which τ_o = 70 ms (L = 0.87 μm) under a field whose amplitude was ±625 V/cm. The alternating component of the birefringence vanished above 40 Hz; the steady component became very small at 1500 Hz. In analyzing the alternating component, only the minima values were considered. Because minima develop while the field strength is low, the distortion near the minima should not be excessive.

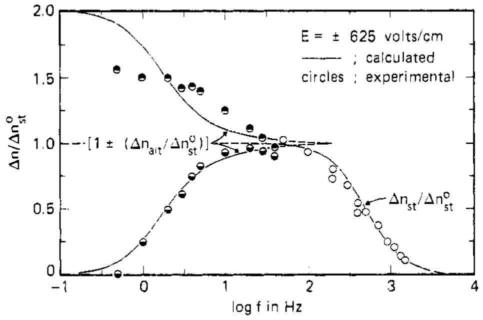

Figure 8. Frequency dependence of the normalized birefringence $\Delta n/\Delta n^\circ_{st}$ determined under a sinusoidal field of ±625 V/cm on a suspension for which τ_o = 70 ms (cf. Figure 4), where Δn°_{st} is the steady (time-independent) component of the birefringence at zero frequency. The half-shaded circles represent the alternating component of the birefringence, Δn_{alt}.

When polarization results solely from a fast-induced moment (i.e., when $\tau_e \ll \tau_o$), the minima and maxima of the alternating component of the birefringence, measured under a low field, are given by eq 9. It was found that experimental values of minima, but not maxima, can be represented rather well by eq 9 upon equating τ_o to 73 ms, in close agreement with 70 ms obtained from the field-free decay of the birefringence. Computed curves and the data (half-shaded circles) are shown in Figure 8 where $\Delta n/\Delta n^\circ_{st}$ connotes $\Delta n_M/\Delta n^\circ_{st}$ when the frequency is below about 40 Hz. In turn, $\Delta n_M/\Delta n^\circ_{st}$ equals (1 ± $\Delta n_{alt}/\Delta n^\circ_{st}$), cf. eq 8, where Δn°_{st} is the high-frequency asymptote given by eq 9. (Δn°_{st} also is the steady component at frequencies below that at which Δn_{st} becomes frequency dependent.) The maxima values of the alternating component deviate from the computed curve, undoubtedly because a field of high amplitude was employed.

The open circles in Figure 8 represent $\Delta n_{st}/\Delta n^\circ_{st}$ at frequencies from 50 to 1500 Hz. The curve was computed from

$$\Delta n_{st}/\Delta n^\circ_{st} = 1/(1 + \omega^2\tau^2) \qquad (17)$$

upon equating τ to 0.32 ms. This τ, which was observed to increase with crystal size, cannot be related to τ_e because a theoretical analysis of the dispersion of Δn_{st} apparently has not been made. It is worth noting, however, that the value of τ (=0.32 ms) is markedly smaller than τ_e = 5.0 ms which was obtained from the reversing-pulse experiment on the suspension of 1.15-μm crystals, as discussed earlier.

The phase angle was measured semiquantitatively at frequencies between 0.05 and 25 Hz on a suspension for which τ_o = 1.2 s (L = 2.2 μm). (Above 25 Hz, the phase angle could not be determined because Δn_{alt} was small.) The data at frequencies between 0.05 and 0.5 Hz are shown by the plot of tan δ vs. f (=$\omega/2\pi$) in Figure 9. Values of δ at all frequencies are plotted against log f in Figure 10.

When polarization results from a fast-induced moment, the phase angle cannot exceed 90° and is given by[11,24]

$$\tan\delta = 2\omega\tau_o \qquad (18)$$

At frequencies below 0.5 Hz, the data obey this relation (Figure 9) and give τ_o = 0.95 s, in fair agreement with 1.2 s obtained from the field-free decay of the birefringence.

