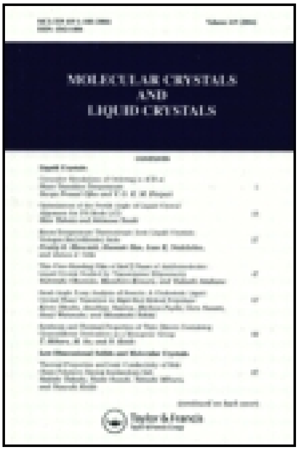

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Comparison of Electro-Optical Response Functions of Nematic Droplet/Polymer Films

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Comparison of Electro-Optical Response Functions of Nematic Droplet/Polymer Films

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Comparisons are made between various electro-optical response functions for nematic droplet/polymer films. The bases behind film dichroism, scattering, and dielectric constant are discussed. It is shown that the measurement of film haze can be related to the specular transmission of the film, and that the scattering electro-optical response is insensitive to the *f/#* of the collection device. The scattering vs. field response for these films is shown to have a strong wavelength dependence. The dichroic, scattering, and dielectric response functions for the same films are compared, and it is seen that the dichroic response requires higher fields for saturation than the scattering or dielectric responses.

INTRODUCTION

Interest continues to grow in dispersions of nematic liquid crystal in polymer films (known as NCAP or PDLC), due to the number of technical applications possible for this class of devices.[1,2] An increasing variety of liquid crystalline materials, matrix materials, and processing methods are being developed to construct these films. These films are typically measured for some sort of electro-optical response, with the exact measurement often depending on the end application in mind for the film. Electro-optical measurements often utilized usually involve film scattering[3,4] and film dichroism.[5] Dielectric properties[6,7] and nuclear magnetic resonance[8,9,10] have also been employed in the study of these films. Comparison of films constructed by different methods and in different laboratories is often made difficult by the different measurement methods used for their evaluation.

Given these disparate measurement methods, it is of interest to compare the various field-dependent response curves for a single film sample. Different electro-optical response functions of these films may have different dependencies on nematic alignment within a droplet, as well as on collective droplet effects. In comparing different measurement methods on a single film, we can gain information regarding the relationship between microscopic nematic alignment within the film and the macroscopic properties of the film.

To date, there has not been a formal comparison of differing electro-optical responses for a well-defined set of films. In this study, we discuss the film characteristics that affect the dichroic, scattering, and dielectric response characteristics of nematic droplet/polymer films. We then report our initial results comparing these different properties for a well-defined set of films. It is our intent that the comparisons described here will form a basis for the comparison of films constructed in different laboratories, and measured in different fashions.

FILM CONSTRUCTION

The films in this study were constructed using an emulsification method, with polyvinyl alcohol as the continuous matrix. The volume-weighted droplet size distributions of the nematic emulsions used to construct these films were characterized prior to coating and film formation, so that the dispersion of droplet sizes within the final film is known. Upon film formation, the cavities containing the nematic adopt the shape of oblate spheroids, with the minor axis of the spheroid aligned perpendicular to the film plane. The nematic within the cavities adopts a bipolar orientation, with the bipolar axis in the unpowered film lying primarily in the film plane. These characteristics, along with other aspects of these films, have been discussed in detail elsewhere.[3,6]

For the comparison of electro-optical properties, nematic mixtures containing a high order parameter yellow dye were used (2% Mitsui SI486 in Merck ZLI 1840). This yellow dye possesses an absorbance maximum near 410 nm, but negligible absorbance at wavelengths > 600 nm. Thus, a helium-neon (HeNe) laser could be used to characterize film scattering at 632.8 nm without interference from the dye. For wavelength-dependent scattering measurements, films containing nematic with no dichroic dye were used. Each film studied was within the thickness range 23 ± 1 μm.

COMPARISON OF MEASUREMENT METHODS

Figure 1 shows schematically three different electro-optical measurement techniques commonly used with nematic droplet/polymer films. Each of these measurements has been employed by a number of workers to evaluate film properties. The film optical response is typically measured as a function of applied field (or voltage).

Figure 1a shows the diffuse transmission of a film containing dichroic dye. The use of an integrating sphere is important in these measurements in order to capture light scattered by the film but not absorbed by the dye. This measurement is most relevant for guest-host nematic droplet films used in display applications.[1] We will suggest in this paper that this measurement is also the most reliable indicator of nematic alignment within a film.

