Notes

Unusual Kerr Effect Transients Explained by the Formation In Solution of Metastable Ordered Structures

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In the Kerr effect literature many unusual Kerr effect transients have been reported. These are typified by those for bentonite,[1] β-lactoglobulin,[2,3] fibrinogen,[4] and TMV[5] which are respectively a disk-shaped clay, two proteins of differing ellipsoidal axial ratio, and a rod-shaped virus. Other materials giving similar unusual transients have recently been surveyed.[6] This survey, however, also includes "funny" transients which change with repeated pulsing and are associated with solution precipitation. This type of nonrepeatable transient must be taken as a special case and will not for the moment be considered here.

The shape of the observed transients is very dependent on the detection method used. The methods that have been used are linear detection, quadratic detection, and birefringence compensation detection, which is a hybrid of linear and quadratic detection and sometimes called quasi-linear detection.[7] This last method was used to obtain the bentonite[1] and β-lactoglobulin[3] result, while linear detection was used for TMV[5] and fibrinogen.[4] Quadratic detection has also been used for β-lactoglobulin.[2] The most useful method for detecting "funny" transients is linear detection as it unambiguously shows both positive and negative birefringence. The relative advantages of these types of detection have been discussed elsewhere.[7]

The birefringence vs. electric field strength behavior has also been recorded for bentonite,[1] fibrinogen,[4] and TMV.[5] The behavior for both bentonite and fibrinogen in this regard appears to correspond to the behavior predicted by Shah[8] for a particle with its permanent electric dipole approximately at right angles to the direction of maximum electrical and optical polarizability. β-Lactoglobulin is also found to have a permanent dipole at right angles to its major axis.[9] It is also noticeable that in each of the above cases the literature shows a marked increase in the negative birefringence contribution with concentration.

There is, however one major difficulty in accepting Shah's steady-state birefringence theory prediction of permanent and induced dipole moments in quadrature. This is because such a system does not give anomolous birefringence decays when the particles experience no external field.[10]

The possibilities which may explain the decay behavior are as follows: (a) two relaxation processes of differing time constant *and* sign, (b) a distortion of the applied field by the impedance of the solution-filled cell, and (c) an hysteresis effect in the local internal field which results from the applied field. Case (b) may be eliminated as this is normally detected by simultaneous recording of the applied electric field pulse. In Figure 1, it is shown how two independent birefringence transients of opposite sign and differing relaxation times can be added to give the observed transients. Possibility (c) would be difficult to infer from one transient and its existence is only likely to be detected after an exhaustive analysis of field strength, concentration, and ionic strength dependence.

Since the unusual traces referred to above appear to fit the composite traces shown in Figure 1, it is appropriate to consider the origins of the different birefringences. It can be postulated that birefringence traces of type (a) may be due to polydispersity or aggregation. One difficulty with the first suggestion is that the larger particles would both have to give a larger rotational diffusion coefficient *and* a birefringence of opposite sign to the smaller particles. Such behavior would be more readily expected of an aggregate with respect to its monomer. There may however be another possibility.

As particles increase in size, surface effects become more important and the effect of solute–solvent interface properties will also tend to become more important as the particle's surface to volume ratio increases, i.e., the particle becomes increasingly anisotropic in shape. There is, however, a further characteristic of anisotropic particles and that is that they go from a close-packed solid to a liquid phase via an intermediate liquid-crystalline phase in which the particles are mobile but have an orientation correlation.[11] It has been suggested[12] that for nematic liquid-crystalline materials at temperatures just above the isotropic–nematic transition temperature metastable nematic liquid-crystalline "flickering droplets" occur. While this concept has met with mixed reactions for conventional liquid crystals,[13] it still forms a useful conceptual approach for investigating concentrated solutions of anistropically shaped particles.

