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Stabilization of Polymer Dispersed Liquid Crystal Systems Using Surface Active Agents

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In this study, surface active agents were used in the preparation of polymer dispersed liquid crystals (PDLCs) by temperature induced phase separation. The surfactants Tween 20, a mixture of long chain carboxylic acids, and oleic acid were used to stabilize the liquid crystal 4-*n*-pentyl-4'-cyanobiphenyl (5CB) in a poly(iso-butyl methacrylate) matrix. The PDLCs formed using the surfactants exhibited more uniform particle sizes and greater particle size stability than comparable systems which contained no surfactant. The stabilized systems maintained their properties after being switched over 100,000 times. Also, the response to an applied electric field was shown to be faster for the stabilized PDLC systems.

Keywords: PDLC; surface active agents; polymethyl methacrylate; relaxation times; infrared spectroscopy

INTRODUCTION

Temperature-induced phase separation (TIPS) has been used to make polymer dispersed liquid crystal (PDLC) devices. These systems are composed of liquid crystal droplets dispersed in a thermoplastic polymer matrix. The presence of liquid crystal acts as a plasticizer, which lowers the glass transition temperature (T_g) of the polymer matrix. In some PDLC systems, such as poly(methyl methacrylate) and E7 (a eutectic mixture of liquid crystals), the T_g of the plasticized polymer remains well above room temperature. In this case, the polymer retains most of its rigidity, and the droplet sizes remain fairly constant with time. In other

systems, such as poly(butyl methacrylate) and E7, the T_g of the polymer matrix is lowered to around room temperature. This causes droplets to undergo Ostwald ripening and coalescence over time[1]. This results in a dramatic decrease in the optical properties of the PDLC system. This behavior also exists in the poly(isobutyl methacrylate) (PiBMA) and 4-*n*-pentyl-4′-cyanobiphenyl (5CB) system. This can be seen in Figure 1, which shows a series of photomicrographs taken from a system composed of 15 percent PiBMA and 85 percent 5CB. As Figure 1 shows, the PDLC sample, which has droplets with an initial average diameter on the order of 200 microns, steadily changes to form large regions of phase separated polymer and liquid crystal. This particle growth causes the opacity of the PDLC to decrease drastically over a short period of time.

This study proposes a new method of size stabilization for PDLC systems. By size stabilization, it is meant that the dispersed particle sizes will remain essentially the same size over extended periods of time. This should allow these systems to be used in applications in which they would have been useless without stabilization.

The proposed method of stabilization chosen for this study is the addition of a surfactant. Latex emulsion paint chemistry was used as a model for the stabilized PDLC systems. In latex paints, the pigment is dispersed as fine particles in a solvent such as water. In this case, the surfactant is used to make a stable emulsion of fine droplets possessing a narrow size distribution.

The hydrophile-lipophile balance (HLB) method, commonly used in emulsion paint chemistry, is used to choose the proper surfactant. This method is based on the balance between the relative hydrophilic and lipophilic strengths of different portions of a pigment molecule. In practice, the HLB of common pigments are found in tables of HLB values or can be calculated if the structure of the pigment is known. Each moiety of the pigment molecule has an associated HLB contribution which can be found in tables from early empirical work in emulsion chemistry[2,3]. The value for each moiety is then added up to give the final HLB value. A surfactant with the same HLB value is then mixed with the pigment and solvent to form the emulsion[4].