Figure 1b shows the measurement of specular transmission for a nematic droplet film, a measure of film scattering. A detector of aperture diameter D is placed a distance L from the film, and measures the intensity of collimated light that passes through the film. The ratio L/D defines the $f/\#$ for the measurement system. This measurement is most relevant for projection display applications for these films.[11,12]

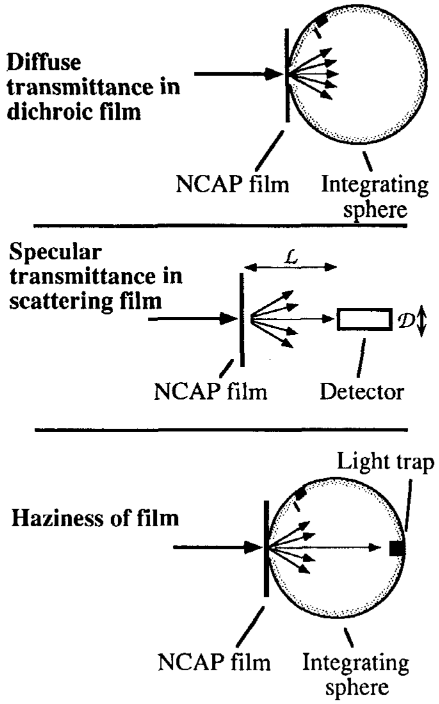

FIGURE 1 Various optical measurement schemes for determining the scattering and dichroic response characteristics of NCAP films.

Figure 1c illustrates the measurement of film haze, another scattering-based measurement related to the perceived clarity of the film. Haze is a measure of the light scattered out of a cone $\pm 4°$ in width, using a well-collimated source.[13] Haze is defined as the ratio of this scattered light to the total light transmission through the film. In the past, we have extensively employed film haze as a measure of nematic orientation within these films.[3,6]

A non-optical measurement technique that we are introducing in this study measures the field-dependent dielectric constant of the film. A 1 Hz square wave is placed across the film, with the rms voltage determining the alignment of the nematic within the film. A 1 KHz AC sine wave with an amplitude 100 times smaller than the 1 Hz signal is summed with the low-frequency square wave, and the impedance and phase angle at 1 KHz are measured. In all cases the voltage:current phase angle measured was greater than 80°, indicating that the 1 KHz impedance was dominated by the film's capacitance. Measurement of the film thickness and area allows for the determination of a dielectric constant for the film. We have previously used this technique to monitor the "effective dielectric constant" of the film in the limits of zero-field and high field.[6] While we find that the values measured in this manner are not true dielectric constants due to the nonideal response of the film,[14] the values are meaningful measures of a film's dielectric response, and are related to the nematic orientation within the film.

The electro-optical response curves plotted in this study are given in terms of applied field, rather than voltage. Nematic droplet films are field-effect devices, and meaningful comparisons between films of different thicknesses can be made if their field-dependent (rather than voltage-dependent) responses are compared.

DICHROIC ABSORBANCE

Perhaps the least ambiguous measure of nematic orientation within an NCAP film is given by the dichroic transmission of the film. In the most general case, the dichroic absorbance A of an NCAP film (excluding losses from reflection and scattering) is approximated by the modified Beer-Lambert expression (1). In (1), S, a,b, and c carry the usual definitions of order parameter, extinction coefficient, cell thickness, and dye concentration, respectively.[15] For droplets with the bipolar configuration, θ is defined as the angle of the bipolar axis of a droplet with the film plane. For a given droplet, the total absorbance is approximated as the sum of the absorbance of light polarized parallel to and perpendicular to the bipolar axis of the droplet. The total film absorbance is determined by summing over all droplets, weighting each term in the summation by the volume $v(\theta)$ of nematic oriented at an angle θ.

$$A_{\text{film}} = -\log T_{\text{film}} = \frac{\text{abc}}{2}\left[\frac{1-S}{3} + \sum_{\theta=0}^{\pi/2} \frac{1}{3}\,[1 + S(3\,v(\theta)\cos^2\theta - 1)]\right] \qquad (1)$$

