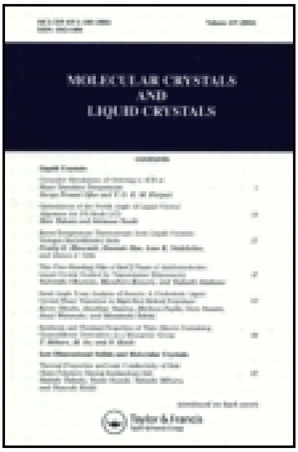

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Liquid Crystal Monomer Additives for Improved Polymer Dispersed Liquid Crystals

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LIQUID CRYSTAL MONOMER ADDITIVES FOR IMPROVED POLYMER DISPERSED LIQUID CRYSTALS

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Abstract The performance of polymer dispersed liquid crystal (PDLC) films was improved markedly by introduction of a monofunctional liquid crystal monomer component into the photopolymerizable solution from which the PDLC was formed by phase separation. Small amounts of an LC-monomer additive enhanced the LC phase separation and slowed the rate of polymerization. Use of 1-10% of LC-monomer in the solution led to the formation of larger LC droplets in a less rigid polymer, resulting in PDLC films with lower threshold and operating voltages and increased the contrast ratio. The effects of LC-monomer additives on PDLC properties were studied as a function of their structure and concentration, particularly in a photopolymerizable solution of Norland NOA65 monomer system with BDH-E9. For example an optimized amount of LC-monomer, such as 4% *p*-butylphenyl *p*-acryloyloxybenzoate in a 1:1 solution of NOA65 and BDH-E9, gave 50% lower threshold and operating voltages, together with 9% higher on-state transmission than the PDLC films without the LC-monomer additive.

INTRODUCTION

The purpose of this study was to seek improved electro-optical properties in polymer dispersed liquid crystal (PDLC) films containing LC droplets and the "Swiss cheese" type of morphology.[1] The general approach was to add small amounts of monofunctional LC-monomers to photopolymerizable solutions of LCs and monomers of the step polymerization type in order to alter the properties of the PDLC formed by polymerization induced phase separation (PIPS).[1,2] Our initial concept was to optimize several inter-related effects which might be expected from the addition of the LC-monomer, namely (a) an increase in the solubility of the LC in the polymerizable solution, based on a "like dissolves like" behavior, (b) a slowing of the rate of polymerization due to the presence of the monofunctional LC-monomer in the otherwise multifunctional monomers, and (c) initial phase separation of some LC-monomer with the LC, followed by its incorporation into the polymer around the LC droplets. As shown in our results, the addition of the LC-monomer had an effect opposite to expectation "a", but was in agreement with the concepts "b" and "c", and gave some very beneficial results.

Several other investigators[1,3-5] have studied the use of non-LC monofunctional acrylate monomer additives in PIPS formation of PDLCs for normal or reverse mode[5] display materials. Recently, the use of siloxane LC-monomers have been described for the preparation of reverse mode PCLCs.[6] Different type of LC/polymer structures have been formed by polymerization of bifunctional LC-monomers to form crosslinked gel type LC-polymers in LC hosts[7,8] to give electro-active layers, including those with chiral additives that give polymer stabilized cholesteric textures.[8]

EXPERIMENTAL

In these studies, the monomer used was the optical cement NOA65 (Norland) which contains its own photoinitiator. The LCs used were BDH-E9 (Merck Ltd.) and HRL-PD50, a proprietary mixture.[9] The phenyl benzoate based LC-monomers (structure I below) were synthesized at HRL, from the reaction of acryloyl chloride with the corresponding *p*-substituted phenyl *p'*-hydroxybenzoate by one of two methods.[10,11] The cyanobiphenyl based LC monomers (structures II and III below) were prepared at Merck Ltd. Compound II was synthesized by reaction of 6-bromohexanoyl chloride with 4-cyano-4'-hydroxybiphenyl followed by reaction with sodium acrylate. Compound III was synthesized by alkylation of 4-cyano-4'-hydroxybiphenyl with 3-bromopropanol, followed by esterification with acryloyl chloride. A commercial benzophenone (Aldrich) was used as an extra photoinitiator additive.