This method, albeit simple, cannot be applied directly to PDLC systems because liquid crystals contain moieties, such as nitrile groups, which are not included in the HLB value tabulations. However, there is another method based on solubilities that will apply if the structure of the molecule is known. An empirical relation has been found between the HLB values and the solubility parameter values of small molecules[5]. To use this method, the solubility parameter is first calculated. This can be accomplished by using a

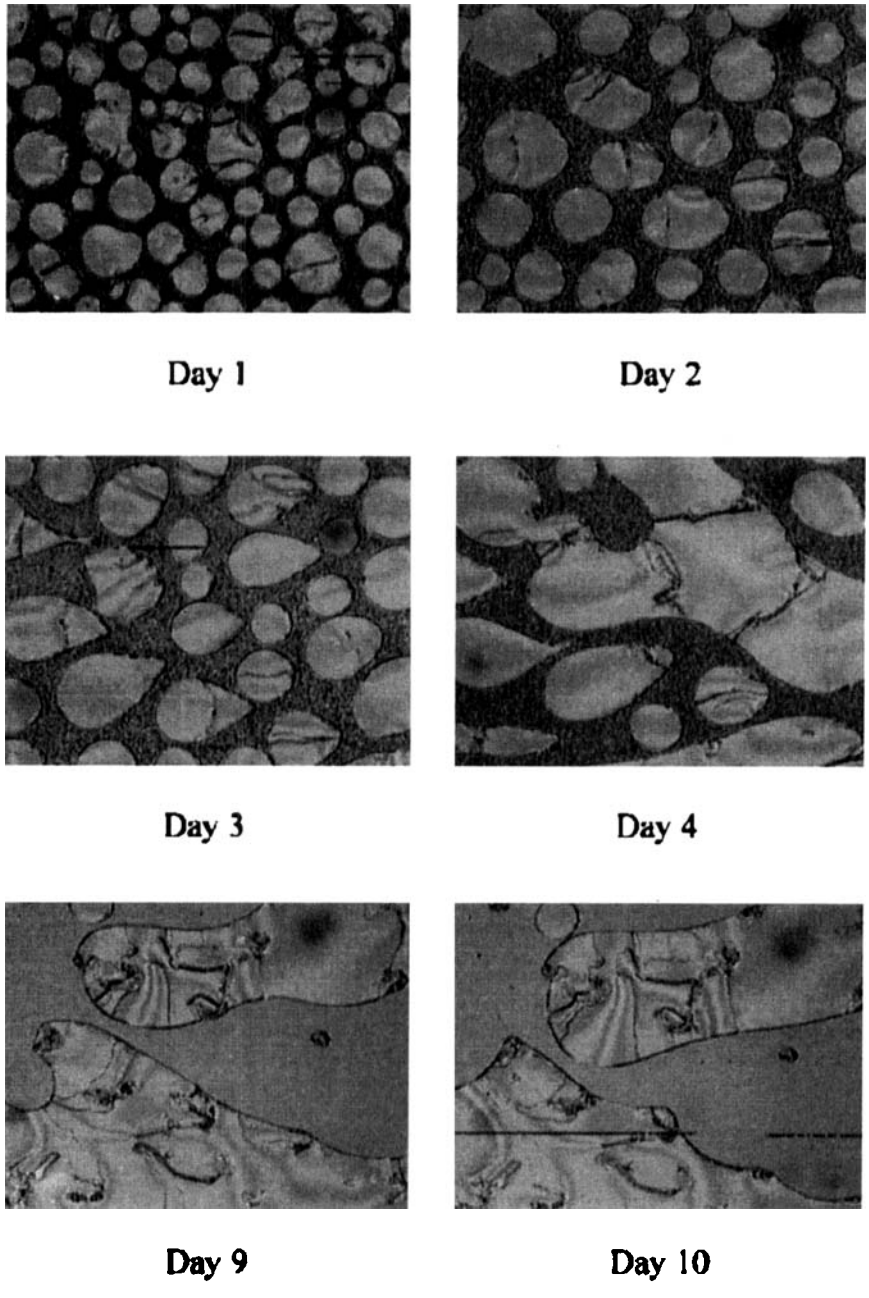

FIGURE 1 Images of a sample containing no surfactant, demonstrating large droplet growth over time. Image dimensions are 1.74 by 1.3 mm.

table of common moieties which have solubility parameter contributions associated with them [6]. Then, knowing the molecular weight, the Hildebrand equation can be used to calculate the solubility parameter value [7].

