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Effect of Accelerators on the Structure, Solar Attenuation Characteristics and Electro-Optic Performance of Polymer-Dispersed Liquid Crystal Films

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Effect of Accelerators on the Structure, Solar Attenuation Characteristics and Electro-Optic Performance of Polymer-Dispersed Liquid Crystal Films

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We have significantly improved the solar attenuation characteristics of ultraviolet-cured polymer-dispersed liquid crystal (PDLC) films by adding chemical accelerators to the materials from which the films are formed. The visual transmittance and response times of the new films are comparable to those of the best ultraviolet-cured films prepared without an accelerator; however, the new films may require higher operating voltages to achieve this performance. In addition, PDLC films prepared with accelerators require approximately 50% less liquid crystal than the best films made without accelerators.

Keywords: polymer dispersed liquid crystals, solar attenuation, light scattering, accelerators, electro-optics, scanning electron microscopy (SEM)

I. INTRODUCTION

Thin films consisting of liquid crystal (LC) microdroplets dispersed in polymer matrices (PDLC films[1–3] and NCAP films[4,5]) are potentially useful for electrically controlled attenuation of solar radiation[6–9] as well as for other electro-optic applications because they can be switched from a light-scattering off-state to a transparent on-state. For optimum performance in solar control applications, these films should backscatter as much of the incoming solar radiation as possible. We recently showed[10] that backscattering of radiation by a polymer-dispersed liquid crystal (PDLC) film at wavelength λ will be maximized when the radius of the LC microdroplets in the film is about $\lambda/7$. We further showed that, since scattering efficiency decreases rapidly with increasing wavelength, backscattering of solar radiation will be determined primarily by backscattering in the visible portion of the solar spectrum. To maximize backscattering at these wavelengths requires droplets with radii near or below 0.1μm. To produce such small droplets requires rapid curing of the PDLC film.[11–13]

In our laboratory we have focused on the development of PDLC films cured by ultraviolet (UV) radiation[14] because radiation curing offers several advantages over

other curing techniques for control of the film fabrication process. For example, by increasing the UV intensity, one can increase the cure rate of a PDLC film, thereby reducing the droplet size. The cure rate of a UV-curable PDLC film can also be increased by including certain chemicals, called (photo)accelerators, in the mixture of polymer precursors from which the film is formed. The use of accelerators to increase the cure rate of thermally cured, epoxy-based PDLC films has been demonstrated previously.[12] In this paper we describe the effects of both increased UV intensity and the addition of accelerators on the performance of UV-cured PDLC films. In particular, we shall demonstrate that addition of accelerators not only can produce PDLC films with significantly improved solar attenuation characteristics and good overall electro-optic performance but also can significantly reduce the amount of liquid crystal needed to form these films.

II. MATERIALS AND FILM FABRICATION

A. Liquid Crystals

In order to determine whether the effects of accelerators were significantly influenced by the LC material in a PDLC film, we made films with ROTN-404 and BL009, two wide-temperature-range LC mixtures which differed considerably in their chemical composition: ROTN-404 is a mixture of cyanobiphenyl and pyrimidine derivatives[15] while BL009 contains cyanobiphenyls[16] but no pyrimidines.

B. Polymer Matrix Materials

P6008-Based Systems. In most of the films we studied, the matrix materials were based on a precursor mixture designated P6008. It contains the diurethane diacrylate Photomer 6008,[17] pentaerythritol tetraacrylate,[18] and pentaerythritol tetrakis-(3-mercaptopropionate).[19] In P6008-based films without accelerator the polymer matrix, designated P6008B, was formed by adding the photoinitiator Darocure 1173[16] to the P6008 mixture.

We also made PDLC films from precursor mixtures containing P6008, Darocure 1173, and the three accelerators N-methyldiethanolamine (MDEA),[20] N,N-dimethylaminoethanol (DMEA)[20] and triethanolamine (TEA).[20] The mixtures containing MDEA, DMEA and TEA are denoted P6008A1, P6008A2 and P6008A3, respectively.

NOA65-Based Systems. A few of our samples utilized the commercially available optical adhesive NOA65[21] as the basis for the polymer matrix. This material is a thiolene system with a benzophenone photoinitiator. To some of these films we added a few % by volume of the photoaccelerator ethyl-4-dimethylaminobenzoate (EPA)[22] to form the mixture designated NOA65A.

The compositions of the samples discussed in this paper are given in Tables I and II, together with their solar attenuation characteristics which will be discussed in Section III.B.

TABLE I

Comparison of ROTN-404-based PDLC samples with and without accelerator

Sample Number	Precursor Mixture	LC:Precursor Volume Ratio β	UV Cure Intensity	% Solar Transmittance	% Solar Reflectance
		Samples made without accelerator			
4893	P6008B	1.1	Low	59.7	17.0
4894	P6008B	1.1	Low	57.7	17.6
4896	P6008B	1.22	Low	48.1	18.8
4897	P6008B	1.46	Low	64.4	16.0
4898	P6008B	1.46	Low	65.4	15.9
4899	P6008B	1.70	Low	63.3	16.4
4900	P6008B	1.70	Low	63.8	16.4
4901	P6008B	2	Low	66.0	16.4
4902	P6008B	2	Low	65.5	15.2
5395	P6008B	1.1	High	49.5	17.0
5396	P6008B	1.1	High	52.8	16.9
5397	P6008B	1.22	High	42.6	22.1
5398	P6008B	1.22	High	44.8	20.3
5399	P6008B	1.46	High	48.0	18.7
5400	P6008B	1.46	High	43.4	19.9
5401	P6008B	1.71	High	62.3	14.8
5402	P6008B	1.71	High	57.0	15.5
		Samples made with accelerator MDEA			
5367	P6008A1	0.71	High	46.5	18.0
5368	P6008A1	0.59	High	35.4	27.1
5370	P6008A1	0.47	High	39.2	22.6

Note: A bold face sample number indicates the sample with the best solar attenuation characteristics in each group.

C. Sample Preparation Prior to UV Cure

All films were prepared by mixing the LC and polymer precursor together and squeezing a small quantity of this mixture between two indium-tin-oxide-coated glass substrates. Spacers were used in all films to control film thickness; in most films, the diameter of the spacers was 20 μm; in a few cases, however, 17.5 μm spacers were used. Nevertheless, scanning electron microscopy (Section III.A) has revealed that the thicknesses of the cured films were sometimes considerably larger than the spacer diameter and, in some samples, nonuniform. Effects of film thickness variation on electro-optic performance will be discussed in Section III.B.