The photopolymerizable solutions containing monomer, liquid crystal, and additives were placed between glass electrodes coated with indium tin oxide separated by a perimeter spacer, to give cells in the range of 10-20 μm PDLC thickness. Ultraviolet exposures were used to initiate polymerization and PDLC formation, as described in prior experiments.[9] The mercury arc system provided a nominal intensity on the test cells of 19 mW/cm^2 in the 300-500 nm range. Electro-optical properties of the PDLC films were evaluated on an optical bench, as previously described,[12] using a small acceptance angle silicon photodiode detector with the sample positioned normal to a beam of green light (from a He-Ne laser, or from a collimated and filtered tungsten lamp).

RESULTS AND DISCUSSION

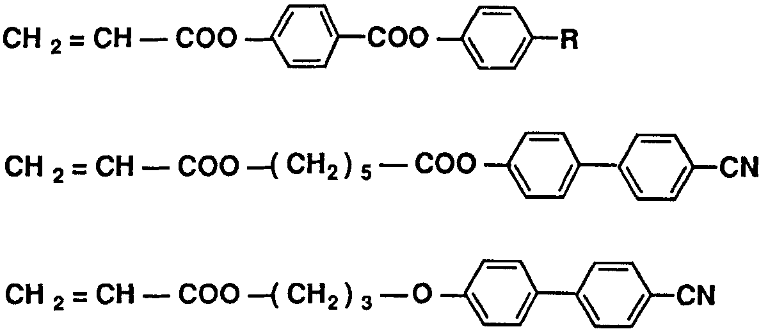
LC-Monomers

The general structure of the LC-monomer additives that we studied is an acryloyloxy derivative with the general structure shown by formula 1, in which all -C_6H_4- groups

$$CH_2{=}CHCOO\text{-}(CH_2)_m\text{-}Z\text{-}C_6H_4\text{-}X \tag{1}$$

are *para-* substituted phenyl rings, and m is an integer for 0 to 10, Z is C_6H_4-COO, COO-C_6H_4, or O-C_6H_4, and X is an alkyl group (C_nH_{2n+1}), alkoxy group (OC_nH_{2n+1}), an alkenyl group (C_nH_{2n-1}), or a CN, Cl, or F group.

The particular LC-monomer structures reported in this work are shown in Figure 1, and their physical properties are given in Table I. We believe that these LC-monomer additives play a dual role in the photopolymerizable solution during the phase separation to form PDLCs. In one role, they act as a mono-functional monomer in a multi-functional step-polymerization system to slow down the polymerization rate and give a less fully cross-linked polymer. In another role, they act as part of the LC content which is initially phase separated during polymerization. The latter role is affected by their affinity for the bulk of the LC molecules in the solution, which in most of our studies was BDH-E9. In Table II we show calculated values of the weight percent (wt.%) LC-monomer, melting point, and clearpoint of six eutectic mixtures, each with a different LC-monomer in BDH-E9. These calculations indicated that theoretically substantial percentages of several of the LC-monomers could be present in such eutectic mixtures. (The values in Table II for compound I-5 are placed in parenthesis because it was less pure than the other LC-monomers, and the wt.%. of I-5 calculated for Table II is probably high due to impurity lowering of its melting point and heat of fusion listed in Table I.) Experimentally we observed that the LC-monomers were less soluble in BDH-E9 than the calculated eutectic values. For example, compound I-4 showed a solubility limit of about 13 wt.% in BDH-E9 at room temperature. In contrast, I-4 is much more soluble in the monomer mixture, with 25 wt.% dissolving easily in NOA65. Also, BDH-E9 has a solubility limit of about 50% in NOA65. Thus, contrary to one of our initial concepts, the addition of these LC-monomers tended to decrease rather than increase the solubility of BDB-E9 in the polymerizable solution, and correspondingly, they also decreased its solubility in the resulting polymer containing LC-monomer. This causes better phase separation of the BDH-E9 during polymerization of solutions containing the LC-monomer. The average



I

II

III

FIGURE 1 Structures of the liquid crystal monomers studied.

TABLE I Properties of liquid crystal monomers used in PDLC formulations.

