Waters
THE SCIENCE OF WHAT'S POSSIBLE.®

Compositional Analysis of Merck E7 Liquid Crystal Intermediates Using UltraPerformance Convergence Chromatography (UPC^2) with PDA Detection

Jane Cooper
Waters Corporation, Manchester, UK

APPLICATION BENEFITS

This application note illustrates the efficient, cost-effective compositional analysis of Merck E7 liquid crystal intermediate compounds using Waters® ACQUITY UPC^2™ System with PDA detection, offering when compared to standard methodology:

- Greater than 20-fold increase in sample throughput, and greater than a 300-fold reduction in the volume of toxic solvents used.

WATERS SOLUTIONS

ACQUITY UPC^2 System

ACQUITY UPC^2 PDA Detector

ACQUITY UPC^2 BEH 2-EP Column

Empower® 3 Software

KEY WORDS

Liquid crystals, Convergence Chromatography, UPC,^{2} Merck E7, liquid crystal intermediates, supercritical fluid chromatography, SFC

INTRODUCTION

Liquid crystals combine the physical and optical properties of both liquids and solids. They flow and pour like liquids, but have some of the optical properties of solids, such as birefringence. They also react predictably to an electric current, which enables the control of light passage. Due to these properties, liquid crystals are used in many items with electronic displays, for example: watches, calculators, mobile phones, desktop monitors, and TVs.

The E7 nematic liquid crystals mixture contains cyanobiphenyl and cyanoterphenol components, at a specific composition, which possess relatively high birefringence and positive dielectric anisotropy. Due to these properties, it is widely used in polymer dispersed liquid crystals.[1,2,3] The specific composition is critical to ensure physical properties and characteristic of the liquid crystal. Even small changes can have pronounced effects on factors such as the nematic to isotropic transition (T_{NI}), and glass transition (T_G) temperatures.

For the compositional analysis typically a chromatographic technique would be used for the analysis of liquid crystal intermediate compounds, for example: HPLC with UV detection,[4] HPLC with MS detection,[5] and GC with MS detection.[6]

Convergence Chromatography (CC) is a normal phase separation technique that uses carbon dioxide as the primary mobile phase, with the use of a co-solvent such as methanol. Waters UltraPerformance Convergence Chromatography™ (UPC^2®) builds upon the potential of CC while using proven and robust Waters UPLC® technology.

Many liquid crystal intermediate compounds are not very stable at high temperatures, have low volatility, and have similar UV spectra. Therefore, utilizing the separation powers of UPC^2 with CO_2 as the mobile phase is an ideal alternative to both HPLC and GC analysis.

This application note describes the compositional analysis of Merck's E7 liquid crystal mixture utilizing UPC^2 with PDA detection offering: robustness, selectivity and sensitivity, with reduced run times, and associated savings in the cost and disposal of toxic solvents.

EXPERIMENTAL

UPC² conditions

System:	ACQUITY UPC²
Run time:	3.00 min
Column:	ACQUITY UPC² BEH 2-EP, 3.0 mm x 100 mm, 1.7 µm
Column temp.:	60 °C
CCM back pressure:	1800 psi
Sample temp.:	20 °C
Mobile phase A:	CO_2
Mobile phase B:	Acetonitrile
Flow rate:	2.0 mL/min
Injection volume:	1 µL
Vials:	Waters Amber Glass 12 x 32 mm Screw neck vial, 2 mL

Mobile phase gradient is detailed in Table 1.

	Time (min)	Flow rate (mL/min)	%A	%B	Curve
1	Initial	2.00	99.0	1.0	–
2	0.75	2.00	99.0	1.0	6
3	1.50	2.00	90.0	10.0	6
4	2.00	2.00	90.0	10.0	6
5	2.10	2.00	99.0	1.0	6
6	3.00	2.00	99.0	1.0	6

Table 1. ACQUITY UPC² mobile phase gradient.