The Derjaguin–Landau–Verwey–Overbeek[14] theory of colloid stability, which is based on short-range London theory attractions and long-range electrostatic repulsions between particles, predicts interparticle separations which are very dependent on solution ionic strength and particle polarizabilities determined at infrared frequencies. It is, therefore, possible that under certain solution conditions, steric including structural bound water effects[15,16] and some form of dipole–dipole interaction[17–19] should encourage the ordering of anisotropic colloidal particles into structures resembling the liquid-crystal "flickering droplets". In fact under conditions of high sol concentration and low electrolyte concentration it is known[20] that colloidal systems containing anisodimensional particles such as TMV separate into two phases. The two phases consist of a dilute isotropic sol and a more concentrated birefringent sol. The behavior of the "flickering droplets" would be expected to differ from that of single particles. In fact their electrical properties would be expected to be derived from the Maxwell–Wagner theory of mixed phases[21] and in fact the droplet envelope shape may also change with solution conditions in a manner analogous to that of a flexible coiled polymer. It is thus possible that such "flickering droplets" provide an alternative explanation of "funny" transient behavior.

The rotatory diffusion coefficient of particles in a droplet will be longer than that of a single particle as the particles will interfere with each other as they rotate so that the droplet reorientates like a pack of cards. A longer relaxation time on its own, however, does not distinguish a droplet particle from an aggregate so it is necessary to look for other distinguishing features.

The Kerr effect orientation function Φ[22] and the liquid-crystal orientation function S[23] are related to the distribution of particle orientations by the same expression

$$\Phi = \int_0^\pi f(\theta)\,\frac{(3\cos^2\theta - 1)}{2}\,2\pi\sin\theta\,d\theta = S$$

In each case $f(\theta)$ is dependent on the particular orientation mechanism. Now since we wish to compare applied electric field orientation with droplet orientation it is useful to relate the droplet orientation to an equivalent orientation produced

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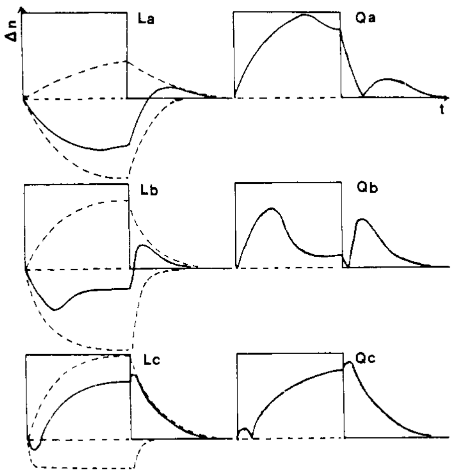

Figure 1. The effect of adding increasing amounts of a positive birefringence to a faster negative birefringence. The solid curves show the resultant traces for linear (L) and quadratic (Q) detection for a square wave applied electric field pulse.

by an electric field E_d. As the droplet is not likely to constitute an electric dipole, the effective droplet field strength has the property that $E_d = -E_d$, i.e., an axis rather than a direction of symmetry is defined. For colloidal particles of bentonite[24] the orientation function has a quadratic field strength dependence for induced dipole orientation up to a value nearly equal to half its saturation value. Thus for droplets with what is likely to be partial orientation we will assume that the orientation can be represented by

$$S = kE_d^2$$

With no external applied field, the orientations of the droplets are initially uncorrelated. The solution birefringence axis will be defined by the field direction. With no droplets to consider the Kerr effect orientation due to the applied field E would be for small field strengths

$$\Phi = kE^2$$

However, in a droplet in which E_d makes an angle θ with the applied field, we can say as a first approximation that Φ becomes Φ_d and now depends on $E + E_d \cos \theta$. Thus

$$\Phi_d = k(E^2 + 2EE_d \cos \theta + E_d^2 \cos^2 \theta)$$

Because E_d cannot have a negative direction when we average over all possible droplet orientations we have

$$\Phi_d = k(E^2 + 2E\langle E_d \cos \theta\rangle + \langle(E_d \cos \theta)^2\rangle)$$

in which $\langle E_d \cos \theta\rangle$ only disappears for a zero value of E_d.