No.	R	MW g	Purity %	MP °C	CLPT °C	ΔH kcal
I-3	C_3H_7	310	93.6	59.9	64.2	5.36
I-4	C_4H_9	324	98.0	48.3	40.9	7.74
I-5	C_5H_{11}	338	91.5	47.2	64.5	3.31
I-7	C_7H_{15}	366	97.8	44.5	64.1	7.10
I-02	OC_2H_5	312	98.0	116.4	117.0	11.31
I-06	OC_6H_{13}	368	94.2	60.3	101.7	7.03
II		363	98.2	72.0	[44.0]	8.51
III		307	98.6	62.0	[32.0]	7.14

TABLE II Calculated eutectic mixtures of LC-monomers in BDH-E9.

LCM	I-4	I-5	I-7	I-06	II	III
Wt.%	14.8	(41.1)	21.4	14.2	6.1	10.3
MP, °C	2.5	(-5.1)	1.3	3.0	4.7	3.4
CLPT, °C	81.3	(80.2)	83.6	88.8	84.8	81.9

refractive index of I-4 and BDH-E9 are 1.552 and 1.595, respectively, so that when a small amount of this LC-monomer is incorporated into the polymerized matrix while displacing residual BDH-E9, the refractive index of the PDLC polymer matrix (n_p) is lowered slightly to give a better index match with the ordinary index of the BDH-E9 droplets (n_o = 1.522).

PDLC Studies

The effects on the electro-optical curves of PDLCs formed with I-4, I-7, and I-O6 present at 4%, 5%, and 5%, respectively, in the polymerizable solution are shown in Figure 2. These concentrations corresponded to 7.4%, 9.1%, and 9.1%, respectively, of the LC-monomer in the total LC plus LC-monomer content of the solutions. The use of these amounts of I-4 and I-7 (curves 2 and 3) resulted in a PDLC with substantially lower threshold voltage (V_{th}) and operating voltage (V_{op}), and also gave higher transmission (%T) at high voltage than the PDLC formed without the LC-monomer. These PDLC films showed less residual microscopic birefringent scattering points in

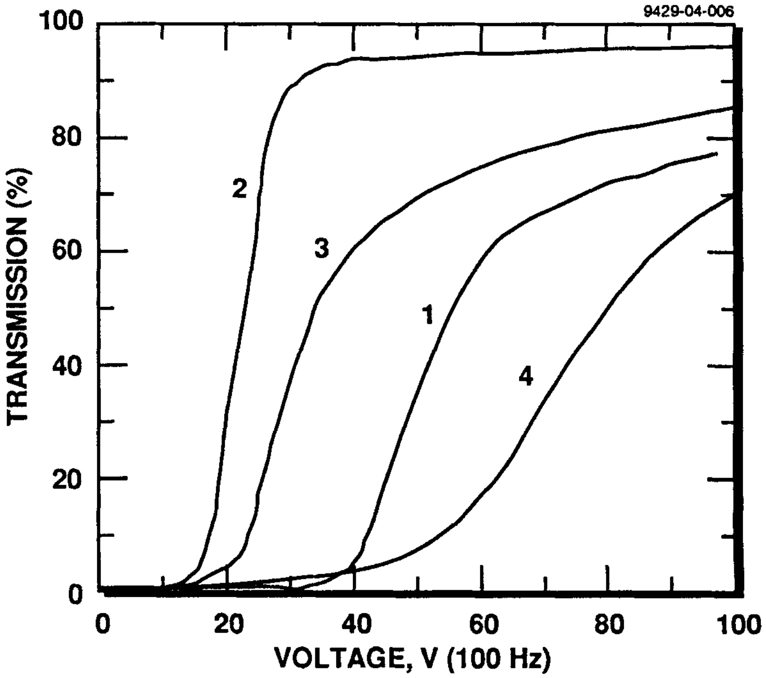


FIGURE 2 Effects of LC-monomers in NOA65/BDH-E9 on 15 μm PDLC film. (Curve 1, none; curve 2, 4% I-4; curve 3, 5% I-7; curve 4, 5% I-O6.)

the on-state than those made without these LC-monomers. The lower voltages for activation, along with the observation of slower on and off response times, indicate that larger LC droplets were formed by the use of I-4 and I-7 in these PDLCs.[13] On the other hand, the use of 5% of I-O6 had the opposite effect on the PDLC characteristics, as shown in curve 4. Also, the initial curve 4 shown for I-O6 in Figure 2 was not reproducible when the voltage scan was repeated, indicating the presence of a different PDLC morphology probably of the "polymer ball" type.[1]