In the PVA films described here (with oblate spheroidal cavities, bipolar orientation), the absorbance of the film in the low-field and high-field cases is well defined: the nematic is aligned primarily in the film plane in the low-field case ($\theta = 0$), and perpendicular to the film in the high-field case ($\theta = \pi/2$). We define the terms A_{off} and A_{on}, representing the absorbance of the film in the low field and high-field limits, respectively.[1] We can simplify equation (1) if we assume that each droplet switches from an in-plane alignment ($\theta = 0$, at low fields) to a perpendicular alignment ($\theta = \pi/2$, at high fields) over a narrow field range. In this case, at a field E the overall absorbance of the film [$A_{\text{film}}(E)$] will be given by (2), where $V_{\text{on}}(E)$ represents the volume of nematic droplets oriented with the field. Taking the derivative with respect to field, Equation (3) describes a simple relationship between the change in film absorbance and the volume of nematic reoriented within the film.

$$\text{A}_{\text{film}}(E) = V_{\text{on}}(E)\,(A_{\text{on}} - A_{\text{off}}) + A_{\text{off}} \qquad (2)$$

$$\frac{d\text{A}_{\text{film}}}{dE} = (A_{\text{on}} - A_{\text{off}})\,\frac{dV_{\text{on}}}{dE} \qquad (3)$$

We can test the validity of equation (3) by comparing the dichroic response of a film to the droplet size distribution. Previous experimental and theoretical work[3,4,16] has shown that there is an approximate inverse relationship between the diameter of the nematic droplet and the field required for reorientation of that droplet.

Using this relationship and equation (3), a plot of $d[\log T]/dE$ vs. field should have the same shape as a plot of the volume size distribution vs. [1/diameter]. The field at maximum $d[\log T]/dE$ will correspond to the peak of the volume size distribution.

Figure 2 shows this comparison for two dichroic NCAP films. For each film, comparison of the $\{d[\log T]/dE$ vs. $E\}$ curve with the {volume fraction vs. [1/diameter]} curve shows a good correlation of the curve shapes. While the shapes of the curves are similar, it is apparent that the assumption that the dichroic response of the film is narrow for each size of droplet has only limited validity. The width of the dichroic response is greater than the width of the droplet size distribution for each film, indicating that the nematic droplets in a given size range reorient over a range of fields.

Even though the width of the absorbance and volume distribution curves differ, the maximum of the $d[\log T]/dE$ curve should correspond to the peak in the droplet size distribution. For the large droplet film, the size distribution peak of 4.6 μm corresponds to a $d[\log T]/dE$ peak of 0.7 ± 0.2 V/μm. Invoking the inverse relation between droplet size and reorientation field, this graph indicates that a field of 3.2 ± 0.9 V/μm is required to reorient a 1.0 μm droplet in this film. For the small