Since several approximations are used for this calculational method, it is often useful to use an empirical method to determine their validity. An empirical method for the determination of the HLB number involves mixing the pigment with water and surfactants of a wide range of HLB values [8]. The resultant emulsions are visually inspected to see the size of the particles and the stability of the emulsions. This method can be applied to any emulsion system, including PDLCs.

Once the desired systems have been made, their stability can be examined by observing the change in the sizes of the droplets over time. By comparing the size changes of the surfactant-treated and untreated systems, the relative advantage of the treated systems can be determined.

Another way to test the quality of the stabilization is through a dynamic switching "stress test", in which PDLC samples are repeatedly switched and periodically visually inspected to see if there are any changes in the structures of the samples.

It is well established that time resolved step-scan infrared spectroscopy can be used to monitor the electric field induced homogeneous to homeotropic transition of a liquid crystal [9–12]. This spectroscopic method provides information about the orientation of the liquid crystal director on a submicrosecond level. This has also been applied to the study of PDLCs [13, 14]. This technique can be used to determine the switching time and the relaxation time of a PDLC. There is also the potential for studying the differential segmental orientation response by comparing the temporal responses of different functional group absorptions by use of this technique.

EXPERIMENTAL

To establish the initial type of surfactant to be used, an attempt was made to calculate the HLB values of the liquid crystals commonly used in PDLC systems. All of the previously mentioned calculations were performed for several liquid crystals commonly used in PDLC systems.

ZLI 3217 liquid crystal, a proprietary mixture of liquid crystals, was used for the initial empirical HLB determination. For each HLB value, 0.5 g of ZLI 3217 was mixed with approximately 2.0 g of water and 5% by liquid crystal weight (0.025 g) of surfactant. These solutions were made up with surfactants with an HLB range from 1 through 17, which was the entire

range available using oleic acid (HLB = 1) and Tween 20, a mixture of long chain carboxylic acids, (HLB = 17). This was accomplished using the simple rule that surfactants can be mixed together in the proper proportions to form a resultant surfactant with any HLB value between the values of the constituents. These mixtures were shaken for about 20 seconds and their stability was observed visually with the naked eye and with the aid of a low power (5x) microscope. These tests were repeated as necessary with 5CB substituted for ZLI 3217.

For the sample preparation, solutions were first made by dissolving PiBMA and 5CB in the ratio of 15:85. To each solution, surfactant was added in an amount equal to five percent by weight of the liquid crystal. Solutions were made using surfactants in the HLB range of 8 through 13. A bulk amount of chloroform was added as a common solvent, and the solutions were stored overnight to allow for complete solvation of the polymer. A solution with no surfactant was used as a control.

For each sample, two one-inch squares of glass were heated to 70°C. One drop of the appropriate solution was placed on one of the squares. Two narrow strips of 25 micron thick polyethylene terephthalate (PET) film were placed on two opposite edges of the square. After allowing 20 minutes for any residual solvent to boil off, the second square was placed directly on top of the first one, forming a sandwich. Due to the low concentration of polymer present, a very small amount of stress can damage the samples. Therefore, it was necessary to use binder clips to hold the samples together. One binder clip was placed directly over each PET spacer. The samples were then allowed to sit at 22°C to allow phase separation to take place. After one day, the first data was collected. This method of preparation allowed small droplets to coalesce and form bigger droplets that could easily be seen through a low power microscope.

Each sample was marked in two different regions. This marking allowed pictures to be taken of the same region for each data collection. Pictures were taken of each of the two spots for the first four days after phase separation and 9, 10, and 11 days after phase separation. A Nikon microscope with a 5X objective lens was used to collect the images. Due to a lack of contrast in the images, a polarizer had to be used when collecting the images. The microscope was equipped with a CCD camera which was connected to a Macintosh Quadra 700 running Mediagrabber frame grabbing software.