A similar phenomenon occurred when using higher concentrations of I-4. This is seen in Figure 3 and Table III, which show the effect of using different concentrations of I-4 in the BDH-E9/NOA65 mixture. The use of 2.5% and 5.0% of I-4 (curves 2 and 3 in Figure 3) greatly decreased V_{th} and V_{op} of the PDLC as well as giving a very high %T above 30 V. (By extrapolation, these results indicate that as little as 1% of I-4 in the polymerizable solution will have a favorable effect on the PDLC characteristics.)

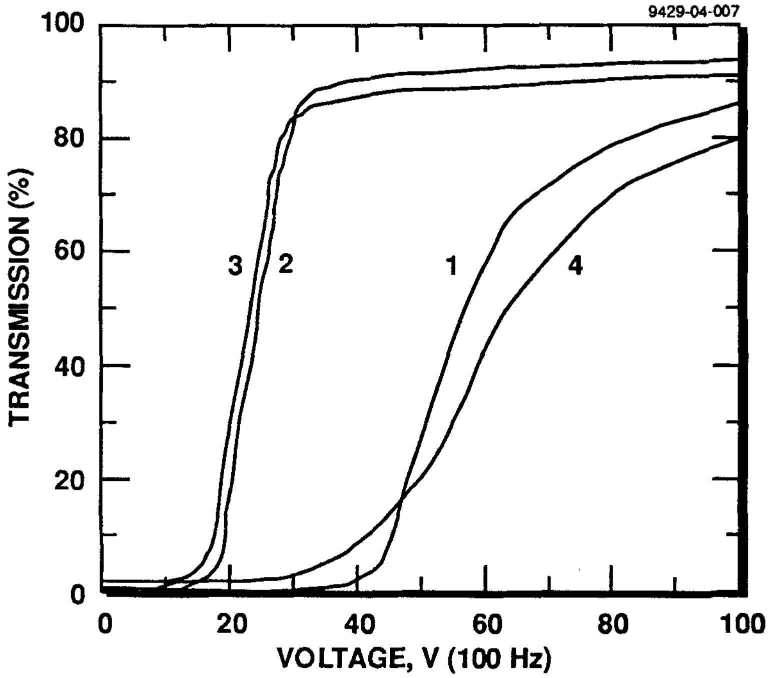


FIGURE 3 Effect of I-4 concentration in NOA65/BDH-E9 on 15 μm PDLC film. (Curve 1, none; curve 2, 2.5%; curve 3, 5.0%; curve 4, 7.5%.)

The data in Table III shows that the addition of the LC-monomer slowed down the time taken to observe the polymerization induced phase separation (PIPS). However, in curve 4 of Figure 3, the use of 7.5% of I-4 (corresponding to 13% of I-4 in the total LC plus LC-monomer content) resulted in a higher V_{op} and a lower %T at most voltages. This curve 4 also showed a "memory" effect (non-reproducibility) indicative of a morphology different than the "Swiss cheese" droplet morphology desired.

TABLE III LC-monomer I-4 effect on PDLC properties for Figure 3 curves.

LC-monomer I-4		PIPS, sec	$\%T_{off}$	$\%T_{on}$	V_{10}	V_{90}
Curve 1	0.0 %	2	0.6	84.8	42.0	72.3
Curve 2	2.5 %	3	0.5	95.0	22.5	37.5
Curve 3	5.0 %	3	1.5	92.6	20.5	34.0
Curve 4 *	7.5 %	4-5	1.8	79.4	38.0	80.5

*Solutions whose PDLCs showed "memory" (non-reproducible voltage scans).

The change of PDLC morphology for curves 4 in Figures 2 and 3 each occurred at the approximate solubility limit of the LC-monomer in BDH-E9, namely 9% for I-O6 and 13% for I-4. However, another factor in our studies was that the polymerizable solutions were made by adding the LC-monomer to the NOA65 and then adding a fixed percentage of the LC. Thus, the addition of the LC-monomer not only introduced a mono-functional acrylate but also diluted the overall concentration of the multi-functional monomers and their photoinitiator. Each of these factors contributed to causing a slower polymerization rate, which may also affect the resultant PDLC morphology.