Calorimetric studies combined with scanning electron microscopy (SEM) have shown that accelerators can greatly increase the cure rate of the polymer matrix in a thermally cured PDLC film, resulting in smaller droplets.[12] However, in a

TABLE II

Comparison of BL009-based PDLC samples with and without accelerator

Sample Number	Precursor Mixture	LC:Precursor Volume Ratio β	Accelerator	% Solar Transmittance	% Solar Reflectance
		Samples made without accelerator			
5387	P6008B	1		58.0	15.4
5389	P6008B	1.5		48.6	20.4
5392	P6008B	2		52.8	19.6
5520	NOA65	2		46.9	24.0
		Samples made with accelerators			
5374	P6008A1	0.59	MDEA	36.2	26.6
5375	P6008A1	0.59	MDEA	37.5	24.6
5383	NOA65A	2	EPA	50.4	16.9
5516	P6008A2	0.59	DMEA	57.7	18.2
5517	P6008A2	0.59	DMEA	59.6	17.1
5518	P6008A3	0.59	TEA	57.1	18.7
5519	P6008A3	0.59	TEA	55.6	18.6

Note: A bold face sample number indicates the sample with the best solar attenuation characteristics in each group.

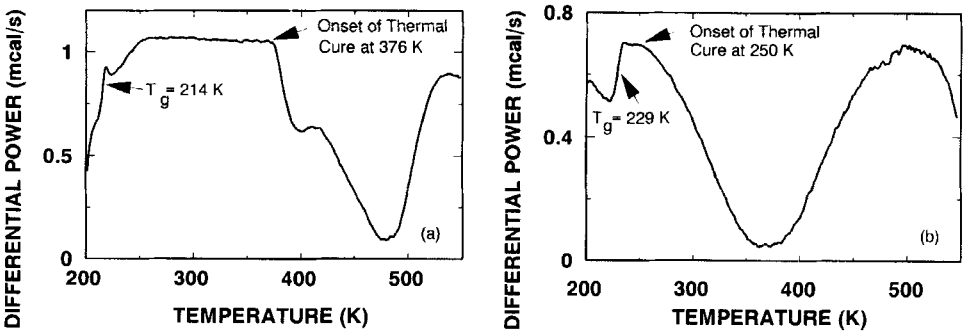

FIGURE 1 (a) DSC thermal scan of an initially uncured polymer precursor, P6008, with no accelerator or photoinitiator. The large exothermic peak commencing near 376 K is due to thermal cure of the photomer. The change in baseline near 214 K is associated with the glass transition of the uncured photomer. (b) DSC scan of initially uncured P6008 containing 1% accelerator (by volume) and no photoinitiator. The accelerator has reduced the onset of cure to about 250 K, well below room temperature. The apparent glass transition temperature (229 K) is high since the sample had partially cured during preparation.

UV-cured system, their use can have an unwanted side effect. Using differential scanning calorimetry (DSC), we have found that addition of an accelerator reduces the onset temperature for thermally-induced cure of P6008 to below room temperature. This is illustrated in Figure 1 which shows DSC thermal scans of initially uncured P6008 without accelerator (Figure 1a) and with 1% by volume of an

accelerator (Figure 1b); the onset of cure is shifted from 376 K to 250 K when the accelerator is added. Therefore, when using accelerators in this UV-curable system, it is necessary to mix the polymer precursors together at as low a temperature as possible. Furthermore, since our samples are typically cured at 40°C or higher, it is necessary to initiate UV cure as soon as possible after preparing the precursor mixture in order to avoid microstructural variations due to inhomogeneous thermal curing. Thermally induced cure may be one reason why we have found it more difficult to control thickness precisely in UV-cured PDLC films prepared with accelerators than in films prepared without an accelerator.

Despite inhomogeneities and thickness variation resulting from incomplete control of some aspects of the cure process in some of our samples, comparison of the microstructure and electro-optic behavior of groups of samples prepared with and without accelerators has revealed important differences between these two classes of samples. In this paper we present our data in a way that best illustrates the major effects associated with the use of accelerators to increase the rate of UV cure.

D. UV Curing Procedures

Films containing ROTN-404 were prepared by several different UV-curing procedures. Some films in Table I were cured with a Fusion Model Super Six[23] UV-curing apparatus which used a six inch lamp with an output intensity of about 200 W/in. The lamp was positioned to irradiate a large area in the sample plane and the sample was positioned at the center of this irradiated area. Typically, samples were irradiated for about 45 s to cure them with this system. The total UV energy reaching unit area of the sample during this period was measured with an International Light IL700A Radiometer equipped with a "UV Light Bug" detector.[24] During the curing period, the average irradiance at the sample, after passing through one sheet of indium-tin-oxide-coated glass, was[25] about 80 mW/cm^2. In column 4 of Table I we characterize this UV intensity as "Low." Films cured with the Super Six system contained no accelerator.

The remaining samples described in Table I were cured with a Fusion Systems Model F460[23] UV-curing apparatus utilizing a ten inch lamp with an output intensity of about 375 W/in. This output was focused to a broad "line" about 5 mm wide and 10 cm long in the sample plane and the samples passed under this "line" on a conveyor belt moving at 4.4 cm/s. Measurements with the "UV Light Bug" indicated that, during the cure, about 1.7 J passed through the glass substrate to each cm^2 of the sample. We found that about half the UV energy of the lamp was contained within the focused "line" and the rest was spread over a distance of about 15 cm measured along the axis of the moving belt. With this system, the average irradiance reaching the sample during the cure[25] was about 500 mW/cm^2. In column 4 of Table I we characterize this UV intensity as "High." Some films cured with the F460 system were prepared without an accelerator while others were prepared with MDEA, as noted in the table.

All films containing BL009 were prepared with the Fusion F460 system described above. Their properties are summarized in Table II. Films in the first group in the

table were prepared without an accelerator; those in the second group were prepared with accelerators.

III. RESULTS

A. Structural and Thermal Characteristics

Film Microstructure. In order to understand more fully the effects of accelerators on the electro-optic performance of PDLC films, we have examined the microstructure of films prepared with and without accelerators by means of scanning electron microscopy (SEM). Figure 2 shows photomicrographs of cross sections through PDLC samples cut from films 5387 and 5392, which were prepared without an accelerator. Figure 3 shows SEM photomicrographs of films 5367, 5368, 5370 and 5374, which were prepared with the accelerator MDEA. Each photomicrograph reveals a distribution of roughly circular cross sections through the droplets of the PDLC film. From the distribution of the radii of these circular cross sections (two-dimensional or areal distribution of radii) one can obtain the distribution of the radii of the three dimensional microdroplets in the film[26-27] (three-dimensional or volume distribution). Figures 4a-4b show the results of such an analysis for the samples of Figure 2, which were prepared without an accelerator; Figures 4c and 4d show similar results for two of the samples of Figure 3, which were prepared with MDEA. In each figure the unshaded histogram shows the distribution of radii