Since the Kerr effect birefringence is proportional to Φ, the occurrence of a linear relationship between birefringence and field strength and particularly if associated with birefringence sign changes or "funny" transients may be signs of droplet behavior.

In this simple treatment it is assumed that the individual droplet's orientation axis is not disturbed, i.e., an elastic deformation of the droplet results from the application of the electric field. In larger electric fields an ordering of the droplet orientations would be expected, with the possible coalescence of some droplets. Such large ordered regions may exist for a period of time after removal of the electric field, and, since their orientation now preserves a memory of the applied field direction, this could create a finite solution birefringence. In essence we have our original hypothesis (c) occurring. However, in the concentrated solutions likely to give such effects the high field strengths will also disturb the ionic distribution, so that irreversible aggregation is likely. Those transients initially excluded from treatment in this paper because of their association with precipitation may now be considered to be the result of fluctuating droplet orientation and coalescence.

Since it is assumed that the droplet because of its nematic structure is non dipolar, although the individual particles of the droplet may be dipolar, its correlation of orientation is only likely to be maintained in an applied electric field if the individual particles orientate under an induced dipole mechanism. A domain structure for the droplet would have to be postulated to cater for permanent dipole orientation without destroying the droplet. This last postulate would seem to require rather excessive ordering in a metastable structure and for the moment will be discounted.

Induced dipole moment orientations occur for high-frequency fields, for example, laser-induced birefringence, and also for high dc fields even when the particles possess a finite permanent dipole.[8] It is thus under these orientation conditions that cooperative droplet orientation effects should be observed. This hypothesis now predicts that for particles with a finite permanent dipole in solutions of sufficient concentration for interparticle interactions to occur, orientation effects at low dc field strengths will be essentially due to individual particles, while at higher fields cooperative orientation in the droplet will dominate. At even higher field strengths ordering and coalescing of the droplets themselves then takes place.

The experimental results for bentonite[1] do in fact show negative birefringence at low field strengths as would be expected for particles with a transverse permanent dipole and a positive birefringence at higher field strengths where the induced dipole dominates. This is also coupled with an increased relaxation time for the positive birefringence which in the middle field strength region creates the funny transients as shown in Figure 1. It is also noticeable that in the region where the induced dipoles are dominating the orientation there is a linear slope of birefringence vs. field strength.

Also since it has been postulated that metastable droplets occur in solutions of TMV and bentonite which change from a single phase to a double phase on increasing the concentration, similar behavior should be observed in flickering droplets in isotropic nematogens near to the isotropic–nematic phase change. In fact it should be noted that the nematogen *p*-methoxybenzylidene-*p*-*n*-butylaniline (MBBA) at a temperature above its nematic–isotropic transition point has for high laser field strengths a transition[25] from a conventional squared to a linear relationship between birefringence and field strength. This is likely to correspond to an electric field induced isotropic nematic transition with the predicted accentuation of the second term in eq 1. Furthermore the funny transients observed[26] in solutions of the positive nematic material 4,4′-*n*-pentylcyanobiphenyl (PCB) at very high dc field strengths can be interpreted as a dominant induced dipole orientation mechanism ordering and coalescing flickering droplets into a short-lived nematic phase which persists for a short while after removal of the orientating field.

In conclusion it may be stated that the occurrence of "funny" transients is a probable indication of the presence of groups of interacting particles forming metastable droplets under conditions which are close to a phase change.

