

Nematic–Isotropic Transition in Polymer-Confined and Polymer-Free Liquid Crystal Mixtures

F. Kuschel, L. Hartmann, M. Bauer

Fraunhofer Research Institution for Polymeric Materials and Composites PYCO, Teltow D-14513, Germany

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ABSTRACT: Depending on the processing conditions in liquid crystal (LC) display manufacturing, LC/polymer composite films may exhibit unusual properties with respect to the compositional and phase behavior of the LC constituents. In particular, we have observed extraordinary large shifts of phase transition temperatures in LC/polymer composites, which can not be explained by preferential solvation or adsorption. Therefore, the influence of real manufacturing conditions such as thermal stress, storage in vacuum, and UV irradiation on the nematic–isotropic (n–i) transition temperatures of commercial nematic mixtures was investigated. Shifts of the clearing temperature of up to 88 K, presumably due to partial evaporation

or UV degradation, were observed. Furthermore, we found that annealing may lead to the replacement of the nematic phase by the smectic A phase at room temperature in both LC/polymer composites and pure LC samples. Among the tested commercial LC blends, the mixtures E7, MLC-6650, and L101 showed the smallest stress effects. Practical consequences of our results are discussed. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 1486–1492, 2010

Key words: polymer/LC composites; phase separation; phase behavior; annealing; morphology

INTRODUCTION

Composites prepared from low molecular weight LCs and polymers are the object of research for several reasons. In basic research, a wide field is opened due to the large number of molecular structures and phases of both partners. Moreover, because of an improved mechanical stability and a better processability of LCs, such composites are of considerable practical interest, in particular for various electro-optical applications. For instance, polymer-dispersed liquid crystals (PDLCs), characterized by a biphasic structure consisting of separated LC droplets distributed in a polymer matrix, have been intensively investigated for applications as displays, light valves, or smart windows.^{1–4} Further on, heterogeneous films prepared from homogeneous LC/polymer mixtures by various phase separation techniques can be used to stabilize the cell gap of LC devices against external mechanical stress, especially if flexible substrates are involved. These composites consist of electro-optically active LC compartments that are isolated by coherent polymer walls.^{5–7}

However, in some cases, the properties of the LCs as component of LC/polymer composites deviate remarkably from those of the pure materials. Such changes concern primarily the composition of the LC-rich domains. Widely used nematic LCs are eutectic mixtures of several single components, for example, E7 and E44 (E. Merck). Besides a certain mutual solubility of the composite parts, in several systems, a fractionation of the LC constituents has been observed. For example, the gas chromatographic analysis of the composition of LC droplets in PDLC films made from E7 and NOA65 (Norland Products Inc.) revealed deviations from the original composition of E7, which have been attributed to different interactions between each of the LC components and the polymer.⁸ Also the heterogeneity of LC droplets formed after photo polymerization of isotropic E44/NOA65 mixtures is attributed to a fractionation caused by different affinities of the LC compounds to the NOA65 networks.⁹ In other investigations of the morphology and the phase behavior of various LC/polymer systems,^{10–14} the n–i transition temperature, that is, the clearing temperature T_c , was identified as a highly sensitive indicator for changes of the composition and was used for the comparison of different samples.

In nearly all systems, a considerable increase of T_c was found as consequence of an enrichment of those LC components with the highest clearing temperatures within the separated droplets.¹⁵ A nematic–

Correspondence to: M. Bauer (monika.bauer@pyco.fraunhofer.de).

isotropic phase transition 7 K higher than the clearing temperature of the pure LC mixture E7 has been found for E7/PMMA composites. This shift has been related to a preferential solvation of specific E7 constituents.¹⁶ The absence of such effects in composites prepared from poly(dimethylsiloxane) and single LC substances, for example, 4-cyano-4'-*n*-pentylbiphenyl or 4-cyano-4'-*n*-octylbiphenyl,^{11,13} provides further evidence for an irregular separation in case of multi-component LC phases.