Somewhat above 0.5 Hz, δ exceeds 90° and becomes about 160° at 25 Hz (Figure 10). This behavior is novel and apparently has not been reported previously for any type of particles whose orientation results from a pure induced moment, and a theoretical treatment does not exist. (When particle orientation results from a pure permanent moment, δ should approach 180° at high frequencies.[24] Under certain conditions, δ can exceed 90° by a sizable amount when both permanent and fast-induced moments are operative, although it approaches 90° at high frequencies.[24])

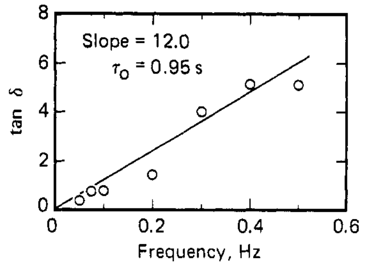

Figure 9. The dependence of tan δ on frequency between 0.05 and 0.5 Hz for a suspension of crystals whose relaxation time from the field-free decay of the birefringence is about 1.2 s. The slope of the above line gives 0.95 s.

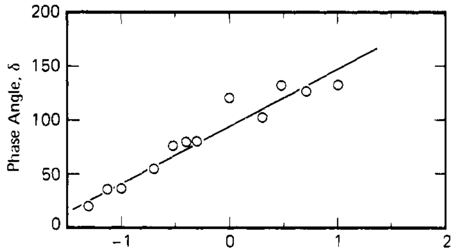

Figure 10. Dependence of the phase angle δ on the logarithm of the frequency. Data at log $f \leq -0.30$ are those shown in Figure 9.

The phase angle undoubtedly exceeds 90° at frequencies above 0.5 Hz because τ_e is not small compared to $1/\omega$ and hence the polarization lags the applied field. (Unfortunately, the frequency dependence of Δn_{alt} was not evaluated.) Below 0.5 Hz the polarization, but not particle orientation, presumably remains in phase with the field. Polarization can then be attributed to a fast-induced moment and therefore eq 18 is applicable, as found.

Dependence of Birefringence on Field Strength and the Polarizability of Crystals. The steady-state birefringence was measured under electric pulses of different intensities on three suspensions whose relaxation characteristics are shown in Figure 4. On one of these suspensions, measurements were also made at 20 Hz. As the alternating component of the birefringence was small, the steady component could be determined readily at different field strengths. The data were analyzed in terms of Shah's[26] equation that applies to a disk-shaped particle in which a moment is induced perpendicular to its unique axis.

To evaluate the normalized birefringence, $\Delta n/\Delta n_s$, plots were first made of $I^{1/2}$ vs. $1/E^2$, where again I is the intensity of the transmitted light. (Linearity is expected when $\Delta n/\Delta n_s$ > 0.6, as indicated by eq 10.) The intercept of each line on the ordinate gave $I_s^{1/2}$. Next, values of $(I/I_s)^{1/2}$ (=$\Delta n/\Delta n_s$) were computed and are plotted in Figure 11. The slopes of the lines give (cf. eq 10) the values of $(\alpha_2 - \alpha_1)$ in Table I. These values were used in preparing Figure 12. The curve represents Shah's equation[26] and the dashed line depicts Kerr's law. As shown, the curve conforms closely to the data, including those obtained on the same suspension (L = 0.87 μm) at 20 Hz and also by the pulse technique. The data in Figure 11 show that the birefringence approaches saturation at a low field strength. The field strength at which $\Delta n/\Delta n_s$ = 0.90 decreases from 875 to 163 V/cm with an increase in crystal size from 0.87 to 2.65 μm, cf. Table I.