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References and Notes

(1) M. J. Shah and C. M. Hart, *IBM J. Res. Dev.*, **7**, 44–57 (1963).
(2) C. L. Riddiford and B. R. Jennings, *Biopolymers*, **5**, 757–771 (1967).
(3) C. L. Riddiford and H. G. Jerrard, in press.
(4) A. E. V. Hashemeyer and I. Tinoco, *Biochemistry*, **1**, 6, 996–1004 (1962).
(5) C. T. O'Konski and B. H. Zimm, *Science*, **111**, 113–116 (1950).
(6) B. L. Brown and B. R. Jennings, *J. Colloid Interface Sci.*, **43**, 170–175 (1973).
(7) C. L. Riddiford and H. G. Jerrard, *J. Phys. D*, **3**, 1314–1321 (1970).
(8) M. J. Shah, *J. Phys. Chem.*, **67**, 2215–2219 (1963).
(9) S. N. Timasheff, *Biopolymers*, **4**, 107–120 (1966).
(10) H. Benoit, *Ann. Phys. (Leipzig)*, **6**, 561–609 (1951).
(11) P. G. de Gennes, "The Physics of Liquid Crystals", Clarendon Press, Oxford, 1974, p 2.
(12) W. L. McMillan and J. de Physique, *Colloq. C. 1 Suppl.*, **36**, 3, 103–105 (1975).
(13) P. G. de Gennes, ref 11, p 103.
(14) E. J. W. Verwey and J. Th. G. Overbeek, "Theory of Stability of Lyophobic Colloids", Elsevier, Amsterdam, 1948.
(15) C. Ballario, A. Bonincontro, and C. Canetti, *J. Colloid Interface Sci.*, **51**, 191–195 (1975).
(16) R. E. Grim, "Applied Clay Mineralogy", McGraw-Hill, New York, N.Y., 1962.
(17) J. G. Kirkwood and J. B. Shumaker, *Proc. Natl. Acad. Sci. U.S.A.*, **38**, 855–862 (1952).
(18) J. G. Kirkwood and J. B. Shumaker, *Proc. Natl. Acad. Sci. U.S.A.*, **38**, 863–871 (1952).
(19) S. N. Timasheff, *Biopolymers*, **4**, 107–120 (1966).
(20) D. J. Shaw, "Introduction to Colloid and Surface Chemistry", 2nd ed, Butterworths, London, 1970, p 174.
(21) H. M. Dintzis, J. L. Oncley, and R. M. Fuoss, *Proc. Natl. Acad. Sci. U.S.A.*, **40**, 2, 62–70 (1954).
(22) E. Fredericq and C. Houssier, "Electric Dichroism and Electric Birefringence", Clarendon Press, Oxford, 1973, p 25.
(23) P. G. de Gennes, ref 11, p 24.
(24) M. J. Shah, *J. Phys. Chem.*, **67**, 2215–2219 (1963).
(25) H. J. Coles and B. R. Jennings, *Mol. Phys.*, **31**, 571–580 (1976).
(26) H. J. Coles and B. R. Jennings, *Mol. Phys.* **31**, 1225–1231 (1976).

Time Resolved Fluorescence Studies of Poly(*N*-vinylcarbazole), Poly(1-vinylnaphthalene), and 1,3-Bis(*N*-carbazolyl)propane

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Excimer emission from polymers with pendant aromatic groups has recently received considerable attention.[1-12] In nearly every case the excimer emission has been shown to arise from a sandwich type excimer in which the π orbitals of the aromatic rings overlap substantially. For example, the excimer fluorescence ($\lambda_{max} \simeq 410$ nm) of poly(1-vinylnaphthalene) (PVN) dominates the relatively weak emission from the naphthyl monomer.[9] However, the excimer emission of poly(naphthyl methacrylate) (PNMA) ($\lambda_{max} \simeq 390$ nm) is approximately equal to the monomer emission ($\lambda_{max} \simeq 340$ nm) in ethyl acetate.[2] In neither case was any type of excimer emission other than that of the low-energy excimer ($\lambda_{max} \simeq 400$ nm) observed.[2,9] In contrast, the emission spectrum of poly(*N*-vinylcarbazole) (PVCz) results from two distinct excimers, a low-energy sandwich type ($\lambda_{max} \simeq 420$ nm) and a high-energy excimer of undefined structure ($\lambda_{max} \simeq 375$ nm).[8] Emission from the high-energy excimer is relatively more intense in a predominately syndiotactic polymer obtained by radical polymerization than in a more isotactic polymer obtained by cationic polymerization.[12] Itaya et al. have proposed that the high-energy excimer has a structure in which only one pair of phenyl rings from the two carbazole chromophores overlaps.[12] The high-energy excimer in PVCz is thought to arise from excimer traps existing prior to the initial absorption of light by the carbazolyl chromophore.[8] The low-energy sandwich excimer can be formed by two possible mechanisms, either directly or by reorientation of the high-energy excimer.