While investigating techniques for cell gap stabilization in flexible displays by use of thermally induced phase separation (TIPS),⁷ we found several further LC/polymer composites with increased values of T_c for the LCs inside the compartments. The elucidation of causes for this effect is of general relevance because it appeared in filled display cells. Apart from a change in composition due to phase separation, changes of the LC mixture in thin films could also appear during the filling process by selective adsorption to the substrate surfaces, for example, in presence of ionic dopants.¹⁷ In our studies, using unsealed cells, we observed remarkable shifts of T_c parallel and perpendicular to the filling direction for several isotropic LC/polymer mixtures. In the latter case, the center line of the cell is a symmetry axis. Furthermore, the T_c shift was found to be dependent on the thermal pretreatment of the samples. For some LC mixtures and irrespective of the polymer agent, the increase of the n-i transition temperature was nearly 90 K. In particular, the observed T_c gradients could not be explained by selective LC separation and preferential solvation. Moreover, it is unlikely that these shifts and the lateral gradient were caused by chromatographic adsorption. Motivated by these observations, we investigated the impact of the conditions applied during the processing of LC/polymer composites (high temperatures, vacuum, UV irradiation) on the T_c of polymer-free commercial LC mixtures. Relatively extreme conditions during the fabrication of such composites are not unusual. For example, a batch composed of poly(vinylbutyral), LC-mixture, and chiral dopant has been processed at 140°C.¹⁸ Also, tetrahydrofuran used as solvent has been removed at room temperature under vacuum during 3 days.¹⁹ In a further example, the mixture of LC material with an UV curable precursor was exposed to UV radiation of 40 mW/cm² up to 800 s.⁹

In this contribution, the measurement of T_c of several nematic mixtures after thermal treatment, after storage in a vacuum degassing equipment, or after UV exposition shows a considerable expansion of the nematic phase toward higher temperatures. Furthermore, in one case, it was even observed that the nematic phase is replaced by the smectic A phase at ambient temperature. Obviously, these shifts of T_c and

TABLE I
Compositions of the Nematic Mixtures L101 and E7

| LC mixture | Component | wt % |
|------------|--|------|
| L101 | 4-pentyl-4'-cyanobiphenyl | 39.1 |
| | 4-heptyl-4'-cyanobiphenyl | 24.7 |
| | 4-octyl-4'-cyanobiphenyl | 13.3 |
| | 4-pentyl-4'-cyanoterphenyl | 9.1 |
| | 4-butylbenzoic acid-4'-cyanophenylester | 8.6 |
| | 4-pentylbenzoic acid-4'-cyanophenylester | 1.7 |
| E7 | 4-heptylbenzoic acid-4'-cyanophenylester | 3.4 |
| | 4-pentyl-4'-cyanobiphenyl | 51.0 |
| | 4-heptyl-4'-cyanobiphenyl | 25.0 |
| | 4-octyl-4'-cyanobiphenyl | 16.0 |
| | 4-pentyl-4'-cyanoterphenyl | 8.0 |

the change of phases are due to partial evaporation and selective UV degradation, respectively. The decreased fraction of higher volatile components is accompanied by the enrichment of constituents having a lower vapor pressure and a higher clearing temperature in the residue of annealed or vacuum-treated samples. This explanation is supported by GC-MS analysis, that is, a combined analysis using gas chromatography accompanied by mass spectroscopy.

EXPERIMENTAL

Materials

The nematic multicomponent LC mixtures used in these experiments are L101 (home made), E7, E63, MDA-00-1795, MDA-01-3250, MLC-6650 (Merck), and ZOC-1001XX, ZOC-1002XX, ZOC1003XX (Chisso Co.). As far as known, the chemical structures and compositions for L101 and E7 are given in Table I.

Both mixtures L101 and E7 contain 4-pentyl-4'-cyanoterphenyl as constituent with the highest T_c (240°C). ZOC-1002XX is a ten-component LC blend containing five compounds with clearing temperatures considerably higher than T_c of the eutectic mixture.²⁰

Poly(cyclohexyl methacrylate) (PCHMA) was used as polymer matrix. The preparation and properties of this polymer have been described elsewhere.⁷

Preparation of the samples

The LC/Polymer composite films were prepared as outlined in a previous paper.⁷

Samples of the unmodified LC mixtures were prepared using microscope slides (25 mm × 25 mm) and cover glasses (18 mm × 18 mm) as sketched in Figure 1.

Small droplets (about 0.5 μL) of the LC material were applied to form a free and a covered part of the sample [Fig. 1(a,b)].