In the process of analysis, the images were doubled in size, smoothed, and converted to the proper image format using several different image processing software packages. The Global Lab Image program was used to analyze the

final images. From this program, droplet area, size, and roundness can be determined. All data on droplet size changes was collected using this software package.

Two stabilized PDLC samples were prepared under the same conditions as before. A function generator/amplifier combination was used to apply an electric field to the samples. A 12 V peak-to-peak 0.5 Hz sine wave with 0 V DC offset was used. The samples were visually inspected after 100, 1000, 10000, and 100000 cycles.

A Bruker ifs88 FTIR spectrometer was used for all step scan measurements. PDLC samples were prepared as before, except that germanium was used as the window material because of its conductivity and infrared transparency. A 5 ms pulse of a 2 kHz sine wave was applied to the samples, and a 300 ms delay was used between pulses to allow for collection of spectra before the pulse and also to allow the samples to relax completely back to the off state. Single beam spectra were collected at both 50 μs and 500 μs time resolution. The resultant spectra were converted to absorbance and the peaks at 2228, 1600, and 1500 cm^{-1} were integrated for each. These area values were subtracted from the area value before the field was applied and plotted to give the time resolved switching curves. These curves were then visually inspected to elucidate the switching and relaxation times.

RESULTS AND DISCUSSION

The HLB calculations of the liquid crystals resulted in values that were outside of the range of values for common nonionic surfactants. This method of HLB determination was abandoned in favor of the empirical method.

The liquid crystal/water/surfactant mixture with no surfactant and with a surfactant with an HLB value of 1 formed large globules of liquid crystal that quickly coalesced to form a large mass in the bottom of the vial. The mixtures that contained surfactants with HLB values between 2 and 7 formed smaller and more stable droplets. Mixtures with surfactants of HLB values between eight and thirteen formed small droplets that did not coalesce extensively, but rather settled to the bottom of the vial. Mixtures with surfactants of HLB values between 13 and 17 formed small droplets that clumped together to form groupings of several droplets. These results show that the most stable emulsions are formed in the HLB range of 8 through 13, which agrees with the commonly accepted range from the literature [15].

These tests were repeated with surfactants in the 8 through 13 HLB range with 5CB to confirm the validity of the observations. The same results were found for this liquid crystal.

All of the PDLC samples phase separated with about the same opacity. One day after the samples were prepared, they had a slightly less opaque appearance. Their appearances remained nearly constant throughout the remainder of the sampling period, except for the sample with no surfactant, which quickly formed droplets large enough to be seen with the naked eye. Images from the sample made with the surfactant with an HLB value of 9 is shown in Figure 2.

The results of particle analysis for the two regions of the sample using the surfactant with an HLB value of 8 are shown in Figure 3 and in Figure 4 for the sample made with the surfactant that had an HLB value of 11. As can be seen, the same trends occur in both regions for a given sample. All samples show the trend of the particles growing larger then smaller either at the beginning or the end of the time period. This may be attributed to errors from measurements, such as inexact positioning of the microscope stage or random image noise. However, the overall change in average particle size for all of the treated samples is quite small, as shown in Table I.

Also, the distribution of droplet sizes in the stabilized samples can be seen to fall in a small range. This is shown in Figure 4a, which shows a histogram of the droplet size distributions for the sample shown in Figure 2.

The samples that were switched repeatedly showed very little change even after 100000 cycles. The droplets did not show any significant growth, but some changes in the internal droplet structures could be seen.

The time resolved switching curves for the carbon-carbon phenyl ring stretching bands, $1500\,cm^{-1}$ and $1600\,cm^{-1}$, and the nitrile stretching band, $2228\ cm^{-1}$ band were all found to follow the same general trend through switching and relaxation. This is as expected, because all three of these bands are aligned parallel with each other in the rigid portion of the liquid crystal molecule. The plots for the untreated and treated PDLC samples at both 50 and 500 μs time resolution can be seen in Figures 6–9. From Figures 6 and 7, it can be seen that the unstabilized PDLC has a switching time of 3 ms, while the stabilized PDLC has a switching time of 2 ms. Switching time here is defined as the time between the onset of the electric field and the time that the absorbance has reached a steady lower value. From Figures 8 and 9, it can be seen that the relaxation time of the stabilized PDLC system is also shorter than the unstabilized system.