PDA conditions

UV system:	ACQUITY UPC² PDA Detector
Range:	190 to 400 nm
Resolution:	1.2 nm
Sampling rate:	20 pts/sec
Filter time constant:	Slow (0.2 sec)

Sample description

The Merck E7 liquid crystal intermediate compounds were purchased from Sigma-Aldrich (their structures are shown in Table 2). Individual stock solutions were prepared to a concentration of 5 mg/mL, dissolved in either heptane/ethanol (9:1) or methanol. Serial dilutions of the stock solutions were carried out in heptane/isopropanol (9:1) in order to prepare mixed standards, or in methanol to prepare infusion MS tuning standards.

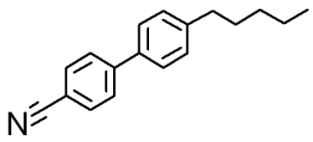
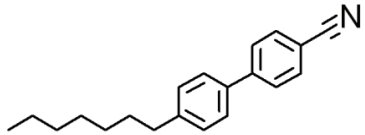
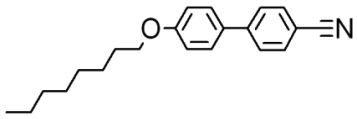
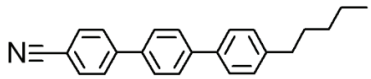
Merck E7 (liquid crystal intermediate compounds)	
4-cyano-4'-n-pentyl-biphenyl $C_{18}H_{19}N$ 	4-cyano-4'-n-heptyl-biphenyl $C_{20}H_{23}N$ 
4-cyano-4'-n-oxyoctyl-biphenyl $C_{21}H_{25}NO$ 	4-cyano-4''-n-pentyl-p-terphenyl $C_{24}H_{23}N$ 

Table 2. Merck E7 liquid crystal intermediate compounds, associated empirical formulas, and structures.

Instrument control, data acquisition, and results processing

Empower 3 Software was used to control the ACQUITY UPC² and the ACQUITY UPC² PDA Detector, as well as for data acquisition.

RESULTS AND DISCUSSION

The UPC^2 conditions were optimized for the analysis of the selected liquid crystal intermediate compounds. Retention times and UV optimum absorbances were established by analyzing single component standards (see Table 3).

Chemical substance		CAS number	Retention time (minutes)	UV optimum absorbance (nm)
4-cyano-4'-n-puntyl-biphenyl	5CB	40817-08-1	0.889	269
4-cyano-4'-n-heptyl-biphenyl	7CB	41122-71-8	1.012	269
4-cyano-4'-n-oxyoctyl-biphenyl	8OCB	52364-73-5	1.469	287
4-cyano-4''-n-pentyl-p-terphenyl	5CT	54211-46-0	1.742	292

Table 3. Merck E7 liquid crystal intermediate compounds, associated CAS number, measured retention times, and the UV optimum absorbance.

The analysis of the four Merck E7 liquid crystal intermediate compounds was achieved using the ACQUITY UPC^2 System with the ACQUITY UPC^2 PDA Detector.

UPC^2 and PDA conditions were optimized, considering different UPC^2 columns, co-solvents, column temperatures, mobile phase temperatures, and system CO_2 back pressures. The elution of all compounds was achieved in a 3-minute run, offering a 20 to 90 fold time saving when compared to HPLC.[4,5]

Mixed calibration standards, 0.01 to 0.40 mg/mL, were prepared and analyzed for all the compounds considered. The calibration curve results generated by Empower Software for 4-cyano-4'-n-puntyl-biphenyl, are shown in Figure 1.

The UV chromatograms for each liquid crystal intermediate compound in a mixed 0.1 mg/mL calibration standard, are shown in Figure 2, and the associated UV spectra, are shown in Figure 3.