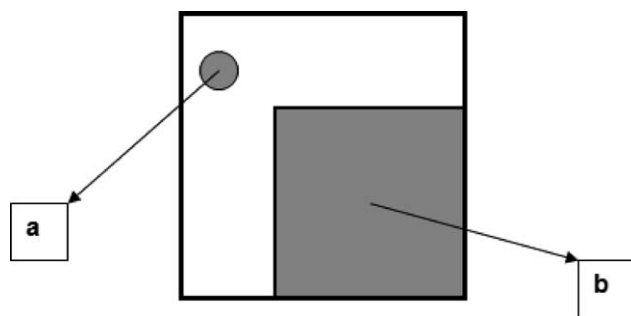


Figure 1 Scheme of sample preparation for thermal, evaporation, and UV exposure tests: (a) open droplet, (b) covered LC layer.

Methods

To study the effect of annealing, the samples were placed on a covered hot stage at 120°C for 90 min. A second set of samples was kept at room temperature in a vacuum chamber at 3×10^{-3} mbar for 240 min. Finally, the effect of UV irradiation was studied by exposure for 40 min with an UV-F 400F/EVG lamp (Panacol-Elosol, Oberursel/Germany) having an estimated power output of 20 mW/cm² at 370 nm. To maintain ambient temperature (25°C), a water-filled Petri dish was arranged between the light source and the samples.

To explore the phase separation and phase transition processes, the samples were placed on a homemade calibrated hot stage of a Nikon Labophot 2 polarizing microscope. Because the n-i phase transition of multicomponent LC mixtures is usually extended over a certain temperature interval, it was monitored during a heating run at 1 K/min crossing the biphasic region accompanied by a cooling run from the isotropic to the nematic phase. T_{c1} is the average of the temperatures at which the first isotropic droplets appeared during the heating run and the last isotropic domains disappeared during a cooling run, respectively. T_{c2} is the average of the temperatures where the last nematic domains disappeared in a heating run and the first nematic droplets were formed in a cooling run, respectively. Because of the local dependence of the n-i transition in open droplets, for each sample, the lowest (T_{c1}) and the highest (T_{c2}) values were registered. In case of covered layers, these data have been recorded at the middle of the samples. Generally, T_c^0 data are given for the unstressed (original) LC material, whereas T_c^{ex} data are refer to the exposed ones.

In addition, the effect of the different sample treatments on the composition of selected LC mixtures has been investigated by a combined gas chromatography and mass spectrometry (GC-MS) analysis using a Trace GC Ultra Gas Chromatograph coupled with a Thermo Scientific DSQ II Single Quadrupole Mass Spectrometer.

RESULTS AND DISCUSSION

Nematic-isotropic transition of unstressed LC mixtures

First of all, the transition temperatures of unstressed nematic mixtures had to be verified in view of the intended comparison with stressed samples. The mean n-i transition temperatures T_c and the transition regions δT_c of original commercial LC mixtures are summarized in Table II. These data are given by

$$T_c = (T_{c1} + T_{c2})/2 \quad \text{and} \quad \delta T_c = (T_{c2} - T_{c1})/2.$$

T_c^s is the clearing temperature taken from supplier's data sheets.

Differences between T_c^s and T_c^0 may be due to variations in different product charges or the use of different measuring techniques, for example, differential scanning calorimetry versus microscopic observation. The data for T_c^0 of Table II served for comparison with the corresponding values of stressed samples, T_c^{ex} .

Nematic-isotropic transition of LC mixtures in polymer matrices

Among the LC/polymer composites investigated previously,⁷ the nematic to isotropic transition in blends containing ZOC-1002XX showed the strongest deviations from the pure LC mixture. Apart from a general increase of T_c of up to 30 K, there was a strong dependence of T_c on the location of the measuring spot in the sample's surface. Generally, a transition gradient parallel and perpendicular to the direction of cell filling was observed. The formation of LC droplets by thermal induced phase separation during cooling the LC/PCHMA composite layers from 120°C started always at the cell edges [Fig. 2(a)]. After reaching room temperature, an insular pattern consisting of nematic droplets surrounded by polymer walls was formed in the middle of the sample [Fig. 2(b)]. A coexistence of nematic and smectic A droplets could be observed in a transition region [Fig. 2(c)]. Finally, a change of the LC mixture's composition caused the