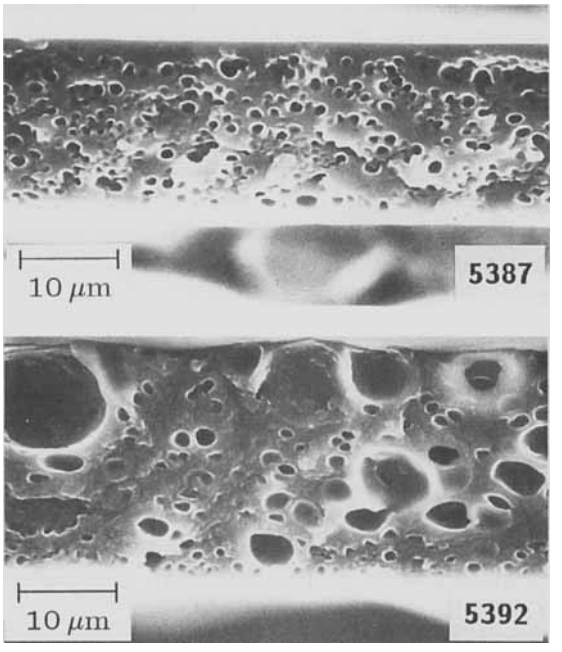

FIGURE 2 Photomicrographs of cross sections through PDLC films prepared without accelerators.

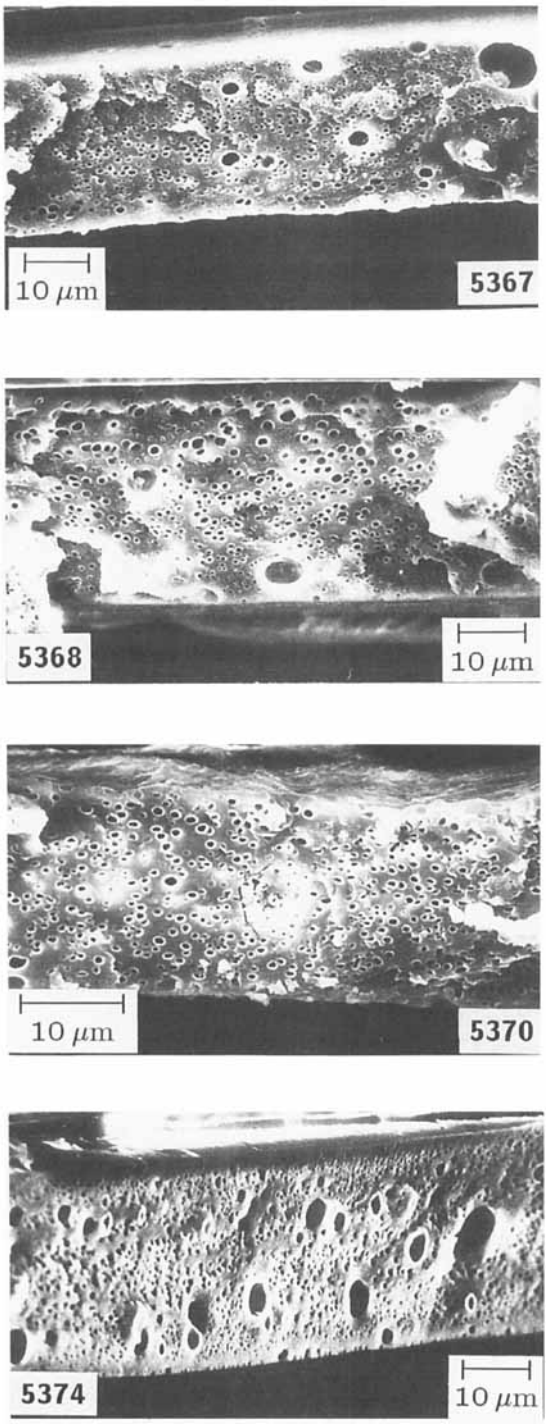

FIGURE 3 Photomicrographs of cross sections through PDLC films prepared with accelerators.

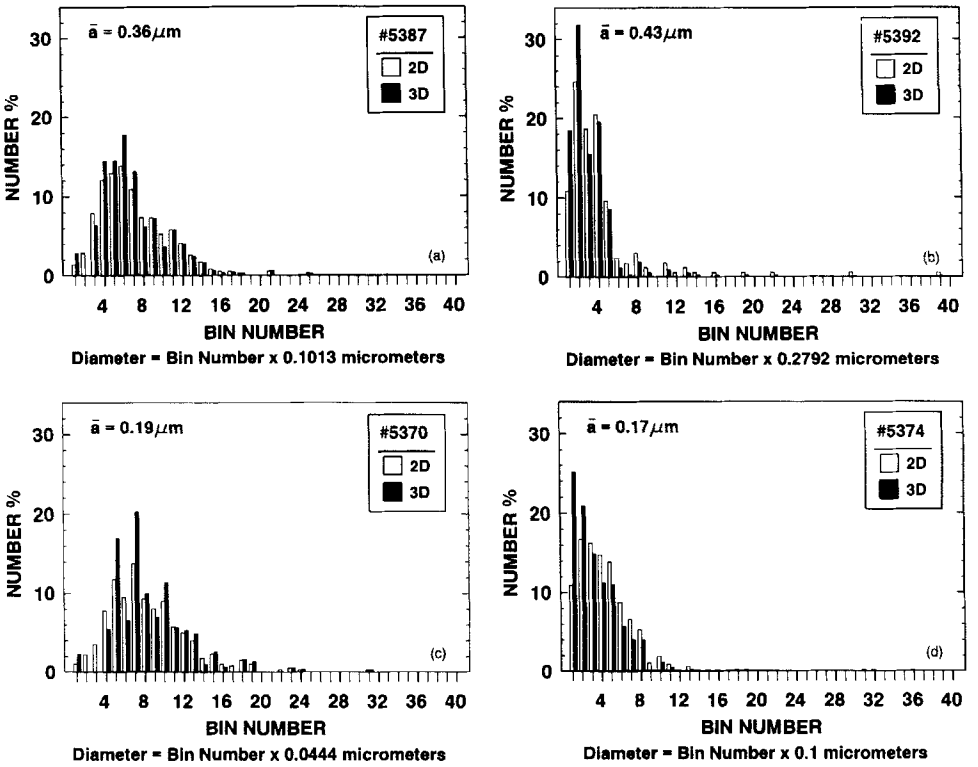

FIGURE 4 Two and three dimensional number distributions of LC microdroplets in PDLC films from analysis of SEM photomicrographs. Films 5387 (a) and 5392 (b) were prepared without accelerators; films 5370 (c) and 5374 (d) were prepared with accelerators.

of the circular cross sections on the photomicrograph and the shaded histogram shows the distribution of the radii of the actual, three-dimensional microdroplets in the film. These figures demonstrate that introduction of accelerators to increase the cure rate does reduce droplet size, as expected. The thickness of each film can also be determined from its SEM photomicrograph.