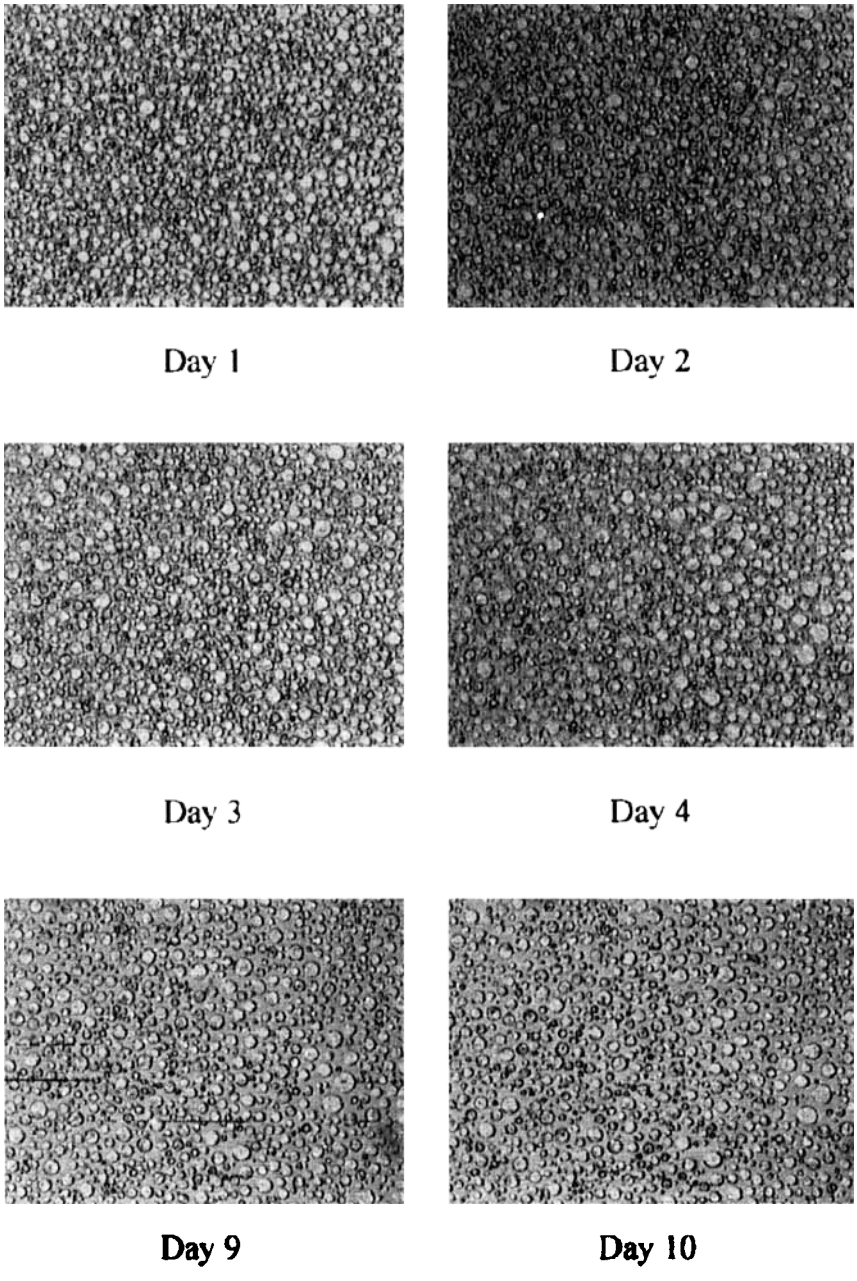

FIGURE 2 Images of a treated sample containing surfactant with HLB 9, demonstrating stable droplet sizes over time. Image dimensions are 1.74 by 1.3 mm.