TABLE II
Nematic-Isotropic Transition Temperatures of Commercial LC Mixtures

| LC mixture | $(T_c^0 \pm \delta T_c^0)/^\circ\text{C}$ | $T_c^s/^\circ\text{C}$ |
|-------------|---|------------------------|
| L101 | 57 ± 1.5 | 60 |
| E7 | 57 ± 1.5 | 60.5 |
| E63 | 85 ± 5.5 | 82 |
| MDA-00-1795 | 101 ± 3.5 | 100 |
| MDA-01-3250 | 117 ± 3.5 | 113 |
| MLC-6650 | 93 ± 7.5 | 90 |
| ZOC-1001XX | 66 ± 2 | 67.2 |
| ZOC-1002XX | 79 ± 2.5 | 79.2 |
| ZOC-1003XX | 77 ± 2 | 76.7 |

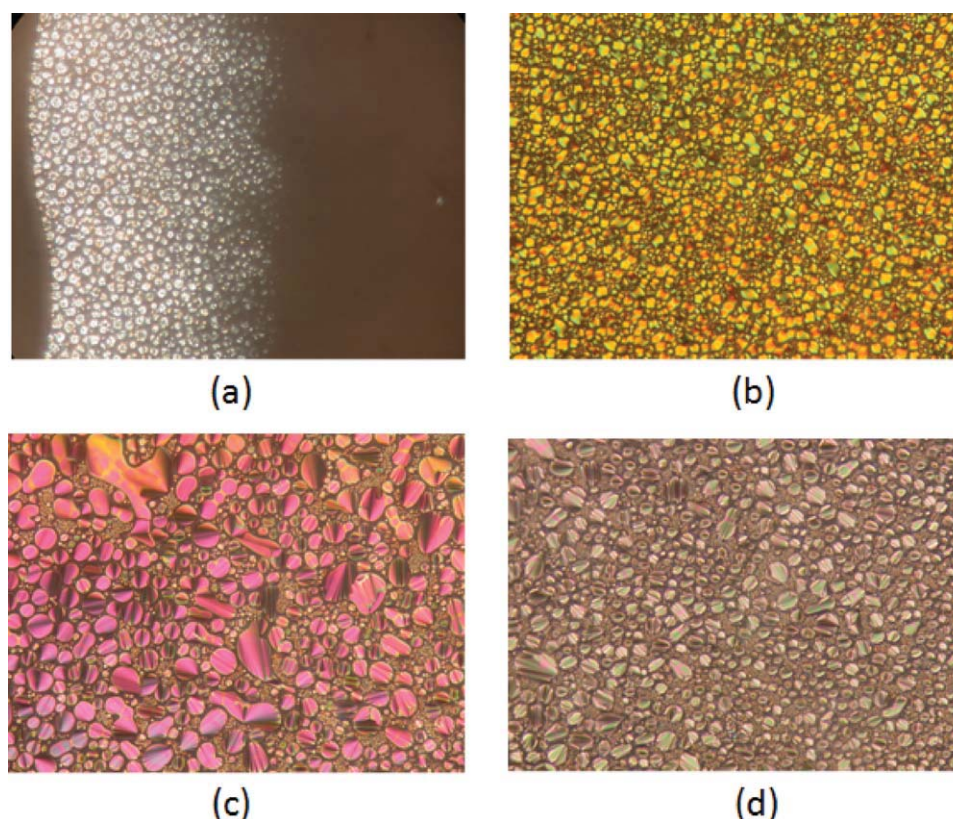


Figure 2 Polarizing optical microscope (POM) images (crossed polarizers) of LC/polymer composite films prepared from ZOC-1002XX/PCHMA (80/20 wt %) in glass cells. (a) Formation of nematic droplets starting from a cell edge (left) at 100°C, (b) Insular pattern of nematic droplets enclosed by polymer walls in the middle of the sample, (c) Transition zone of nematic to smectic A droplets, (d) Smectic A droplets close to the filling hole of the cell. (b)–(d) are captured at 25°C. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

formation of smectic A droplets in close vicinity to the edges [Fig. 2(d)].

To explore the essential cause of these effects, comparative studies with polymer-free samples of different room temperature nematic mixtures were performed.