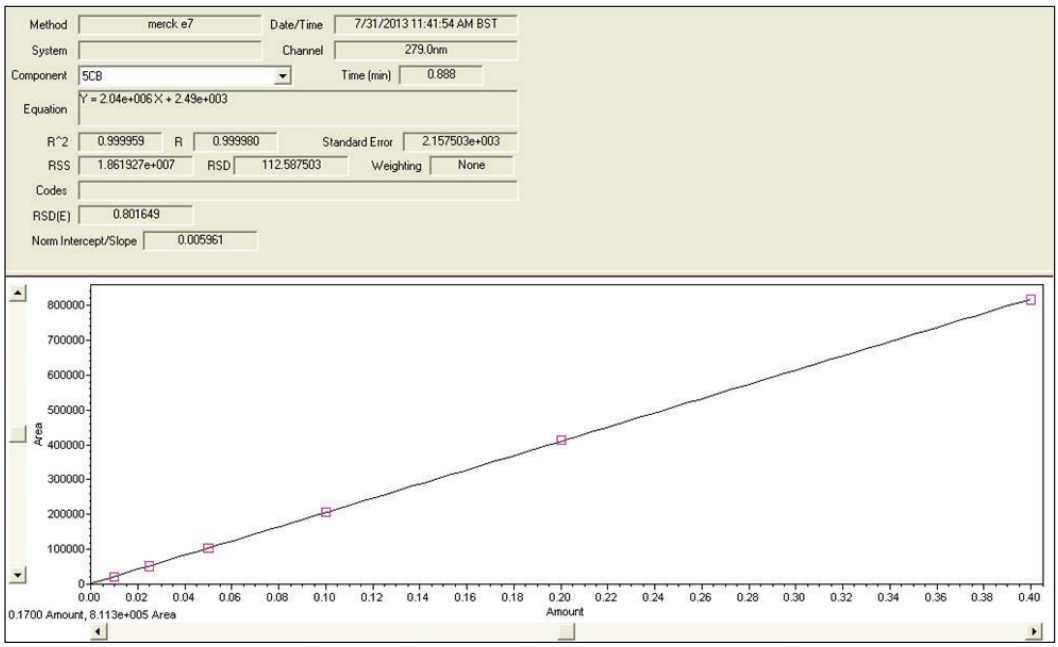


Figure 1. Empower Software calibration curve for 4-cyano-4'-n-puntyl-biphenyl.

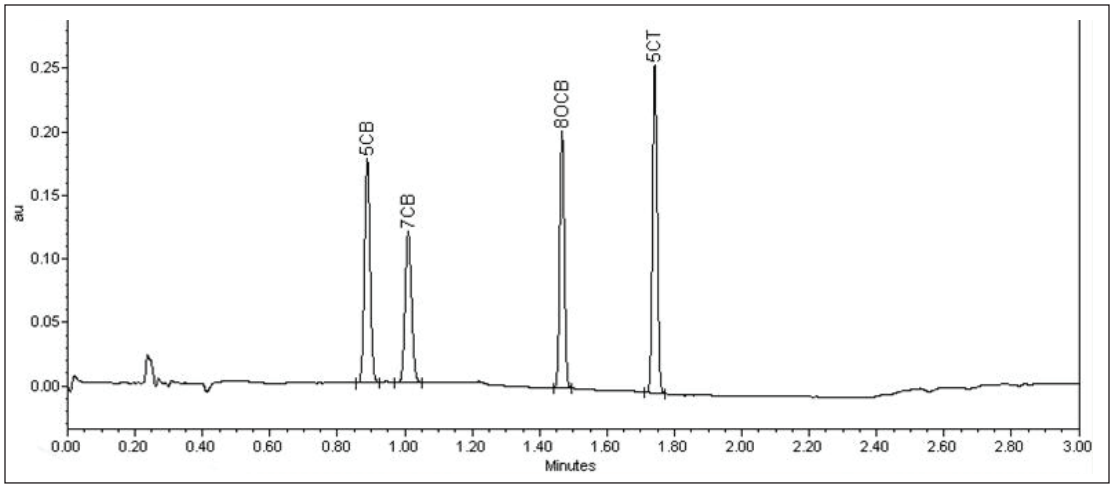


Figure 2. UV chromatograms for each liquid crystal intermediate compound, at wavelength of 279 nm, in a mixed 0.1 mg/mL calibration standard.