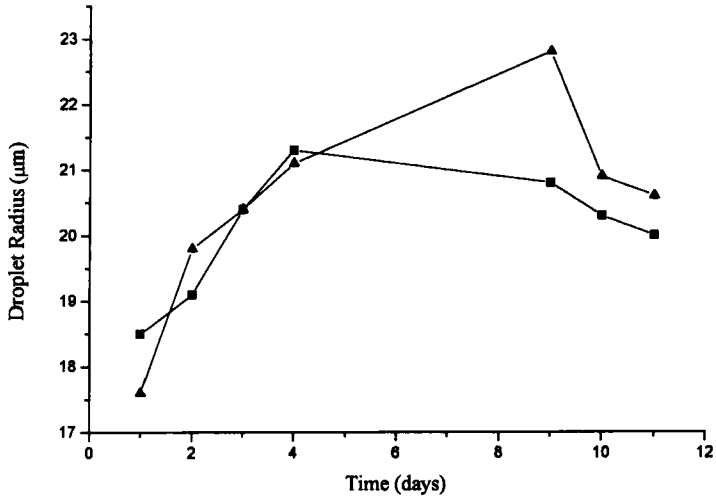

FIGURE 3 Droplet radius over time for two regions of a sample treated with a surfactant with an HLB of 8.

TABLE I Overall change in particle size, averaged for the two regions of each treated sample. (All dimensions are in microns)

Surfactant HLB	*Initial Radius*	*Final Radius*	*Change in radius*
8	18.1	20.3	2.2
9	14.5	16.3	1.8
10	18.5	18.5	0.0
11	17.2	19.3	2.1
12	17.7	17.0	−0.7
13	15.2	15.7	0.5

CONCLUSIONS

It was shown that surfactants can be used to stabilize PDLC systems. By using paint chemistry as a model, the appropriate range of surfactants for stabilization was chosen. Electronic image processing was used to show that the systems were indeed stable over a short time period. When the treated (Fig. 1) and untreated (Fig. 2) systems are compared, the effects of adding surfactant to stabilize PDLCs can be clearly seen. It was shown that the stabilized PDLCs did not undergo any considerable loss of properties after being switched repeatedly. In addition, the switching and relaxation times of the stabilized systems was shown to be faster than those of the unstabilized one.

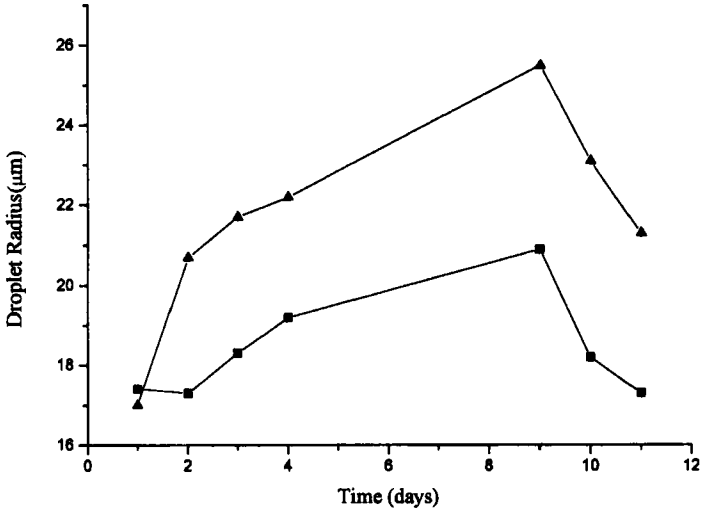

FIGURE 4 Droplet radius over time for two regions of a PDLC sample treated with a surfactant of HLB 11.