Annealing

For the samples subjected to the annealing program, the ($T_c^{\text{ex}} \pm \delta T_c^{\text{ex}}$) data are collected in Table III. In addition, the shift of T_c caused by thermal stress is indicated as

$$\Delta T_c = T_c^{\text{ex}} - T_c^0.$$

Table III reveals an increase of T_c of up to 88 K after the thermal treatment and for the uncovered material. However, a remarkable broadening of the transition interval was not detected. These observations evoked the interest to explore the properties of thin LC films obtained after filling of display-like glass cells at elevated temperatures. For this purpose, ZOC-1002XX was filled at 115°C by capillary forces in a 30 mm × 10 mm glass cell of 3.5 μm cell gap. After cooling at 1 K/

min, the inner surface of the heating chamber's lid was fogged indicating partial sample evaporation. The LC film showed a clear dependence of T_c on the location of the measuring spot. In Figure 3(a), the disappearance of the nematic phase starting from the middle of the cell toward the filling edge during slow heating is recorded at 96°C. Filling another cell in the same manner at 125°C and cooling it to room temperature yielded textures in the vicinity of the filling edge as shown in Figure 3(b,c). While in close proximity of the edge, the typical fan-shaped texture of the SmA phase²¹ was formed [Fig. 3(b)], in the inner area of the cell, a gradual transition to a nematic Schlieren texture has been observed [Fig. 3(c)]. Such transition regions could be observed near all edges of the cell.

In a further attempt, a small droplet of ZOC-1002XX was annealed at 150°C for 30 min. After cooling to room temperature, the microscopic texture formed between the glass slides is shown in Figure 3(d). It reveals a disordered broken fan-shaped texture.

Vacuum test

The results obtained after storage of the samples in a vacuum degassing equipment are given in Table IV.

TABLE III
Nematic–Isotropic Transition after Annealing

| LC mixture | Open droplet | | Covered layer | |
|-------------|---|------------------|---|------------------|
| | $T_c^{\text{ex}} \pm \delta T_c^{\text{ex}}$ (°C) | ΔT_c (K) | $T_c^{\text{ex}} \pm \delta T_c^{\text{ex}}$ (°C) | ΔT_c (K) |
| L101 | 69 ± 3 | 12 | 58 ± 1 | 1 |
| E7 | 57 ± 2 | 0 | 57 ± 1.5 | 0 |
| E63 | 101 ± 8 | 16 | 85 ± 5.5 | 0 |
| MDA-00–1795 | 127 ± 8 | 26 | 106 ± 2 | 5 |
| MDA-01–3250 | 137 ± 3 | 20 | 122 ± 3 | 5 |
| MLC-6650 | 100 ± 18 | 7 | 95 ± 6.5 | 2 |
| ZOC-1001XX | 151 ± 5 | 85 | 75 ± 2.5 | 9 |
| ZOC-1002XX | 122 ± 2 | 43 | 109 ± 1.5 | 30 |
| ZOC-1003XX | 165 ± 2 | 88 | 121 ± 1 | 44 |

Partial evaporation from free material can also cause a considerable shift of T_c toward higher temperatures.

UV irradiation

The effect of UVA irradiation on the n–i transition of the covered composite samples shown in Table V is marginal except mixture MDA-01-3250. Here, a relative large T_c depression of -10 K showed up and the sample was partly discolored.

GC-MS studies

Because Tables III and IV reveal exceptionally large annealing and vacuum effects for ZOC-1003XX, this mixture has been subjected to a GC-MS analysis prior and after these sample treatments. Figure 4 shows the gas chromatograms of the original sample [Fig. 4(a), ZOC/O] and of the stressed samples [Fig. 4(b–d)].