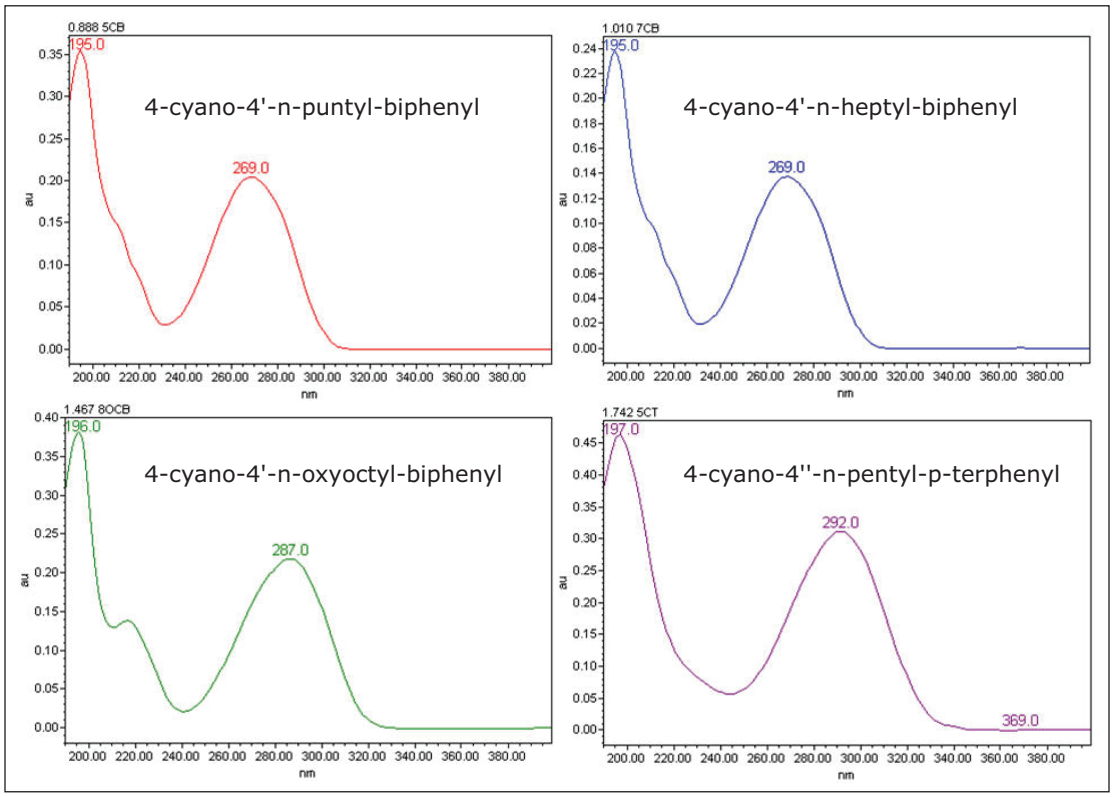


Figure 3. UV spectra for each liquid crystal intermediate compound in a mixed 0.1 mg/mL calibration standard (all compounds were resolved by retention time).

Compositional analysis

The ratio of the individual liquid crystal intermediate compounds in the required mix is paramount to achieving optimum optical quality, performance, and lifetime of the electronic device. Therefore the ability to quantify the ratio is critical to ensure optimum efficiency of the liquid crystal.