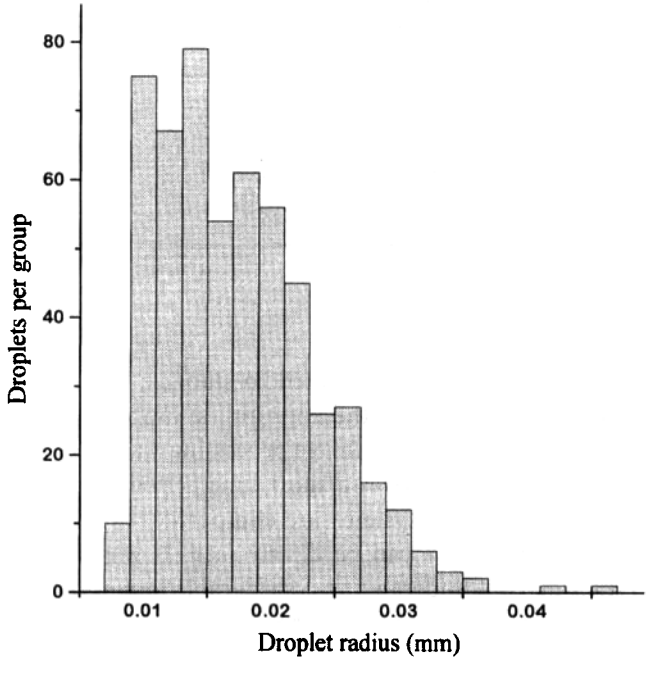

FIGURE 5 Histogram of droplet size distribution for day 11 of the sample from Figure 4.

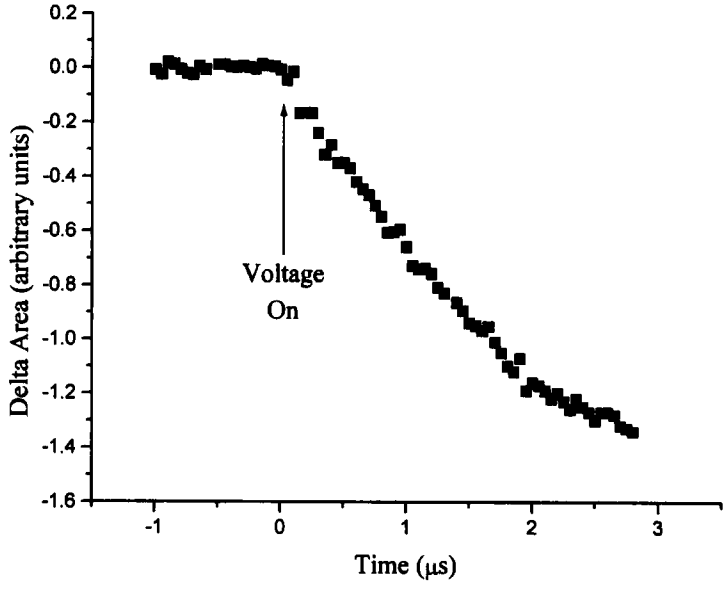

FIGURE 6 Change in nitrile peak area after field was applied for the unstabilized sample, 50 μs resolution.