The comparison discloses clearly the following effects: After annealing, the gas chromatogram of

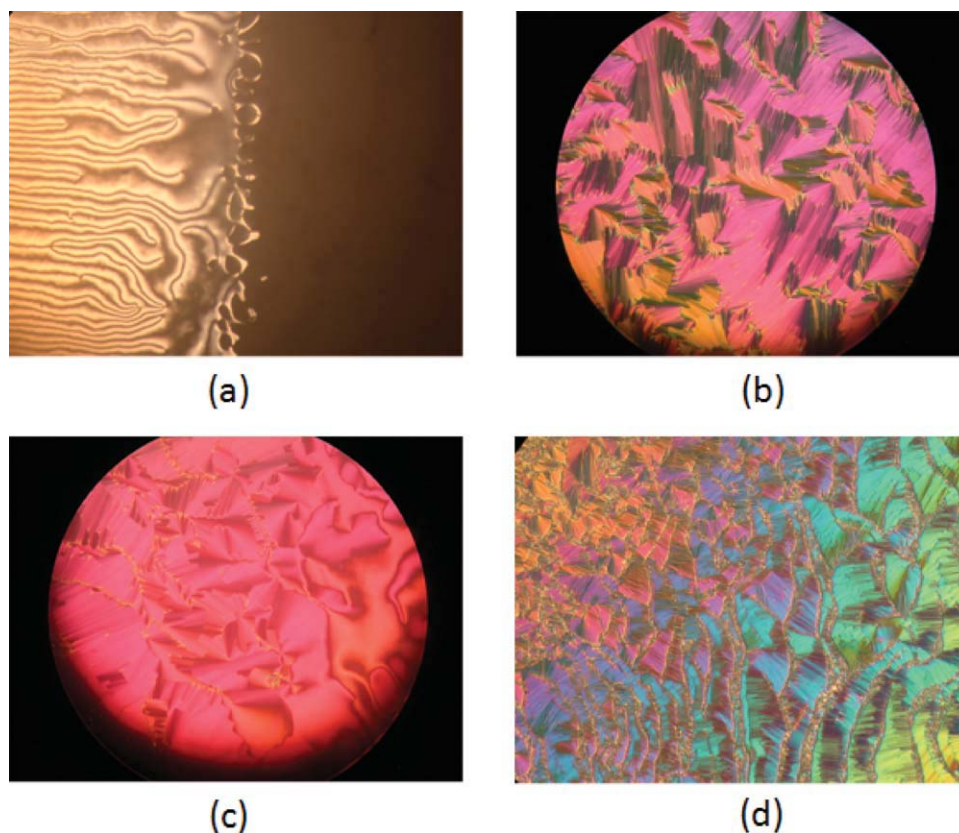


Figure 3 POM images (crossed polarizers) of ZOC-1002XX in glass cells after thermal stress. (a) Growing of the nematic phase starting from the cell edge (left) toward the middle of the cell during cooling, recorded at 96°C . (b) Smectic A fan-shaped texture formed directly at the filling edge. (c) Coexistence of the nematic and the smectic A phase in a transition region. (d) Broken fan-shaped texture after annealing at 150°C . (b)–(d) are captured at room temperature. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE IV
Shifts of the Nematic–Isotropic Transition Temperatures after Storage under Vacuum

| LC mixture | Open droplet | | Covered layer | |
|-------------|---|------------------|---|------------------|
| | $T_c^{\text{ex}} \pm \delta T_c^{\text{ex}}$ (°C) | ΔT_c (K) | $T_c^{\text{ex}} \pm \delta T_c^{\text{ex}}$ (°C) | ΔT_c (K) |
| L101 | 55 ± 1 | −2 | 57 ± 1.5 | 0 |
| E7 | 55 ± 3 | −2 | 57 ± 1.5 | 0 |
| E63 | 90 ± 7 | 5 | 85 ± 5.5 | 0 |
| MDA-00-1795 | 109 ± 8 | 8 | 101 ± 2.5 | 0 |
| MDA-01-3250 | 127 ± 7 | 10 | 117 ± 2.5 | 0 |
| MLC-6650 | 91 ± 11 | 2 | 93 ± 8 | 0 |
| ZOC-1001XX | 110 ± 3 | 44 | 71 ± 2.5 | 5 |
| ZOC-1002XX | 126 ± 1 | 47 | 87 ± 1 | 8 |
| ZOC-1003XX | 165 ± 3 | 88 | 83 ± 1.5 | 6 |

the residue (ZOC/R) taken from the heating chamber shows a relative decrease of peaks at short retention times which is attributed to the evaporation of the most volatile components of the mixture. Furthermore, a relative increase is observed at longer times originating from the remaining less volatile components. In the chromatogram of the condensation film taken from the lid of the heating chamber (ZOC/C), in a complementary manner the peaks at long retention times disappear, while those at short times remain almost unchanged. The chromatogram of the vacuum-treated sample (ZOC/V) is similar to that of ZOC/R.