Table III summarizes PDLC film characteristics obtained from analysis of the photomicrographs in Figures 2 and 3. The average droplet radius $\bar{a}$ (column 4 of the table) is defined by:

$$\bar{a} = \frac{\Sigma_i N_i \cdot a_i}{\Sigma_i N_i} \tag{1}$$

where N_i is the number of droplets per unit volume having radius a_i. Radii a_{10}, a_{50} and a_{90} are defined so that 10% of the total volume occupied by the droplets in the film is contained in droplets with radii below a_{10}, 50% of the volume is in droplets with radii below a_{50}, and 90% of the volume is in droplets with radii below a_{90}. The spread parameter S is used to characterize the distribution as monodisperse ($S < 2/3$) or polydisperse ($S \geq 2/3$).[25] The ninth column in the table shows the

TABLE III

Microstructural properties of selected PDLC films

Sample Number	LC:Precursor Ratio β	Thickness (μm)	Droplet Radii (μm) $\bar{a}$	a_{10}	a_{50}	a_{90}	Spread Parameter S	LC Droplet Volume Fraction η	η/β
Samples made without accelerator									
5387	1.00	19.0	0.36	0.30	0.56	0.88	0.50	0.15	0.15
5392	2.00	24.0	0.43	0.54	2.62	5.42	0.82	0.27	0.14
Samples made with accelerator MDEA									
5367	0.79	26.5	0.15	0.17	0.31	1.21	0.75	0.18	0.25
5368	0.59	32.8	0.16	0.23	0.49	0.71	0.46	0.17	0.29
5370	0.59	20.0	0.19	0.15	0.27	0.50	0.53	0.11	0.23
5374	0.47	28.6	0.17	0.21	0.45	1.78	0.79	0.25	0.42
5375	0.59	36.0	0.32	0.23	0.33	0.46	0.34	0.17	0.29

droplet volume fraction η, i.e., the fraction of the total film volume occupied by LC microdroplets. This parameter is important for determining the light scattering behavior of a PDLC film: in general, both forward scattering and backscattering will increase with increasing volume fraction, at least for volume fractions below 0.5.

We can also determine droplet volume fractions from calorimetric measurements[12] of α, the fraction of the initial LC which is confined to microdroplets in the final PDLC film. The volume fractions derived from DSC measurements are generally larger than those obtained from SEM analysis. This is reasonable. SEM is likely to underestimate the volume fraction by overlooking some (small) droplets. DSC is likely to give an overestimate since it responds to any "free" LC, whether it is contained in droplets or present as puddles or surface layers.

Several important points are illustrated by the data of Table III.

1. The ratio of the volume fraction η to the LC:Precursor volume ratio β is much larger in the films prepared with the accelerator MDEA than in the films prepared without an accelerator. This indicates that, for a given polymer precursor volume, a higher droplet volume fraction is produced in the cured film per unit initial volume of LC when the film is prepared with an accelerator.
2. Samples containing accelerators can be either monodisperse or polydisperse. Even in the polydisperse samples, however, the droplets tend to be smaller than in the samples without accelerator. This result is consistent with our expectation that addition of accelerators to increase the cure rate would produce PDLC films with smaller droplets.
3. The volume fractions occupied by the droplets in the monodisperse films are lower than those in the polydisperse films and lower than those typically observed in films containing larger droplets. Examination of the volume distribution of the polydisperse sample containing MDEA indicates that this film

contains a few large droplets whose volume is a significant fraction of the total droplet volume.

4. Although all the samples containing MDEA were formed using 20 μm diameter spacers, film thicknesses determined from the SEM photomicrographs vary from film to film. This result was mentioned earlier in connection with sample preparation and will be discussed further in Section III.B in connection with its effect on electro-optic performance.

Degree of Cure. Calorimetric studies of several UV-cured PDLCs containing accelerators have revealed that some films were incompletely cured by the F460 conveyor belt system, which uses a relatively high belt speed to avoid overheating the sample and increasing the cure temperature. DSC scans showed behavior similar to that previously observed for incompletely cured PDLC films prepared using electron-beam curing.[27] The initial DSC spectrum of a P6008-based PDLC (Figure 5a) shows an incipient exotherm (due to additional curing) above 370 K. In a subsequent scan (Figure 5b), the exotherm is missing, indicating that the sample is now more completely cured. Further evidence for incomplete cure is the fact that small amounts of LC would diffuse from the PDLCs. The samples studied by calorimetry contained LC mixture ROTN-403, which is similar, although not identical in composition to ROTN-404; consequently, at least the ROTN-404-based films described in this report are expected to show similar effects and the BL009-based films may show them as well. Obviously, it is important to guard against incomplete cure in preparing PDLC films using accelerator-assisted UV cure. In

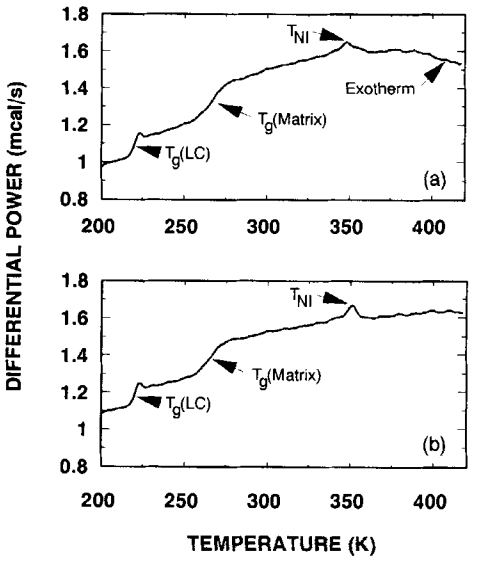

FIGURE 5 (a) DSC thermal spectrum of a P6008-based PDLC sample after preparation in the F460 conveyor system. Three transition temperatures are indicated: $T_g(LC)$, the glass transition of the LC in the microdroplets; $T_g(Matrix)$, the glass transition of the polymer matrix; and T_{NI}, the nematic-isotropic transition temperature. The presence of an exotherm above about 370 K indicates that the sample is incompletely cured. (b) DSC spectrum for the same sample as in (a) after heating to above 400 K. The sample is now more fully cured, as indicated by the absence of the exotherm.

films cured to differing degrees, different amounts of LC may remain dissolved in the polymer matrix; this will produce films with different matrix refractive indices and, hence, different light-scattering characteristics. (Effects of matrix refractive index are discussed in Section IV.)