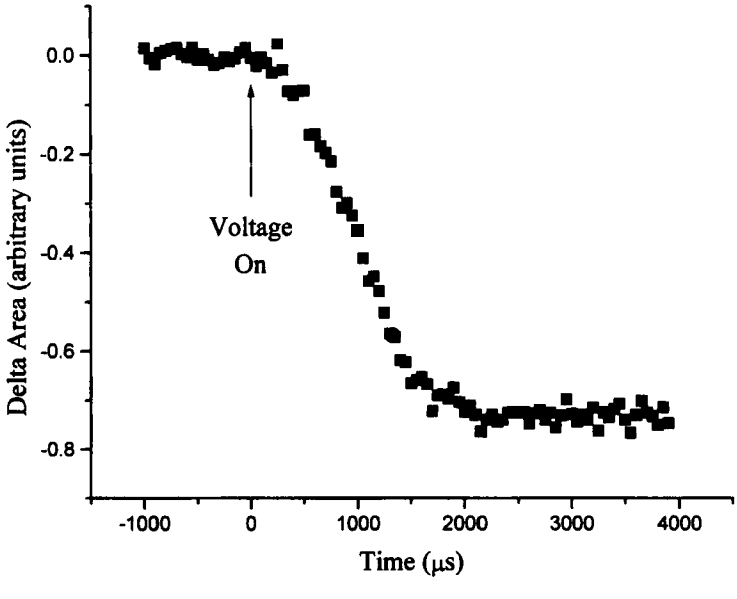

FIGURE 7 Change in nitrile peak area after field was applied for the stabilized sample, 50 μs resolution.

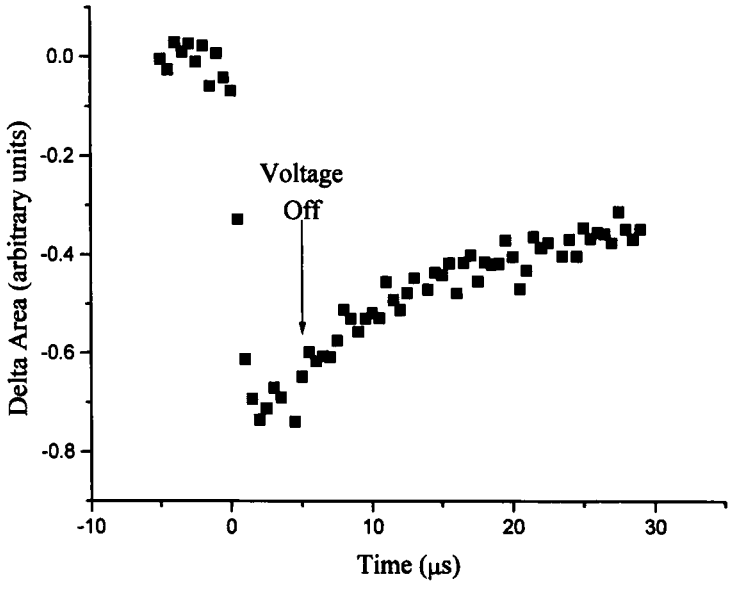

FIGURE 8 Change in nitrile peak area after the field was removed for the stabilized sample, 50 μs resolution.

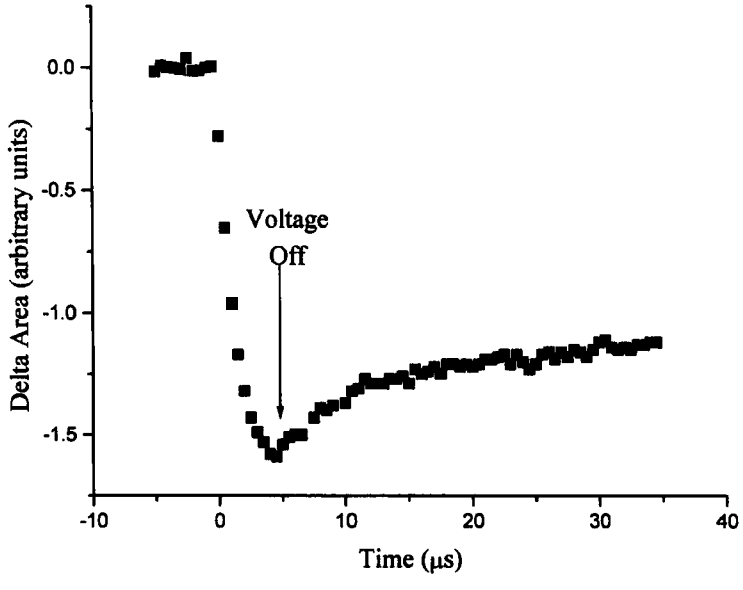

FIGURE 9 Change in nitrile peak area after the field was removed for the unstabilized sample, 500 μs resolution.

Acknowledgements

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