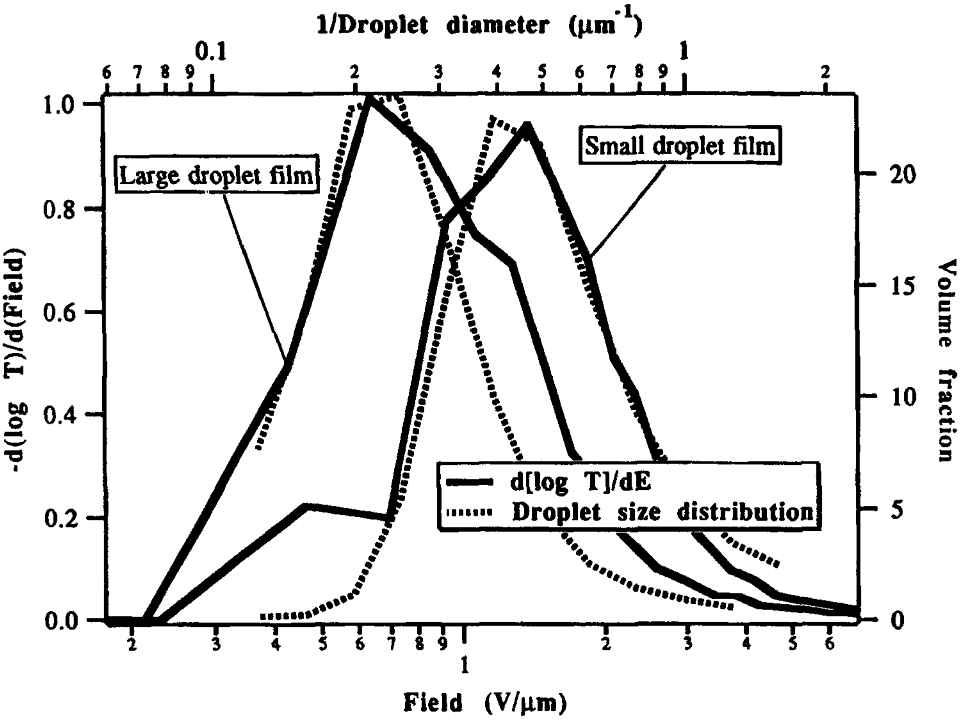

FIGURE 2 Comparison of dichroic film response and droplet size distribution for two NCAP films. The solid lines (—) correspond to the first derivative of [log T] with respect to the field, and are plotted on the left and bottom axes. The dotted lines (---) correspond to the volume-weighted size distribution of nematic droplets, plotted vs. [1/diameter]; these curves are plotted using the top and right hand axis. The right hand pair of curves correspond to a small droplet distribution (mean volume diameter = 2.3 μm), and the left-hand pair of curves correspond to a larger mean diameter (4.3 μm).

droplet film, we get a similar value. The size distribution peak of 2.4 μm corresponds to a $d[\log T]/dE$ peak of 1.25 ± 0.35 μm. This gives a reorientation field for a 1.0 μm droplet of 3.0 ± 0.8 V/μm. While the errors associated with deriving these fields are rather large, the data here indicate that both films do share the approximate relationship between droplet size and field, and that droplets of similar size in each film require about the same fields for reorientation.

SCATTERING BASED MEASUREMENTS

In films that do not contain dichroic dyes, scattering properties (both haze and specular transmission) are important measurements of the film response. Comparing Figures 1a and 1c, it is obvious that the specular transmission and haze measurements are related, as shown by Equation (4). Thus, haze is no more than a variant on a specular transmission measurement. This is readily seen in Figure 3, which shows the electro-optical response curve for a single film measured under a variety of methods. Figure 3 plots field vs. transmission at three different L/D ratios: $f/4$, $f/16$, and $f/64$, along with a plot of (1-haze)*$T_{f/0}$. It is readily seen that the general electro-optical response curves for these films are nearly identical, with the curves possessing the same threshold and shape. In comparing the field-dependence of film scattering, the choice of $f/\#$ is not an important function.

$$\text{Haze} = 1 - (T_{f/?}/T_{f/0}) \tag{4}$$

$$-\log T = \text{abc} \tag{5}$$

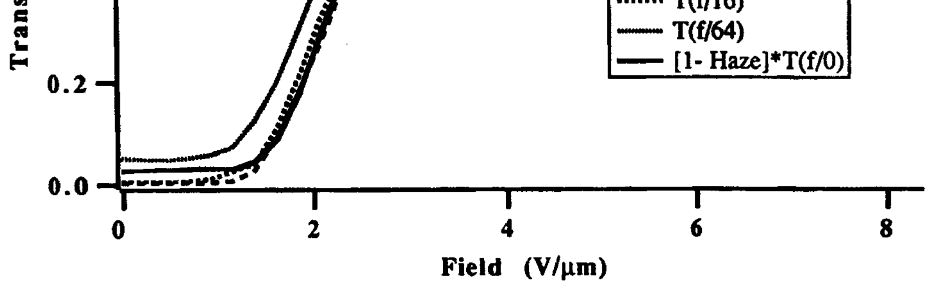

FIGURE 3 Comparison of the specular transmission response of an NCAP film, as a function of $f/\#$. The similar shape of the [1-Haze]* $T_{f/0}$ curve to the specular transmission curves shows the intrinsic relationship between specular transmission and haze measurements.