In order to demonstrate compositional analysis, a mix of the four compounds in the E7 was prepared, one containing the correct ratio and one at an incorrect ratio; both were then analyzed using the developed UPC^2 conditions with PDA detection. The resulting UV chromatograms acquired are shown in Figure 4, and the achieved results are provided in Table 4.

Utilizing the custom calculation function of Empower 3, results can be quickly reported, highlighting preset pass/fail criteria. This removes the need for manual calculations and in doing so, eliminates potential human calculation errors. Generated compositional custom QC reports are shown in Figure 5.

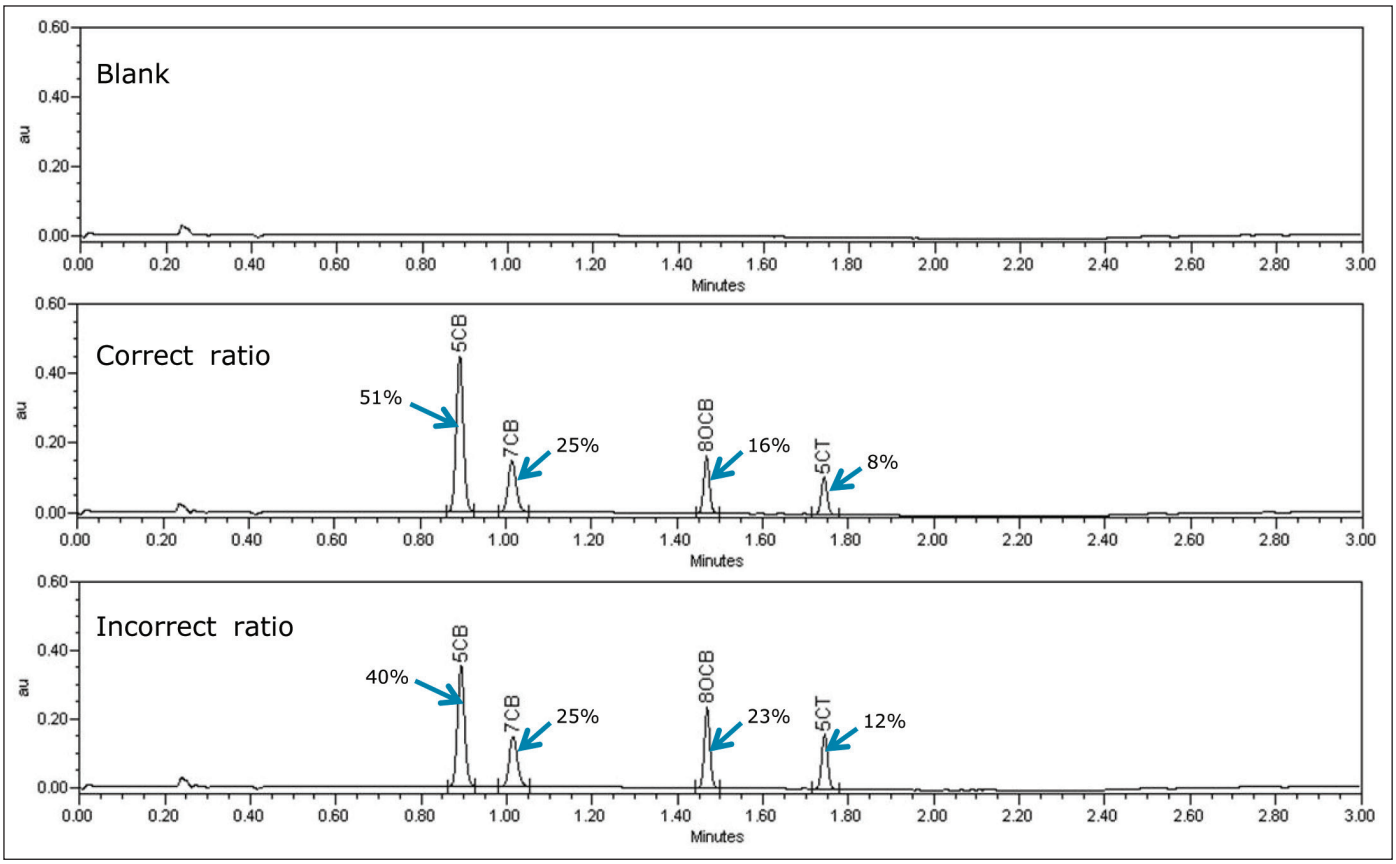


Figure 4. Merck E7 liquid crystal compositional UV chromatograms.