The data in Figure 4 and Table IV show that the addition of a small amount (0.2%) of benzophenone (BP) photoinitiator to photopolymerizable solutions stabilized a droplet type PDLC structure when using 7.5% of the I-4 LC-monomer, as illustrated by the lower voltages for curve 4 compared to curve 3 in Figure 4 and also by the response characteristics in Table IV. The use of 0.6% BP with 12.2% I-4 initially showed favorable results (Table IV), however, this PDLC had an unstable memory effect, indicating that a different morphology was formed. Other results in Table IV show very favorable improvements in the three PDLC films made by the addition of just 2.4% of LC-monomers I-O6, II, and III, respectively, indicating that a wide range of acrylic LC-monomers are effective additives for lowering the voltages and improving the on-state transmission of the BDH-E9/NOA65 type systems.

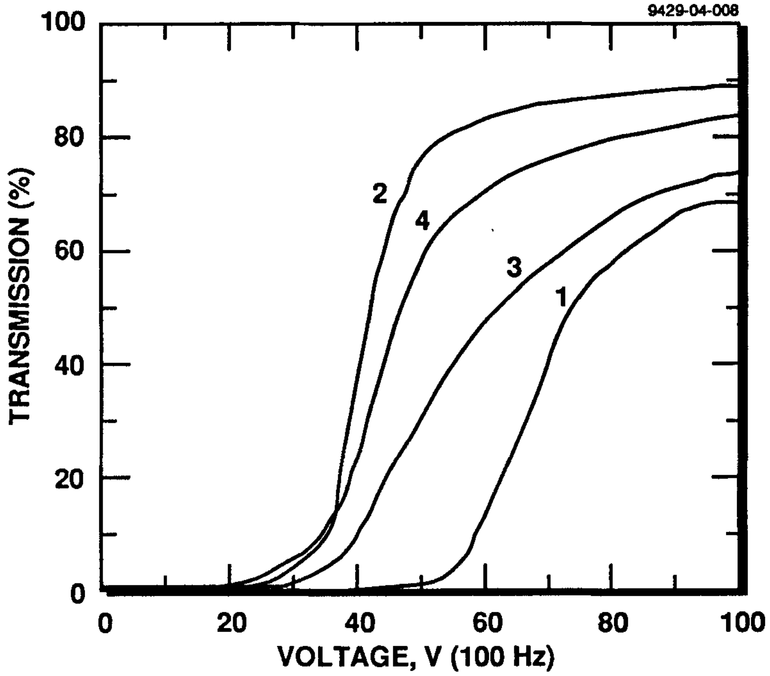


FIGURE 4 Effect of I-4 concentration and BP in NOA65/BDH-E9 on 20 μm PDLC. (Curve 1, none; curve 2, 2.4%; curve 3, 7.5%; curve 4, 7.4% + 0.2% BP.)

As a comparison, the effects of adding the non-LC monomer phenylacrylate (PA), which has the structure CH_2=CH-COO-C_6H_5, to the BDH-E9/NOA65 system are shown in Figure 5 (curve 3) and in Table IV. When 2.8% of PA was added, it lowered the V_{th} and V_{op} of the resultant PDLC, but it did not give a high on-state %T even in relatively thin cells of 12μm thickness. Increasing the amount of PA additive to 6.5% of the polymerizable solution resulted in a PDLC with a significantly lower clearpoint and a morphology that had non-reproducible electro-optical properties.

The addition of LC-monomers was also studied in PDLCs made with HRL-PD50, a Hughes proprietary LC mixture of phenylcyclohexane, cyanobiphenyl, and cyanoterphenyl components which forms a sunlight stable PDLC.[9] The LC-monomer I-4 was used in the concentration range of 1 to 7% of the photopolymerizable solutions of this LC with NOA65. The optimum concentration was about 3% of I-4 (with 47%

TABLE IV. Solutions polymerized and the properties of the PDLCs formed.