In the analysis of a film's scattering response, we often want to measure an optical parameter which is proportional to the numbere of aligned droplets within the film. For a dilute collection of scatters, the transmission of a collimated light source through the scattering medium scales as Equation (5).[17] In 5, a is the cross section of scatterers, b, is the cell thickness, and c concentration of scatterers. This equation is similar in form to the Beer-Lambert law used in dichroic systems. Deviations from (5) occur when multiple scattering is involved, as some fraction of light will be scattered back into the original propagation direction. Despite its shortcomings, Equation (1) does imply that as individual droplets switch from strong scatterers to weak scatterers with increasing field, the attenuation of light through the film decreases exponentially with the number of strong scattering sites. In relating film scattering to the reorientation of individual cavities within the film, log transmission is the proper method of analysis.

This distinction between T and $\log(T)$ has practical importance, as the electro-optic response curve depends strongly on which parameter is plotted. The exponential dependence of T described in (5) indicates that plots of T vs. field will reflect the film thickness and concentration of scatterers, as well as the orientation of the nematic droplets within the film. While the measurement of T is often of practical importance for the evaluation of a film as a device, the measurement of $\log(T)$ vs. field is a more reliable indicator of droplet orientation within the film.

Figure 4 shows that the apparent threshold and saturation fields for a film can vary by $2\times$, depending on whether T or $\log(T)$ is plotted vs. the field E. Estimating the reorientation fields for droplets within a film using T vs. E curves in this case results in values much higher than are warranted. Given the correspondence between haze and transmission (Equation 4), this analysis also shows that using film haze to estimate reorientation fields for individual droplets will produce fields that are artificially high.

Film scattering will provide an approximate measure of nematic orientation within the film. It is difficult to draw an exact correspondence between film scattering and nematic orientation, however. The difficulties in relating film scattering to nematic orientation can be appreciated by a cursory glance at the theory of light scattering.[17–20] Light scattering from an arbitrary particle is a nonlinear function of the particle size, its refractive index, and wavelength. In NCAP films, the variables that affect film scattering include wavelength, droplet size and shape, nematic orientation, nematic and polymer refractive indices (which are also wavelength dependent), and film thickness. *A priori* prediction of light scattering profiles from individual droplets is difficult at best, and the presence of multiple scattering due to the high concentration of droplets makes the relationship between macroscopic film scattering and microscopic orientation difficult to relate.

An example of this problem is shown in Figure 5, which shows $\log(T)$ at $f/8$ for a non-dyed NCAP film as a function of wavelength. Depending on the wavelength chosen, the threshold and saturation fields vary by up to 50% across the spectrum, despite the fact that at any particular field the orientation of the nematic droplets within the film is independent of wavelength. Thus, the transmission of a film based on film scattering is not a unique measure of the response of the film, but will depend to some degree on the measurement method and film samples chosen for

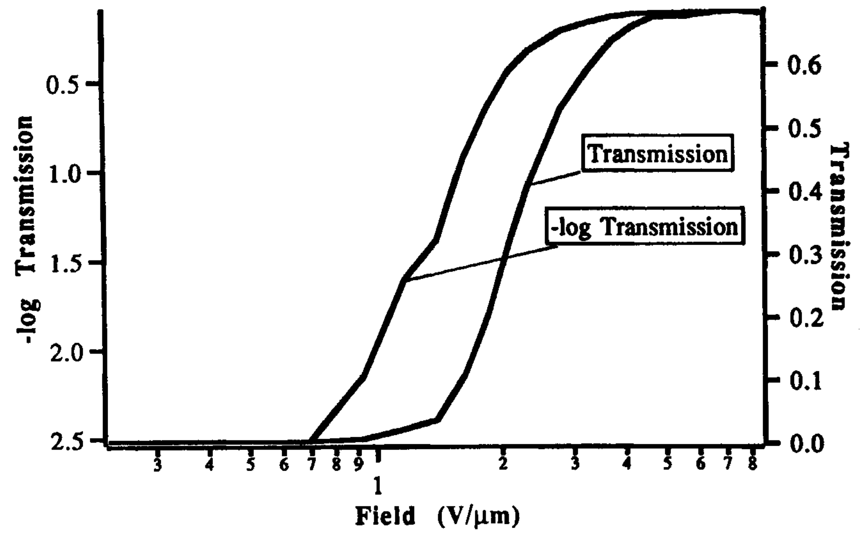

FIGURE 4 Comparison of the specular transmission curve of an NCAP film at $f/16$. The apparent threshold and saturation values for this film will depend on which parameter is plotted.