B. Electro-Optic Performance

Solar Attenuation Characteristics. The hemispherical transmittance and reflectance of each sample were measured as a function of wavelength from 200 nm to 2500 nm using a Perkin-Elmer λ-9 spectrophotometer equipped with an integrating sphere. Illustrative spectra of samples without accelerator (5389) and with accelerator (5370) are shown in Figures 6a and 6b, respectively. The spectral transmittance and reflectance data were weighted with the air-mass-two (AM2) spectral distribution of solar irradiance at the earth's surface and integrated to obtain the

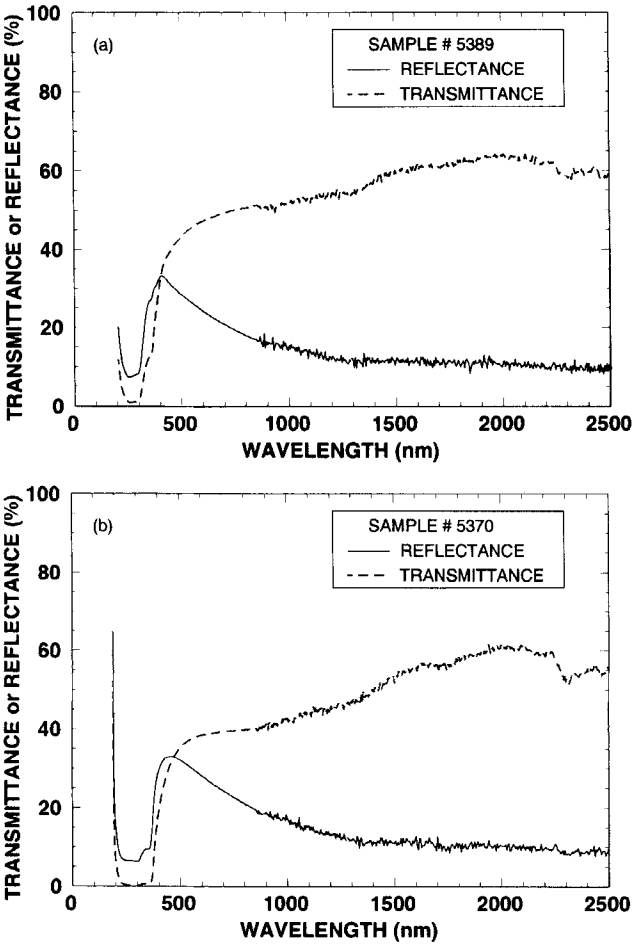

FIGURE 6 Representative hemispherical transmittance and reflective spectra of PDLC films: (a) Film prepared without accelerator (5389); (b) Film prepared with accelerator MDEA (5370).

fraction of the incoming solar energy which would be transmitted or reflected by each film. The resulting solar transmittances and reflectances are shown in Tables I and II for films containing ROTN-404 and BL009, respectively.

Comparison of the solar transmittance and reflectance data for the ROTN-404-based films made without accelerator but cured with different UV intensities (Table I) shows several interesting results.

1. For a given film composition, the solar attenuation characteristics appear to be more reproducible from film to film when the films are cured at the lower intensity than when they are cured at high intensity.
2. Increasing the UV irradiance during cure generally improves the solar attenuation characteristics. If we compare the solar transmittance of each film in the second group with the average transmittance of the films in the first group having the same composition, we find that the average reduction in solar transmittance achieved by curing at the higher intensity is 14.4%. However, the reduction in transmittance varies from 2% to 33.1% depending on the film composition. Similarly, the average increase in solar reflectance due to increased UV cure intensity is 6.0% but the reflectance may increase or decrease depending on composition.
3. Regardless of the cure intensity, the best solar attenuation characteristics were obtained when the LC:Precursor ratio in the starting mixture was 1.22. For this composition, increasing the cure intensity reduced the solar transmittance by about 11% and increased the solar reflectance by about 18% (compare samples 5397 and 4896).

Comparison of the ROTN-404-based films made with and without the accelerator MDEA (Table I) shows that addition of MDEA to the polymer precursor mixture significantly improves the solar attenuation characteristics of P6008-based PDLC films. In particular:

1. The solar transmittance decreases and the solar reflectance increases when MDEA is added.
2. The improved performance in samples containing MDEA is achieved with significantly lower initial liquid crystal concentrations than those required to give the best solar attenuation in films prepared without an accelerator. For example, the concentration of liquid crystal in sample 5368, which contains MDEA, is 50% lower than in sample 5397, which has the best performance of cells without accelerator; yet sample 5368 has a 17% lower solar transmittance and a 23% higher solar reflectance than sample 5397. In all cases where MDEA has been added, we have observed substantial improvement in performance with reduced liquid crystal concentrations. This improvement may be due, at least in part, to the more efficient use of LC, i.e., higher values of η/β, in the samples prepared with MDEA.
3. No further improvement in performance could be obtained by varying either film composition or UV intensity. Increasing or decreasing the ROTN-404:Precursor ratio above or below the ranges shown in Table I reduced solar attenuation by the resulting films. It is possible, however, that UV intensities

higher than the maximum available in our systems might produce additional improvement or permit use of still lower liquid crystal concentrations.

Table II shows the characteristics and performance of PDLC films made with the LC mixture BL009. Samples in the first group in the table were prepared without an accelerator; those in the second group were prepared with various accelerators. Samples 5374 and 5375, which contained MDEA, had substantially lower solar transmittance and substantially higher solar reflectance than the P6008-based films 5387, 5389 and 5392 which contained no accelerator. Moreover, the samples with MDEA used 60% less liquid crystal than sample 5389, which had the best solar attenuation characteristics of the samples without accelerator. As in the case of the films containing ROTN-404, no improvement in performance could be achieved by increasing the BL009:Precursor ratio beyond the ranges given in Table II.

Use of the accelerators DMEA (samples 5516 and 5517) and TEA (samples 5518 and 5519) did not improve the solar attenuation characteristics of P6008-based films. However, as discussed below, these accelerators did improve other electro-optic characteristics while substantially reducing the amount of liquid crystal in the films. Similarly, addition of the accelerator EPA to NOA65 to form the matrix material NOA65A did not improve the solar attenuation properties (compare films 5383 and 5520); however, we have generally used NOA65A to enhance other aspects of electro-optic performance[25] and more work needs to be done with different LC concentrations to determine fully the effect of the accelerator EPA on solar performance.

Transmittance vs. Voltage. For many of our samples we measured transmittance at 543.5 nm as a function of applied voltage using a collimated, spatially filtered HeNe laser beam.[13] The detection system in these measurements collected only light propagating within a cone of 2° half angle about the direction of the incident laser beam.

Figures 7a–7e show transmittance vs. voltage curves for several samples to illustrate effects of different accelerators on the electro-optic performance of PDLC films. Figures 7a and 7b show the effect of adding MDEA to a P6008-based PDLC film containing the LC mixture BL009. In each figure, the diamonds and triangles denote data taken with increasing and decreasing voltage, respectively. The solid (dashed) curves are least squares cubic spline fits to the data for increasing (decreasing) voltage. In all cases, the hysteresis (i.e., the difference between curves for increasing and decreasing voltage) is small.