POLYMERIZABLE SOLUTION						PDLC PROPERTIES			
Acrylate		BP	NOA65	E9	CLPT	V_{10}	T_{0v}	T_{100v}	Decay
Cmpd.	Wt.%	Wt.%	Wt.%	Wt.%	°C	volt	%T	%T	ms
None	0		50.0	50.0	78.0	55.5	0.1	66.5	11.5
I-4	2.4		47.6	50.0	76.2	31.3	0.2	89.0	26.5
I-4*	7.5		42.5	50.0	73.9	37.5	0.4	69.0	4.5
I-4	7.5	0.2	42.3	50.0		32.0	0.7	83.5	15.0
I-4*	12.2	0.6	37.2	50.0		11.0	2.0	79.0	
I-06	2.4		47.6	50.0		30.0	1.0	79.5	
II	2.4		47.6	50.0		24.0	0.2	88.0	
III	2.4		47.6	50.0		32.6	0.1	84.0	
PA	2.8		47.2	50.0	76.4	21.8	0.3	70.5	20.5

*Solutions whose PDLCs showed "memory" (non-reproducible voltage scans).

NOA65 and 50% HRL-PD50), for the best combination of lower operating voltage and higher %T on-state. In 15 μm thick PDLC cells, the contrast ratio was 22% higher with 3% I-4 than without it when using $(100\text{-}T_{on})/(100\text{-}T_{off})$ for the contrast ratio calculation.[12] Curve 2 in Figure 6 shows the favorable results on a 10 μm thickness PDLC by use of just 1.6% of I-4 in the polymerizable solution (with 48.4% NOA65 and 50% HRL-PD50). In addition to the favorable voltage and %T characteristics of curve 2, the I-4 additive eliminated the presence of all tiny birefringent scattering centers observable in the full on-state of the PDLC, which are frequently present in PDLCs and may be due to small LC droplets or clusters of droplets that are too small to be aligned by the applied field.

CONCLUSION

The properties of PDLC films are strongly affected by the addition of small amounts of monofunctional LC-monomers to solutions used for photopolymerization induced phase separation (PIPS). The addition of a few percent of acrylic LC-monomers results in PDLCs with lower operating voltage and higher on-state transmission. In

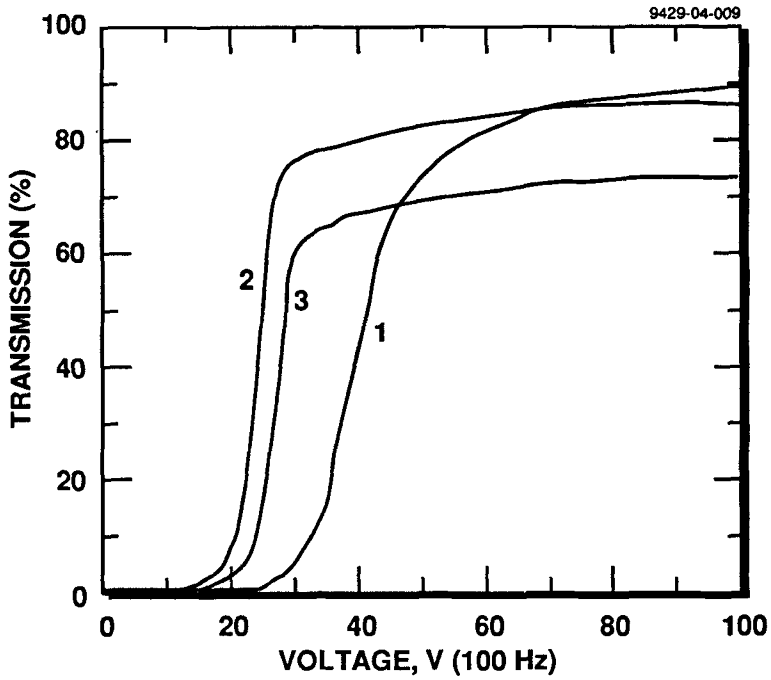


FIGURE 5 Comparison of I-4 and PA effects in NOA65/BDH-E9 on 12 μm PDLC film. (Curve 1, none; curve 2, 2.5% I-4; curve 3, 2.8% PA.)

photopolymerizable solutions of cyanobiphenyl base LCs (such as BDH-E9) and step-polymerization monomers (such as NOA65), the optimum results are obtained with about 1 to 8% of LC-monomer, so long as this amount is less than its solubility limit in the LC. If too much LC-monomer is added, the PDLC morphology is altered to give non-reproducible electro-optical effects. The mechanism of the favorable LC-monomer additive effect is complex, but includes a slowing of the PIPS, the formation of larger LC droplets, and better index matching of the LC with the polymer matrix. It appears likely that better phase separation of the LC occurs, that part of the LC-monomer initially separates with the LC, and that upon completion of polymerization this phase-separated LC-monomer ends up in the polymer immediately surrounding the LC droplets.