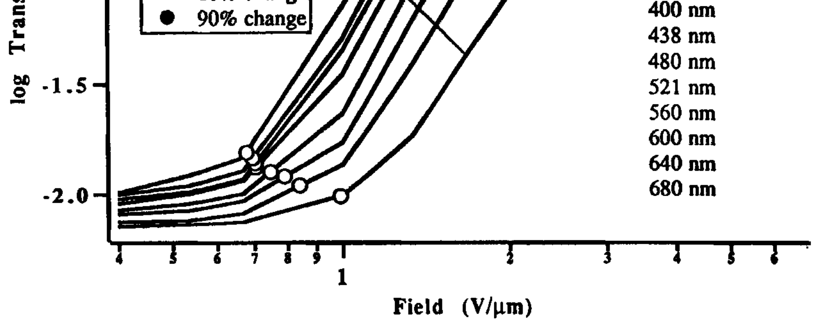

FIGURE 5 Comparison of the specular transmission of and NCAPfilm at $f/16$ as a function of wavelength.

the film. In reporting scattering-based measurements of NCAP films, it is important that the complete measurement conditions, as well as film parameters, be reported.

DIELECTRIC RESPONSE

Film dielectric constant has been used previously to examine nematic droplet NCAP films.[6,7] Semi-empirical mixture formulas, such as Böttcher's formula (6) (and others) have been shown to correlate reasonably well with the low and high-field limits for nematic droplet films.[6] In (6), ε_m refers to the film dielectric constant, ε_1 and ε_2 refer to the matrix and nematic dielectric constants, respectively, and ν refers to the volume fraction of nematic within the film.

$$\varepsilon_m = \varepsilon_1 + \frac{3\,\nu\varepsilon_m\,(\varepsilon_2 - \varepsilon_1)}{2\,\varepsilon_m + \varepsilon_2} \tag{6}$$

In many nematic mixtures, either $\varepsilon_\perp$ or $\varepsilon_\parallel$ may be close to ε_{pol} in value. Under these conditions, nematic droplets at low fields (for $\varepsilon_{pol} = \varepsilon_\perp$) or at high fields (for $\varepsilon_{pol} = \varepsilon_\parallel$) will be dielectrically equivalent to the matrix. In an attempt to simplify the analysis of the dielectric response to nematic reorientation process as much as possible, we make the approximation that each nematic droplet has a dielectric constant equal to either ε_1 or ε_2. The field dependent variables in (6) are then ε_m and ν, where ν now represents the volume fraction of nematic with dielectric constant equal to ε_1.

Nevertheless, even under these rather charitable approximations we still find that the mean dielectric constant of the film ε_m scales as some fractional power of ν. Other semiempirical mixture rules also predict a nonlinear response. Compounding this difficulty, the matrix dielectric constant ε_2 is often uncertain; in many cases the polymer absorbs a significant amount of nematic, and ε_2 is some average of the matrix and liquid crystalline dielectric constants. In general, the field-dependence of ε_m will be a measure of the film response, but it will not be readily related to the microscopic orientation of nematic within the film.

COMPARISON OF DICHROIC, SCATTERING, AND DIELECTRIC MEASUREMENTS

Given the disparate methods available for monitoring the nematic orientation within nematic droplet films, it is of interest to compare the various responses in a well-defined set of films. To this end, we have measured the scattering and dichroic-based transmissions, as well as the effective dielectric constant, of two different films as a function of applied field. As described earlier, dichroic transmission is measured at 410 ± 10 nm (maximum dye absorbance), while scattering-based transmission values were measured at 632.8 nm (with negligible dye absorbance). The two films are the same as those used to generate Figure 2.