The transmittance of sample 5389, which contained no accelerator, begins to rise at about 25 V_{rms} (Figure 7a). By about 85 V_{rms}, it has reached 90% of its 140 V_{rms} value but it never fully saturates at high voltage. The transmittance of sample 5374, which contains MDEA, does not deviate noticeably from zero until the applied voltage reaches about 50 V_{rms} (Figure 7b). It continues to rise rapidly with increasing voltage, even for voltages as large as 140 V_{rms}. These differences in the transmittance vs. voltage characteristics are probably to the increased film thickness and smaller droplets in sample 5374. (Although we have not studied sample 5389 by SEM, its composition lies between those of samples 5387 and 5392 (Table II)

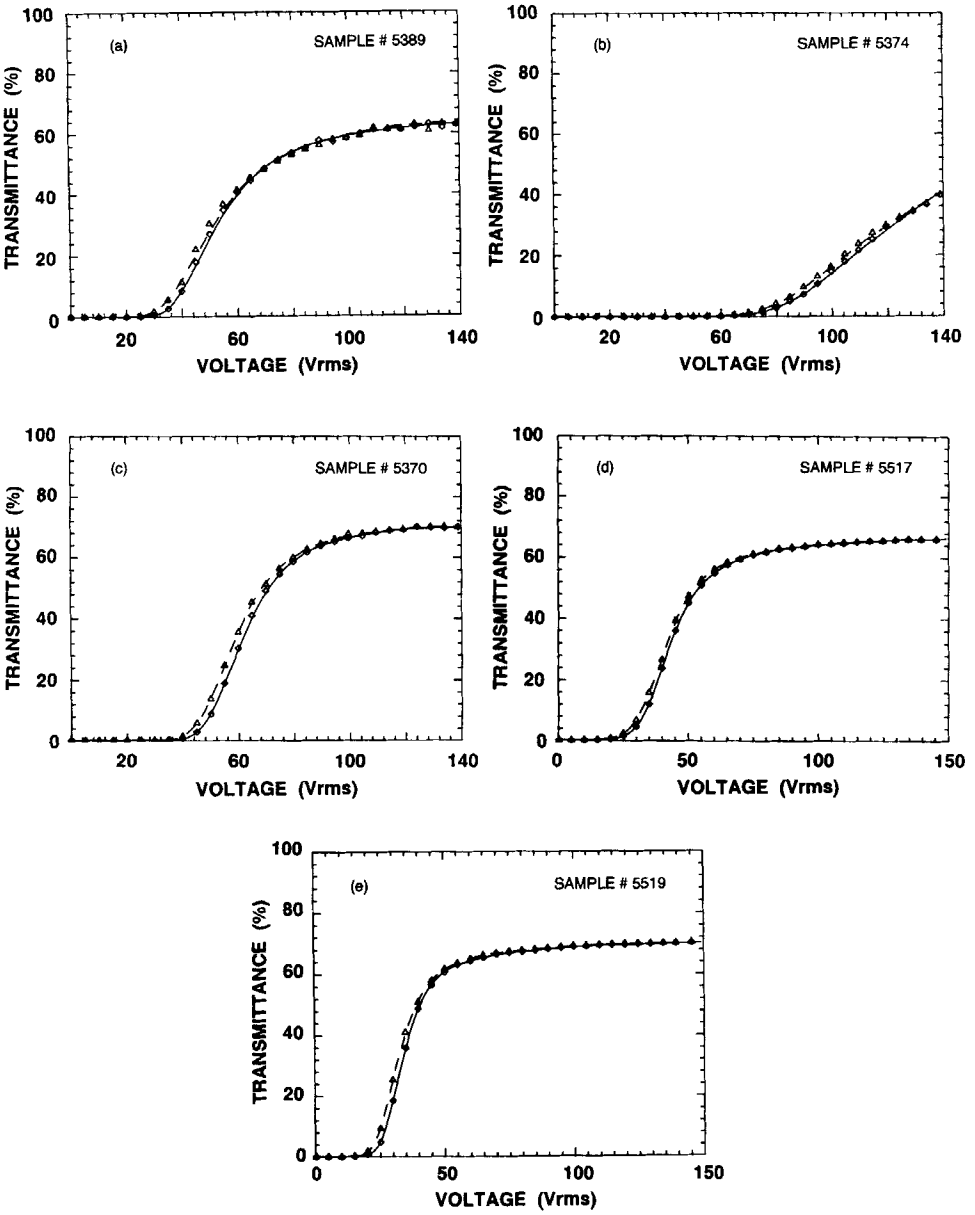

FIGURE 7 Transmittance vs. voltage curves for PDLC samples: Sample 5389 (a) was prepared without accelerator; samples 5374 (b) and 5370 (c) were prepared with MDEA; sample 5517 (d) was prepared with DMEA; and sample 5519 (e) was prepared with TEA.

and it was prepared under otherwise identical conditions; therefore, we might expect its droplet size distribution and, perhaps, its thickness, to lie between those of samples 5387 and 5392.)

Comparison of these results with the transmittance vs. voltage curves of sample

5370 (Figure 7c), which also contained MDEA but a different liquid crystal (ROTN-404) in slightly lower concentration, demonstrates that changes in LC can substantially affect the electro-optic performance of PDLC films containing accelerators. In sample 5370 the threshold voltage, at which the transmittance becomes noticeably non-zero, lies between those of samples 5389 and 5374; however, the transmittance of sample 5370 rises much more rapidly and reaches a higher maximum value than in either sample 5374 or 5389.

Finally, in Figures 7d and 7e, we show the transmittance vs. voltage curves of two additional P6008-based samples containing LC mixture BL009. Sample 5517 contained the accelerator DMEA while sample 5519 contained TEA. These samples have the lowest threshold voltages, the lowest operating voltages, and the highest transmittances of any samples in this study. Furthermore, these samples also used much less LC than samples prepared without accelerator. Since the LC material is one of the most expensive components of PDLC films at the present time, films containing DMEA and TEA probably merit further study even though, as noted earlier, their solar attenuation characteristics were not enhanced by use of these accelerators.

Response Times. We measured response times of the films containing BL009 with and without accelerators and of films containing ROTN-404 with accelerators by monitoring the change in film transmittance as a 4kHz driving voltage was gated on and off.[13] The excitation voltage was 140 V_{rms} in all samples except 5517 and 5519, which were driven at 150 V_{rms}. Results of these measurements are summarized in Table IV.