Table I shows that $(\alpha_2 - \alpha_1)$ increases in direct proportion

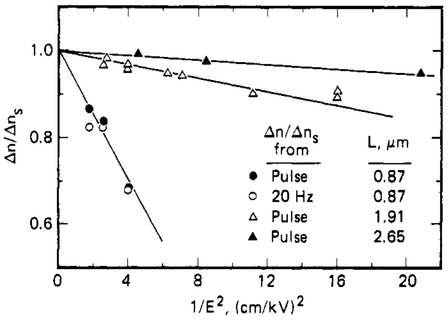

Figure 11. Dependence of the normalized birefringence on $1/E^2$, where Δn_s is the birefringence (saturation) when the particles are fully oriented and E is the field strength. The three suspensions are those whose birefringence relaxation is shown in Figure 4.

Table I
Quantities Derived from Dependence of the Birefringence on Field Strength

L, μm	$(\alpha_2 - \alpha_1)^a \times 10^{29}$, Fm^2	$(\alpha_2 - \alpha_1)/L^3 \times 10^{11}$, F/m	$E_{0.9}$,^{b} V/cm
0.87	1.69	2.57	857
1.91	15.5	2.23	283
2.65	46.9	2.52	163

[a] To convert the polarizabilities into units of cm^3, the above values should be divided by $4\pi\epsilon_0 \times 10^{-6}$, which equals 1.113×10^{-16} and where ϵ_0 (8.854×10^{-12} F/m) is the permittivity of a vacuum. [b] Field intensities at which $\Delta n/\Delta n_s = 0.90$.

to L^3. This finding is consistent with the treatment by O'Konski and Krause[17] of the Kerr constant of a dilute suspension of conducting ellipsoids. For a suspension of highly oblate ellipsoids whose anisotropic electric conductivities are manyfold greater than that of the solvent and whose anisotropic dielectric constants are roughly equal to that of the solvent, their treatment indicates that $(\alpha_2 - \alpha_1)/L^3$ should be a constant whose magnitude is similar to that derived from the experimental data.

According to eq 12 in ref 17 (in their notation, $\alpha_2 - \alpha_1 = kTQ_{21}$),

$$\alpha_2 - \alpha_1 = \frac{\epsilon V}{4\pi}(\chi_2 - \chi_1) \tag{19}$$

where ϵ is the low-frequency dielectric constant of the solvent, V is the volume of the ellipsoid, and

$$\chi_i = (\kappa_i/\kappa - \epsilon_i/\epsilon)B_i^2 + (\kappa_i/\kappa - 1)B_i \tag{20}$$

where κ_i and ϵ_i ($i = 1, 2$) are, respectively, the conductivity and dielectric constant along axis i of an ellipsoid, κ is the conductivity of the solvent, and B_i is the internal field function given by

$$B_i = [1 + (\kappa_i/\kappa - 1)A_i]^{-1} \tag{21}$$

where A_i is the shape-dependent depolarization factor. For highly oblate ellipsoids, i.e., $a/b \lesssim 0.01$, it has been shown (see Table I in ref 36) that $A_2 \ll A_1 \simeq 1$ and that $A_2 \simeq 0.78a/b$. When $A_1 = 1$, it follows that $B_1 = \kappa/\kappa_1$ and $\chi_1 = 1 - (\kappa/\kappa_1)^2\epsilon_1/\epsilon$. Upon assuming that $\kappa_2/\kappa \gg \epsilon_2/\epsilon$ and that $\kappa_2/\kappa \gg 1$, it can be shown that $\chi_2 = (1/A_2)[1 - 1/(1 + \kappa_2 A_2/\kappa)^2]$. Substitution of these relations for χ_1 and χ_2 in eq 19 gives

$$\alpha_2 - \alpha_1 = \frac{\epsilon V}{4\pi A_2}\{1 - 1/(1 + \kappa_2 A_2/\kappa)^2 - A_2[1 - (\kappa/\kappa_1)^2\epsilon_1/\epsilon]\} \tag{22}$$