Chemical substance		Correct ratio		Incorrect ratio	
		Prepared %	Calculated %	Prepared %	Calculated %
4-cyano-4'-n-puntyl-biphenyl	5CB	51.0	51.3	40.0	40.4
4-cyano-4'-n-heptyl-biphenyl	7CB	25.0	24.9	25.0	24.9
4-cyano-4'-n-oxyoctyl-biphenyl	8OCB	16.0	15.9	23.0	22.7
4-cyano-4''-n-pentyl-p-terphenyl	5CT	8.0	8.0	12.0	12.1

Table 4. Merck E7 liquid crystal compounds, correct and incorrect ratios, and the achieved results.

Incorrect ratio

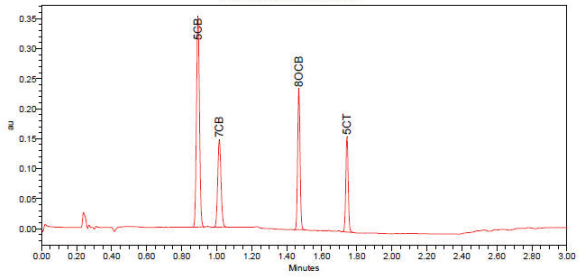
Empower 3

Merck E7 QC Report

SAMPLE INFORMATION

Sample Name:	26_june_2013_041	Acquired By:	
Sample Type:	Unknown	Sample Set Name:	13 june 2013
Vial:	1	Acq. Method Set:	Import
Injection #:	1	Processing Method:	merck e7
Injection Volume:	1.00 ul	Channel Name:	279.0nm@1
Run Time:	3.0 Minutes	Proc. Chnl. Descr.:	PDA 279.0 nm
Date Acquired:	6/26/2013 5:51:05 PM BST		
Date Processed:	10/7/2013 5:46:29 PM BST		

Auto-Scaled Chromatogram



Peak Results

	Name	Retention Time (min)	Area (µV*sec)	Percentage	Amount	E7_5CB	E7_7CB	E7_8OCB	E7_5CT
1	5CB	0.893	415376	40.33	0.203	Fail			
2	7CB	1.015	191991	24.84	0.125		Pass		
3	8OCB	1.469	223639	22.77	0.114			Fail	
4	5CT	1.744	152768	12.07	0.061				Fail

Sample Pass / Fail = Fail

Reported by User: System
Report Method: Merck E7 QC Report
Report Method ID: :2605
Page: 1 of 1

013_02_UPC2_FSC_LCD_JAC\2013_06_UPC2_FSC_E7_JAC
Date Printed:
10/8/2013
12:50:38 PM Europe/London

Correct Ratio

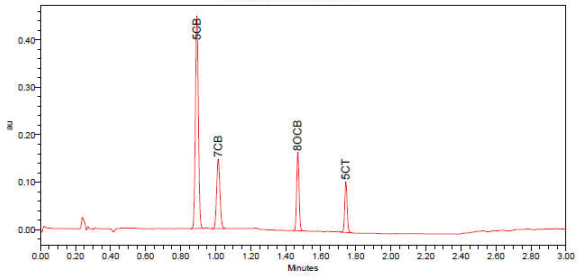
Empower 3

Merck E7 QC Report

SAMPLE INFORMATION

Sample Name:	26_june_2013_039	Acquired By:	
Sample Type:	Unknown	Sample Set Name:	13 june 2013
Vial:	1	Acq. Method Set:	Import
Injection #:	1	Processing Method:	merck e7
Injection Volume:	1.00 ul	Channel Name:	279.0nm@1
Run Time:	3.0 Minutes	Proc. Chnl. Descr.:	PDA 279.0 nm
Date Acquired:	6/26/2013 5:42:18 PM BST		
Date Processed:	10/7/2013 5:29:21 PM BST		