Inspection of the data of Table IV shows that the rise times of films 5374 and 5375 (44.9 ms and 53.3 ms, respectively), are considerably longer than those of the other films. Of all the films containing BL009, the transmittance vs. voltage

TABLE IV

Response times of selected PDLC films

Sample Number	Liquid Crystal	Accelerator	Rise Time (ms)	Decay Time (ms)
		Films made without accelerator		
5389	BL009		2.9	3.9
5392	BL009		2.3	2.4
		Films made with accelerators		
5367	ROTN-404	MDEA	2.6	12.8
5368	ROTN-404	MDEA	11.6	5.9
5370	ROTN-404	MDEA	6.9	20.2
5374	BL009	MDEA	44.9	7.0
5375	BL009	MDEA	53.3	7.6
5517	BL009	DMEA	2.6	20.6
5519	BL009	TEA	2.5	23.5

curves for these two samples (see Figure 7b for sample 5374) show the lowest but most rapidly rising transmittances at 140 V_{rms}, indicating that electric-field-induced molecular reorientation is less complete in these films than in the other samples. Incomplete reorientation is consistent not only with the long rise times but also with the fact that the decay times are much shorter than the rise times in these systems. We have observed previously [8,9,13] that, when the molecular reorientation within the droplets of a PDLC film is incomplete, the film generally relaxes rapidly to its offstate. (In view of these remarks, the behavior of film 5392 is anomalous. Its transmittance vs. voltage curves are similar to those of Figure 7b, yet its rise time, 2.3 ms, is very short.) We believe that the incomplete molecular reorientation and increased rise times of films 5374 and 5375 are probably caused, at least in part, by their larger film thickness compared with the other BL009-based films (Table III).

Despite the anomalies discussed above, Table IV shows that the response times of films made with and without accelerators are similar. They are also similar to response times we have measured in other P6008- and NOA65-based films containing ROTN-404 and BL009.[13]

Spectral Transmittance. To evaluate the effect of accelerators on film performance in applications in which switching of visible transmittance is important, we measured the transmittance of our samples in both the on- and off-states as a function of wavelength from 200 nm to 900 nm using a Perkin-Elmer λ-5 spectrophotometer. Representative results are shown in Figure 8 for the same samples whose transmittance vs. voltage characteristics were discussed previously. The on-state transmittance data of Figure 8 agree well with the laser transmittance data of Figure 7; since the spectrophotometer detection system has a larger collection solid angle than the laser system, transmittances measured with the spectrophotometer are slightly larger in both the on- and the off-states.

At wavelengths in the red portion of the visible spectrum above 600 nm, the off-state transmittances illustrated in Figure 8 are higher in the films containing accelerators than in those without accelerators. We found increased off-state transmittance at these long wavelengths in the other films containing accelerators (samples 5367, 5368 and 5375) as well. If we assume, as discussed earlier, that the droplet size distribution in film 5389 lies between those of 5387 and 5392 (see Table III), we can attribute the increased off-state transmittances of the films containing accelerators to the fact that they contain smaller droplets than film 5389. The transmittance characteristics of sample 5387 (not shown) are similar to those of sample 5389 and are consistent with this explanation. Film 5392, which has large microdroplets (Table III), has high off-state transmittance at long wavelength; this result, while not understood, is at least consistent with the unexpected transmittance vs. voltage characteristics of this film.

In practical applications requiring good broadband visible performance, the undesirable increase in off-state transmittance in the red portion of the visible spectrum is largely offset by the low sensitivity of the human eye to red light.[28] If the high driving voltages needed for the films containing MDEA are acceptable, these films should be adequate for visual applications as well as for applications requiring their superior solar attenuation characteristics.

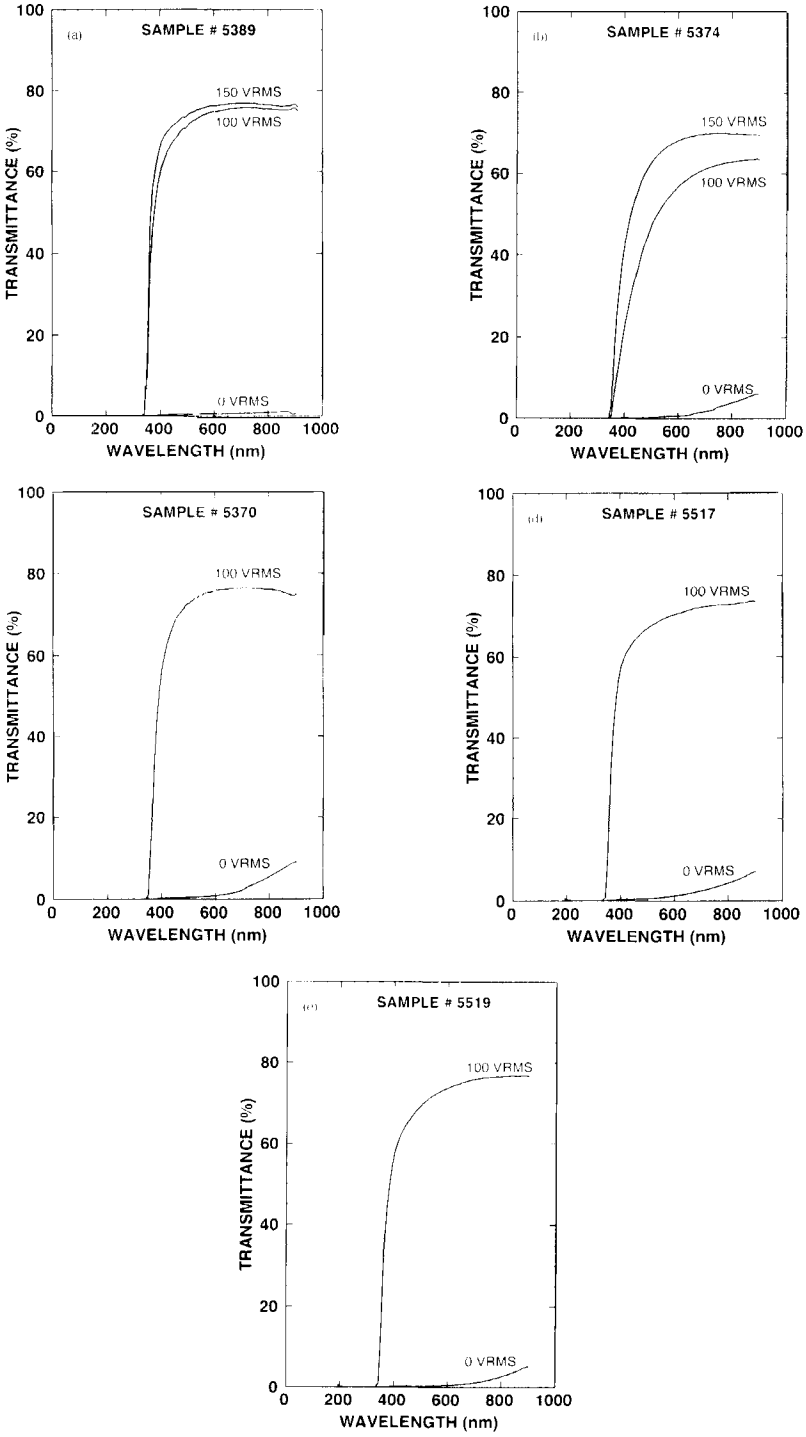

FIGURE 8 Spectral transmittance of the PDLC films of Figure 7 in their on- and off-states.