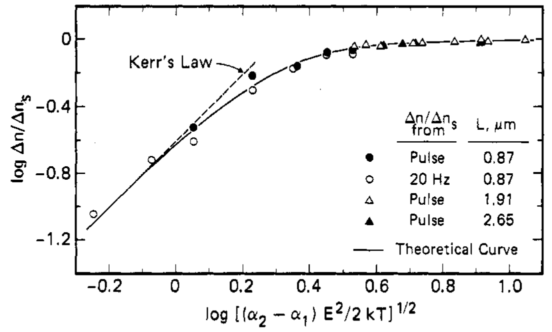

Figure 12. Demonstration that the reduced birefringence over the range $0.1 < \Delta n/\Delta n_s \leq 1.0$ conforms to the equation derived by Shah[26] for the orientation of disk-shaped particles in which a moment is induced perpendicular to the unique axis of a particle. Values of $(\alpha_2 - \alpha_1)$ were obtained from the slopes of the lines in Figure 11.

As considered in the discussion of the rotary diffusion coefficient, $b = L2^{-1/2}$ and $a = 0.955\,(h/2)$. For the present crystals, $h \simeq 0.01$ μm and L ranges from 0.87 to 2.65 μm. Because $A_2 = 0.78a/b$, as mentioned above, it follows that A_2 ($=5.3 \times 10^{-9}/L$, where L is here expressed in meters) ranges from about 0.002 to 0.006. Thus for any realistic values of κ/κ_1 and ϵ_1/ϵ, the term $A_2[1 - (\kappa/\kappa_1)^2\epsilon_1/\epsilon]$ in eq 22 is much less than unity and can be neglected. As the dielectric constant of the solvent (ethylbenzene) is 2.41 (2.68×10^{-10} F/m) and $V = 4\pi ab^2/3$, it follows that $\epsilon V/4\pi A_2 = 4.05 \times 10^{-11} L^3$ F m^2. Thus eq 22 becomes

$$\frac{\alpha_2 - \alpha_1}{L^3} = 4.05 \times 10^{-11}[1 - 1/(1 + 5.3 \times 10^{-9}\kappa_2/\kappa L)^2] \tag{23}$$

where L is again expressed in meters.

If $\kappa_2/\kappa \gtrsim 10^3$, eq 23 becomes $(\alpha_2 - \alpha_1)/L^3 = 4.05 \times 10^{-11}$ F/m, in acceptable agreement with 2.44×10^{-11} F/m, the latter being the average of the three values in Table I. For reasons mentioned in the discussion of the field-free decay of the birefringence, the values of L obtained from τ_0 are possibly somewhat large. If b in fact equals $0.84L2^{-1/2}$ instead of $L2^{-1/2}$, then the average experimental value of $(\alpha_2 - \alpha_1)/L^3$ agrees precisely with the theoretical value.

It seems reasonable to consider that $\kappa_2/\kappa \gtrsim 10^3$ and thus, because $\kappa \simeq 10^{-11}$ ohm^{-1} cm^{-1} (see discussion of materials), that $\kappa_2 \gtrsim 10^{-8}$. The specific conductivity of undiluted poly(ethylene oxide) in vacuo has been reported[37] to be about 10^{-9} ohm^{-1} cm^{-1}, which is some nine orders of magnitude higher than that of most saturated organic polymers. While this latter value cannot be related to the anisotropic conductivities of the crystals in ethylbenzene, it is not unlikely that κ_2 would be at least 10^{-8}. Whether the conduction process occurs within a crystal or along the interface between a PEO crystal and the attached PPO chains is not known.

As indicated by the above discussion, the net electric polarizability depends on the electric conductivities and dielectric properties of the particles and solvent and also on the volume and shape of the particles. Considerable experimental and theoretical work[11,12,17] has been directed toward understanding the polarizability of aqueous solutions of polyelectrolytes for which the electric conductivity is several orders of magnitude greater than that of the suspensions of PEO crystals considered here. Although a detailed discussion of different types of solutions and suspensions is beyond the scope of this paper, it is of possible interest to note that the polarizabilities of certain polyelectrolytes dissolved in water and of PEO crystals dispersed in ethylbenzene are rather similar.