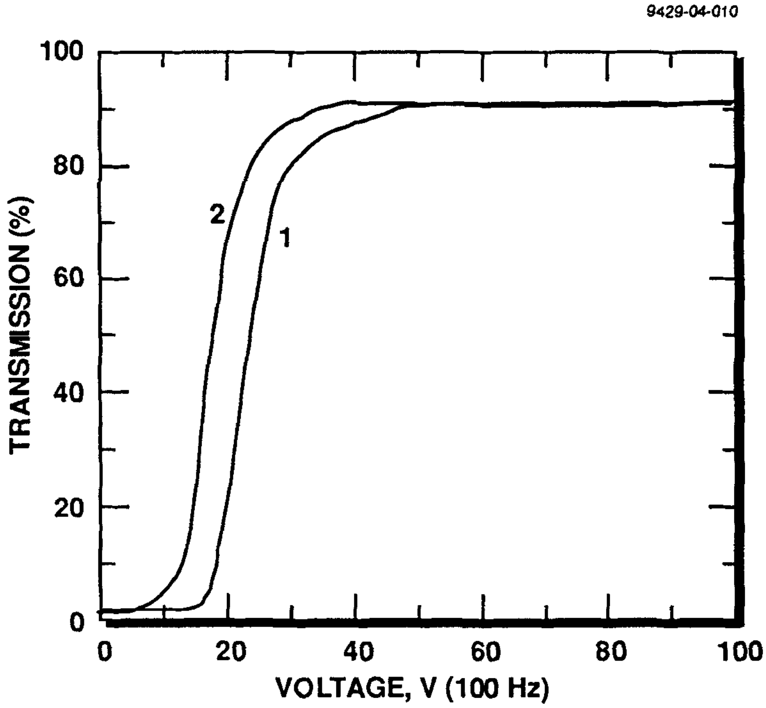


FIGURE 6 Effect of LC-monomer I-4 in NOA65/HRL-PD50 on 10 μm PDLC film. (Curve 1, none; curve 2, 1.6% I-4.)

REFERENCES

1. F. G. Yamagishi, L. J. Miller, and C. I. van Ast, SPIE, Liq. Crystal Chem., Physics, and Applic., 1080, 24 (1989).
2. N. A. Vaz, G. W. Smith, and C. P. Montgomery, Mol. Cryst. Liq. Cryst., 146, 1 (1987).
3. Y. Hirai, S. Niiyama, H. Kumai and T. Gunjima, SPIE, 1257, 2 (1990).
4. J. D. Margerum, F. G. Yamagishi, A. M. Lackner, E. Sherman, L. J. Miller, and C. I. van Ast, Liq. Cryst., 14, 345 (1993).
5. T. Gotoh and H. Murai, Appl. Phys. Lett., 60, 392 (1992).
6. J. Wang, USP 5,270,843, Dec. 14, 1993.
7. R. A. M. Hikmet, J. Appl. Phys., 68, 4406 (1990).
8. D. K. Yang, L.-C. Chien, and J. W. Doane, Appl. Phys. Lett., 60, 25 (1992).
9. A. M. Lackner, E. Ramos, and J. D. Margerum, SPIE., Liq. Crystal Chem., Physics, and Applic., 1080, 267 (1989).
10. L. Stryelecki and L. Liebert, Bull. Soc. Chim. Fr. #2, Part 2, 597 (1973).
11. A. R. Banks, R. F. Fibiger, and T. Jones, J. Org. Chem., 42, 3965 (1977).
12. A. M. Lackner, J. D. Margerum, E. Ramos, S.-T. Wu, and K.-C. Lim, SPIE, Automotive Displays & Industrial Illumination, 958, 73 (1988).
13. A. M. Lackner, J. D. Margerum, E. Ramos, and K.-C. Lim., SPIE, Liq. Crystal Chem., Physics, and Applic., 1080, 53 (1989).