Figures 6 and 7 shows the comparisons. In both films it is observed that the

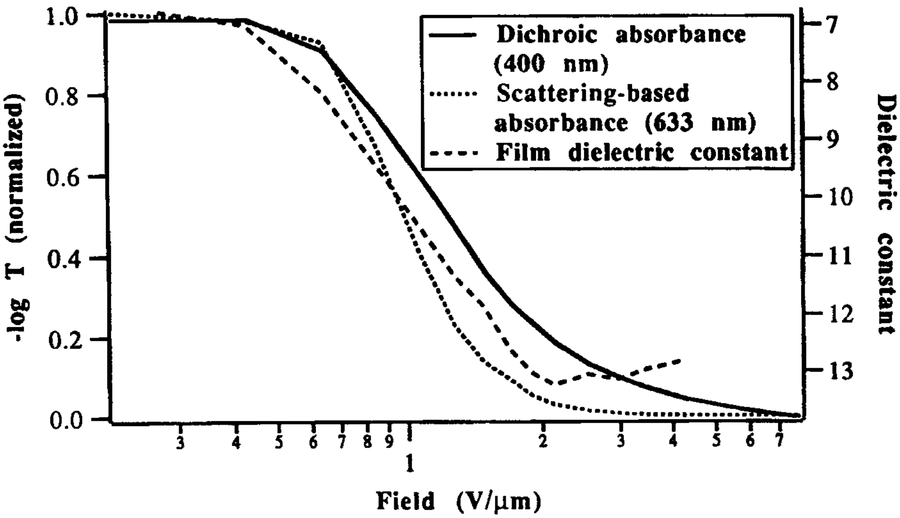

FIGURE 6 Comparison of the dichroic, scattering, and dielectric response functions of an NCAP film (mean volume diameter = 4.3 μm).

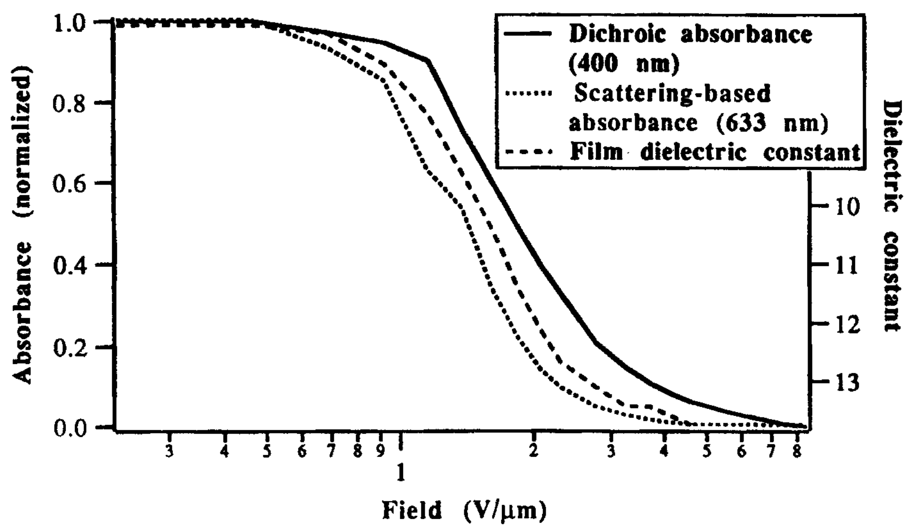

FIGURE 7 Comparison of the dichroic, scattering, and dielectric response functions of an NCAP film (mean volume diameter = 2.3 μm).

threshold responses for the three measurements are similar. It is also seen, however, that the scattering and dielectric response curves reach saturation much more rapidly than the dichroic response. For example, in Figure 7 the scattering and dielectric responses appear to saturate at 4 to 5 V/μm. The dichroic response continues to decrease well past this value, and doesn't reach saturation until at least 8 V/μm.

The most likely explanation for the apparent difference is that the scattering and dielectric properties require less perfect alignment of the nematic within the droplet cavities in order to achieve a saturated response, compared to the dichroic effect. This explanation is consistent with the more rapid falloff of the scattering and dielectric properties in Figures 6 and 7, compared with the dichroic response. The scattering and dielectric film properties are more sensitive to the initial changes in nematic orientation, and less sensitive to the final changes of orientation, compared to the dichroic response. This difference in response curves can be important in devices which rely on both scattering and dichroic effects for their performance.[1]

CONCLUSIONS

In reviewing the scattering, absorbance, and dielectric properties of nematic droplet/polymer films, we find that absorbance measurements of dichroic dye-doped films are the best measure of nematic orientation within the film, as well as the most readily interpreted. Scattering and dielectric-based measurements not only are more complicated in their interpretation, but contain a number of arbitrary elements which makes it more difficult to determine the extent of nematic orientation within the film.

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