For an aqueous suspension of bentonite particles whose mean size is 0.61 μm and whose thickness[38] is 0.01–0.015 μm, the net polarizability[26] (average of values for two fractions) is 4.1×10^{-29} F m^2 which is only about twofold greater than that for the 0.87-μm crystals (Table I). The polarizability of the rodlike TMV in aqueous solution[25] is 0.4×10^{-29} F m^2. While the polarizability of the suspension of 0.87-μm crystals is fourfold greater than that of the aqueous solution of TMV, the volume of a 0.87-μm crystal is about 100-fold greater than that of a TMV particle, whose volume[17] is 5.3×10^{-17} cm^3.

Summary

The data obtained by employing electric pulses and alternating fields show that crystal orientation arises from an induced dipole moment and that the associated polarization is a slow process. The magnitude of the polarization thus depends, in general, on both the field strength and the time. It was considered, as assumed by Tinoco and Yamaoka,[18] that the polarization rate can be characterized by an electric relaxation time, τ_e. The time and frequency dependence of the birefringence are functions of both τ_e and the birefringence relaxation time, τ_o, or equivalently the rotary diffusion coefficient. From the response to a pulse of rapidly reversed polarity, τ_e was estimated to be 5 ms for crystals approximately 1 μm in length.

Some of the present data reflect clearly the finite rate of polarization whereas other data can be treated by considering that polarization is a fast process. This behavior is expected because the relative magnitudes of τ_e and τ_o depend on crystal size and thus on the particular suspension studied.

The results that reflect the finite rate of polarization are: (a) the zero initial slope of the rise curve, observed most clearly on a suspension of large crystals; (b) the transient birefringence found in reversing-pulse experiments when the crystals were smaller than 1.5 μm; (c) the dispersion in the steady component of the birefringence at high frequencies; and (d) the phase angles greater than 90°, observed on a suspension of 2.2-μm crystals at frequencies above 0.5 Hz.

The findings that are unaffected by the finite rate of polarization are: (a) no detectable transient in the birefringence upon pulse reversal when the crystals are larger than 1.5 μm; (b) the frequency dependence of the alternating component of the birefringence for a suspension of 0.87-μm crystals; and (c) the frequency dependence of the phase angle determined on a suspension of 2.2-μm crystals at frequencies below 0.5 Hz.

From the dependence of the steady-state birefringence on field strength, $(\alpha_2 - \alpha_1)$ was evaluated for three suspensions of crystals whose lengths are 0.87, 1.91, and 2.65 μm. It was found that $(\alpha_2 - \alpha_1)/L^3 = 2.44 \times 10^{-11}$ F/m in acceptable agreement with 4.05×10^{-11} F/m obtained from a treatment of the excess electric polarizability of a highly oblate ellipsoid in a fluid whose electrical conductivity is markedly less than that of the ellipsoid.