IV. DISCUSSION

In this study we have demonstrated that the solar attenuation characteristics of PDLC films can be significantly improved by adding a small amount of the proper accelerator to the polymer precursor mixture prior to curing the film by UV irradiation. This improved performance is obtained using only about half the LC needed to give the best solar attenuation in the absence of any accelerators. For example, when the accelerator MDEA was used with the polymer precursor mixture P6008, solar transmittances between 35 and 45% and solar reflectances above 20% were frequently achieved, compared with the 40–55% transmittance and 15–20% reflectance typically measured in P6008-based films made without accelerators. These results were obtained using two different LC mixtures, ROTN-404 and BL009, indicating that the beneficial effects of accelerators can be achieved with LC materials which differ significantly in their chemical composition. In the films containing ROTN-404, the increased performance was achieved while the LC:Precursor volume ratio in the mixture from which the films were formed was reduced from 1.22 to 0.59. In films containing BL009, the LC:Precursor ratio was reduced from 1.5 to 0.59.

In view of our previous studies[10] of droplet size effects in light scattering, it is tempting to attribute the improved solar attenuation characteristics of the films containing MDEA to the small droplet sizes in these films. The small size is undoubtedly an important factor; however, other film parameters such as film thickness and the volume fraction occupied by the droplets in the cured film will also influence PDLC solar attenuation characteristics. In the films made with MDEA, these parameters vary from film to film because we have not yet achieved complete control over all aspects of film fabrication when accelerators are used in conjunction with UV cure. Because of these variations, unambiguous correlation of improved solar attenuation with reduced droplet size has not yet been possible.

Control of film thickness in PDLC films containing accelerators is necessary if these films are to be produced on a large scale for practical applications. It is also important if we are to separate effects of film thickness from other parameters affecting film performance. We have learned that controlling the temperature of the precursor mixture prior to cure is one important aspect of thickness control; other factors still need to be identified.

Solar attenuation by a PDLC film will depend not only on droplet size, film thickness and the volume fraction occupied by the LC droplets in the film but also on the relative refractive indices of the LC droplets and the surrounding polymer matrix. The matrix refractive index depends on the volume of LC from the starting mixture which remains dissolved in the matrix instead of phase-separating into droplets. We let v_{LC}^{matrix} denote the volume of this residual dissolved LC and $v_{precursor}$ denote the initial volume of the polymer precursors in the starting mixture. We neglect any change in the precursor volume during polymerization. Then, the matrix volume in the cured PDLC film is just $v_{precursor} + v_{LC}^{matrix}$ and it is easy to show that γ, the volume fraction of dissolved liquid crystal in the cured matrix, is given by

$$\gamma \equiv \frac{v_{LC}^{matrix}}{v_{LC}^{matrix} + v_{precursor}} = \frac{\beta - \eta(1+\beta)}{(1-\eta)(1+\beta)} \tag{2}$$

where β is the LC:Precursor volume ratio and η is the volume fraction occupied by the LC droplets in the cured PDLC film. For purposes of discussion, we assume that the refractive index of the LC in the droplets is approximately equal to the refractive index of the LC in its isotropic phase, which we denote by n_{LC}. If n_p is the refractive index of the cured polymer matrix material in the absence of any LC, the refractive index of the matrix in the PDLC film can be approximated by

$$n_{matrix} \approx \gamma \cdot n_{LC} + (1 - \gamma) \cdot n_p \tag{3}$$

Using the LC:Precursor ratios of Tables I and II and the volume fractions of Table III, we have estimated n_{matrix} for some of the films in our study using Equation 3. In our calculations we used $n_p = 1.52$ and $n_{LC} = 1.58$; these are representative values for the materials commonly found in PDLC films. The results of the computations are summarized in Table V.

The scattering cross section of a LC droplet is proportional to $|m - 1|^2$, where $m = n_{LC}/n_{matrix}$. We give values for m and for $|m - 1|^2$ in the last two columns of Table V. We find that all the films containing MDEA have lower values of γ and larger values of $|m - 1|^2$ than the two films which contain no accelerator (5387 and 5392). These results obviously are one reason for the increased solar attenuation in the films containing MDEA. Note also that very small differences in m can lead to significant differences in $|m - 1|^2$. Consequently, it is very important to control the degree of cure of the matrix in a PDLC film since it will directly affect n_{matrix}, m, and the scattering efficiency.

TABLE V

Effect of dissolved liquid crystal on matrix refractive index and light scattering

Sample Number	LC:Precursor Ratio β	Volume Fraction η	γ	n_{matrix}	m	$10^3 \cdot \lvert m - 1\rvert^2$
		Samples made without accelerators				
5387	1.00	0.15	0.412	1.5447	1.0228	0.522
5392	2.00	0.27	0.543	1.5526	1.0176	0.311
		Samples made with accelerator MDEA				
5367	0.71	0.18	0.287	1.5372	1.0278	0.774
5368	0.59	0.17	0.242	1.5345	1.0296	0.877
5370	0.47	0.11	0.236	1.5341	1.0299	0.877
5374	0.59	0.25	0.161	1.5297	1.0329	1.081
5375	0.59	0.17	0.242	1.5345	1.0296	0.878

Notes:

1. $\gamma = \frac{v_{LC}^{matrix}}{v_{LC}^{matrix} + v_{precursor}}$

2. $m = \frac{n_{LC}}{n_{matrix}}$

We found that addition of MDEA frequently increased the voltage needed to switch a PDLC film from its light-scattering off-state to its transparent on-state. This effect was most apparent in the films containing BL009. We could not separate the effects of droplet size, droplet concentration and film thickness on switching voltage because of sample-to-sample variations in these parameters. When we achieve better control over the formation of UV-cured films made with accelerators, it may be possible to reduce the switching voltages in films containing MDEA. Except for the high switching voltages, the electro-optic characteristics of PDLC films containing MDEA are comparable to those achieved in our best films prepared without accelerator and should be adequate for most applications.

Adding the accelerators DMEA and TEA to the polymer precursor mixture P0008 did not improve the solar attenuation characteristics of the resulting PDLC films; however, the other electro-optic characteristics of these films were as good as those of our best films prepared without an accelerator. Furthermore, the films with DMEA and TEA used significantly less LC than the films made without accelerators. Further evaluation of these two accelerators with other polymer precursor and LC mixtures is clearly desirable.

Combining the accelerator EPA with NOA65 has produced good electro-optic performance in PDLC films made with several different LC materials. In those films the LC concentrations were adjusted to maximize visual performance rather than solar attenuation. Further studies aimed at improving the solar attenuation characteristics of films containing NOA65 and EPA are needed.

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