No high-energy excimer occurs from 1,3-bis(*N*-carbazolyl)propane (BCP), the low molecular weight model compound of PVCz.[13] Only monomer emission ($\lambda_{max} \simeq 350, 370$ nm) and low-energy excimer emission ($\lambda_{max} \simeq 420$ nm) can be detected for BCP. The low-energy excimer emission is very weak, suggesting little interaction between the neighboring carbazolyl chromophores. The absence of a high-energy excimer emission suggests that the conformational constraints imposed by the stiff polymer chain in PVCz are not present in BCP.

The formation of two distinct excimers, one of high energy and one of low energy, in PVCz, is, therefore, unique among vinyl aromatic polymers. In order to elucidate further the nature of the excimers formed in polymers and in certain model compounds, we have measured the time resolved spectra of various vinyl aromatic polymers and one model compound, BCP. Time resolved fluorescence spectroscopy has been previously used to study the energy transfer mechanism in a copolymer of naphthyl methacrylate and 9-vinylanthracene and in the poly(naphthyl methacrylate) homopolymer.[14]

Experimental Section

The PVCz (Monomer–Polymer) was purified by threefold precipitation into methanol followed by chromatography on silica gel. The ultraviolet spectrum, fluorescence emission spectrum, fluorescence decay times, and excitation spectrum all agree with literature data for PVCz. BCP was synthesized by the method of Lewis et al.[15] and purified by preparative thin-layer chromatography. PVN was prepared by spontaneous polymerization and purified by successive precipitation from benzene solution into methanol. Benzene was twice distilled from phosphorus pentoxide retaining the middle fraction each time. Ethyl acetate was distilled and stored in the dark.

Steady state fluorescence spectra were taken on a Hitachi MPF-2A fluorescence spectrometer and corrected for phototube response using quinine sulfate in aqueous sulfuric acid as a standard. The time resolved fluorescence spectra were taken using the single photon counting apparatus in the multichannel scaling mode.[16] A Spex Minimate monochromator (1.25 mm slit width) was installed with a Rapid-Syn-28PS stepping motor attached to rotate the grating. The multichannel analyzer was employed in the multichannel scaling repeat mode with the analog to digital converter serving as a single channel analyzer. The complete wavelength spectrum was scanned over 20 times in each case in order to correct for noise and lamp fluctuation. The steps were made in increments of 0.14 nm with 0.1 s per step. The time window employed was determined by setting the upper and lower voltage (or time) limits for the single channel analyzer. The time limits were calibrated by observing the decay of a lamp profile scattered off a Ludox scattering solution. Since the sample is continually being excited over a finite period defined by the decay of the low-pressure nitrogen lamp intensity profile, it is difficult to assign the exact time values of the time windows for the time resolved spectra.[16b] The time settings are given as the time difference of the upper (or lower) limit, determined by the discriminator settings on the analog to digital converter, from the maximum of the exciting lamp.[17] The time resolved spectra are adjusted to fit on the same time scale. Time resolved fluorescence spectra are uncorrected for photomultiplier tube response. All samples were degassed with five freeze–pump–thaw cycles before sealing in quartz test tubes.

Results and Discussion

The steady state fluorescence spectra of PVCz (5×10^{-4} M) and BCP (2×10^{-4} M) in benzene are shown in Figure 1. The low-energy excimer emission (above 420 nm) is seen for both PVCz and BCP. The time resolved emission spectra for PVCz are shown in Figure 2 at several time intervals. (In curve a, the points from the multichannel analyzer are actually plotted.) The spectrum in curve a was taken at an upper "time setting" of 0.23 ns from the peak maximum of the exciting lamp intensity. From a consideration of the intensity of exciting light as a function of time, it follows that >96% of the

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