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References and Notes

(1) Postdoctoral fellow sponsored by IBM Germany.
(2) H. Benoit, P. Rempp, and E. Franta, *C. R. Hebd. Seances Acad. Sci.*, **257,** 1288 (1963).
(3) Y. Gallot, E. Franta, P. Rempp, and H. Benoit, *J. Polym. Sci., Part C,* **4,** 473 (1963).
(4) E. Franta, *J. Chim. Phys. Phys.-Chim. Biol.*, **63,** 595 (1966).
(5) C. Picot, C. Hornick, G. Weill, and H. Benoit, *J. Polym. Sci., Part C,* **30,** 349 (1970).
(6) C. Picot and G. Weill, *J. Polym. Sci., Polym. Phys. Ed.*, **12,** 1733 (1974).
(7) D. J. Blundell, A. Keller, and A. J. Kovacs, *J. Polym. Sci., Part B,* **4,** 481 (1966).
(8) B. Lotz and A. J. Kovacs, *Kolloid Z. Z. Polym.*, **209,** 97 (1966).
(9) B. Lotz, A. J. Kovacs, G. A. Bassett, and A. Keller, *Kolloid Z. Z. Polym.*, **209,** 115 (1966).
(10) A. J. Kovacs, J. A. Manson, and D. Levy, *Kolloid Z. Z. Polym.*, **214,** 1 (1966).
(11) C. T. O'Konski and A. J. Haltner, *J. Am. Chem. Soc.*, **79,** 5634 (1957).
(12) C. T. O'Konski, "Encyclopedia of Polymer Science and Technology", Vol. 9, N. Bikales, Ed., Wiley, New York, N.Y., 1968, p 551.
(13) E. Fredericq and C. Houssier, "Electric Dichroism and Electric Birefringence", Clarendon Press, Oxford, 1973.
(14) C. T. O'Konski and S. Krause, "Molecular and Electro-Optics", Part I, C. T. O'Konski, Ed., Marcel Dekker, New York, N.Y., 1976, Chapter 3.
(15) F. Perrin, *J. Phys. Radium,* **5,** 497 (1934).
(16) S. H. Koenig, *Biopolymers,* **14,** 2421 (1975).
(17) C. T. O'Konski and S. Krause, *J. Phys. Chem.*, **74,** 3243 (1970).
(18) I. Tinoco, Jr., and K. Yamaoka, *J. Phys. Chem.*, **63,** 423 (1959).
(19) K. Nishinari and K. Yoshioka, *Kolloid Z. Z. Polym.*, **235,** 1189 (1969).
(20) M. Matsumoto, H. Wantanabe, and K. Yoshioka, *J. Phys. Chem.*, **74,** 2182 (1970).
(21) C. T. O'Konski and B. Zimm, *Science,* **111,** 113 (1950).
(22) H. Benoit, *Ann. Phys. (Paris)*, **6,** 561 (1951).
(23) A. Peterlin and H. A. Stuart, "Doppelbrechung insbesondere künstliche Doppelbrechung, Hand- und Jahrbuch d. Chem. Physik", Vol. 8, Part 1B, A. Eucken and K. L. Wolf, Ed., Akad. Verlaggesellschaft, Leipzig, 1943; Ann Arbor, Mich., 1948.
(24) G. B. Thurston and D. I. Bowling, *J. Colloid Interface Sci.*, **30,** 34 (1969).
(25) C. T. O'Konski, Y. Yoshioka, and W. T. Orttung, *J. Phys. Chem.*, **63,** 1558 (1959).
(26) B. J. Shah, *J. Phys. Chem.*, **67,** 2215 (1963).
(27) C. Booth and D. V. Dodgson, *J. Polym. Sci., Polym. Phys. Ed.*, **11,** 265 (1973).
(28) C. Booth and C. J. Pickles, *J. Polym. Sci., Polym. Phys. Ed.*, **11,** 249 (1973).
(29) P. C. Ashman and C. Booth, *Polymer,* **16,** 889 (1975).
(30) P. C. Ashman, C. Booth, D. R. Cooper, and C. Price, *Polymer,* **16,** 897 (1975).
(31) D. R. Beech and C. Booth, *J. Polym. Sci., Part B,* **8,** 731 (1970).
(32) A. E. Skoulios, G. Tsouladze, and E. Franta, *J Polym. Sci., Part C,* **4,** 507 (1963).
(33) D. J. Blundell and A. Keller, *J. Macromol. Sci., Phys.*, **2,** 301 (1968).
(34) D. J. Blundell and A. Keller, *J. Macromol. Sci., Phys.*, **2,** 337 (1968).
(35) C. T. O'Konski and A. J. Haltner, *J. Am. Chem. Soc.*, **78,** 3604 (1956).
(36) C. T. O'Konski, *J. Phys. Chem*., **64,** 605 (1960).
(37) A. E. Binks and A. Sharples, *J. Polym. Sci., Part A-2,* **6,** 407 (1968).
(38) M. J. Shah, D. C. Thompson, and C. M. Hart, *J. Phys. Chem.*, **67,** 1170 (1963).