Auto-Scaled Chromatogram



Peak Results

	Name	Retention Time (min)	Area (µV*sec)	Percentage	Amount	E7_5CB	E7_7CB	E7_8OCB	E7_5CT
1	5CB	0.893	527644	51.29	0.258	Pass			
2	7CB	1.015	192513	24.91	0.125		Pass		
3	8OCB	1.469	156050	15.86	0.080			Pass	
4	5CT	1.744	102247	7.94	0.040				Pass

Sample Pass / Fail = Pass

Reported by User: System
Report Method: Merck E7 QC Report
Report Method ID: :2605
Page: 1 of 1

013_02_UPC2_FSC_LCD_JAC\2013_06_UPC2_FSC_E7_JAC
Date Printed:
10/8/2013
12:50:00 PM Europe/London

Figure 5. Merck E7 liquid crystal compositional custom QC reports.

CONCLUSIONS

By utilizing the efficiency of ACQUITY UPC^2 with PDA detection, a cost-effective, sensitive, and selective compositional analysis of E7 liquid crystal mixtures can be achieved.

The ratio of the individual liquid crystal intermediate compounds in the required mix is paramount to achieving optimum optical quality, performance, and lifetime of the electronic device. Therefore the ability to quantify the ratios is critical to ensuring optimum efficiency of the liquid crystal.

Many business and analytical benefits are provided when compared to HPLC for the analysis of E7 liquid crystal mixtures, with typically greater than a 20 fold increase in sample throughput and a 300 fold reduction in the volume of toxic solvent required.

Using the custom calculation functions available in Empower 3, results can quickly by reported, highlighting preset pass/fail criteria. By removing the need for manual calculations helps to eliminate potential human calculation errors.

References

1. Mouquinho A, Petrova K, Barros M T, and Sotomayor J. New Polymer Networks for PDLC Films Application, New Polymers for Special Applications, Chapter 5: 139-164. (2012) [cited 2013 August 6]. Available from: http://www.intechopen.com/books/new-polymers-for-special-applications/new-polymer-networks-for-pdlc-films-application.
2. Bedjaoui L, Gogibus N, Ewen B *et al.* Preferential salvation of the eutectic mixture of liquid crystal E7 in a polysiloxane. *Polymer.* (2004) 45: 6555-6560.
3. Mucha M. Polymer as an important component of blends and composites with liquid crystals. *Progress in Polymer Science.* (2003) 28: 837-873.
4. Brás A, Henriques S, Casimiro T, *et al.* Characterization of a Nematic Mixture by Reversed-Phase HPLC and UV Spectroscopy: Application to Phase Behavior Studies in Liquid Crystal-CO_2 Systems. Electronic-Liquid Crystal Communications. March 28, 2005. [cited 2013 May 20]. Available from: http://www.e-lc.org/tmp/M.___Dion%EDsio_2005_03_21_07_41_31.pdf .
5. Martin T, Hass W. Analysis of Liquid Crystal Mixtures. *Analytical Chemistry.* (1981) 53(4): 593-602.
6. Laclercq P, van den Bogaert H. Mass Spectra of Liquid Crystals. *Organic Mass Spectrometry.* (1991) 26: 276-278.

Waters

THE SCIENCE OF WHAT'S POSSIBLE.®

Waters Corporation
34 Maple Street
Milford, MA 01757 U.S.A.
T: 1 508 478 2000
F: 1 508 872 1990
www.waters.com