Based on simulations of the mass spectra, the following explanation has been derived: The retention times below 22 min may be attributed to two-ring aromatic or cyclohexane mesogens, such as 2-(3,4-difluorophenyl-5-propylpyrimidine) (18.43 min), 4-(4-ethylcyclohexyl)benzotrile (19.61 min), and 4-(4-pentyl-cyclohexyl)benzotrile (20.65 min). On the other hand, at longer retention times mainly three-ring mesogens, for example, 5-alkyl-2-(4'-fluorobiphenyl-4-yl)-pyrimidines (26.32 min and further) are displayed. As it is known,²² the vapor pressure of LC components decreases and the clearing temperatures increases with increasing number of rings which are directly bonded to each other.

TABLE V
Shifts of the Nematic–Isotropic Transition Temperatures after Storage under UV Irradiation

| LC mixture | $T_c^{\text{ex}} \pm \delta T_c^{\text{ex}}$ (°C) | ΔT_c (K) |
|-------------|---|------------------|
| L101 | 55 ± 2 | −2 |
| E7 | 57 ± 1.5 | 0 |
| E63 | 83 ± 4.5 | 2 |
| MDA-00-1795 | 102 ± 3 | −1 |
| MDA-01-3250 | 107 ± 8.5 | −10 |
| MLC-6650 | 93 ± 8 | 0 |
| ZOC-1001XX | 65 ± 2 | −1 |
| ZOC-1002XX | 81 ± 2 | −2 |
| ZOC-1003XX | 75 ± 1.5 | −2 |

CONCLUSIONS

This study has been initiated by numerous reports on an increase of the clearing temperature T_c of up to 10 K in LC/polymer composite films prepared from multicomponent nematic LC mixtures. This increase is explained by preferential solvation of certain LC components in the polymer matrix or by selective chromatographic adsorption on substrates.

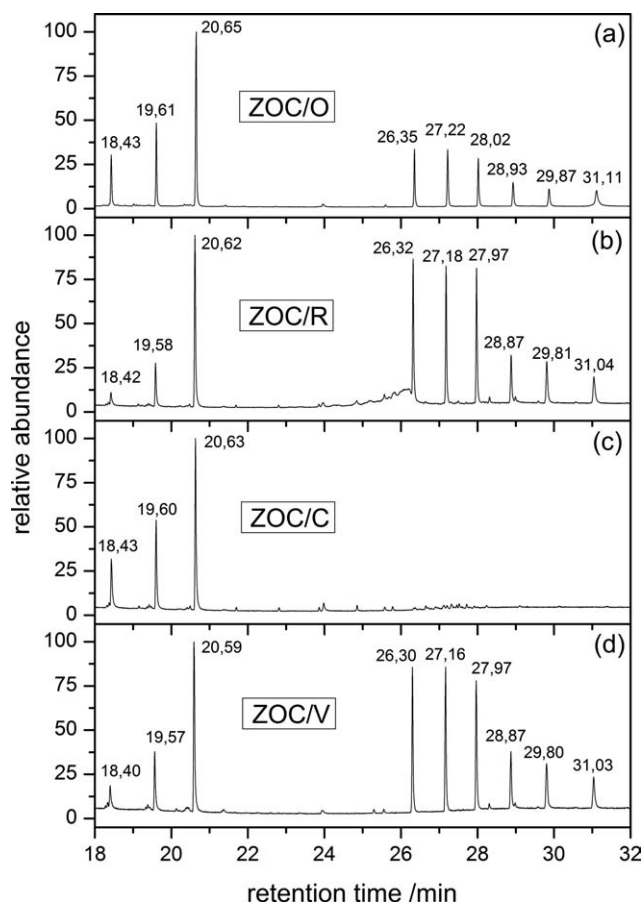


Figure 4 Gas chromatograms of ZOC-1003XX: (a) original mixture (ZOC/O), (b) residue (ZOC/R), (c) condensate after annealing (ZOC/C), and (d) after vacuum treatment (ZOC/V). All curves are normalized to the peak at a retention time of around 20.62 min.

In our previous studies on the formation of nematic LC compartments in polymer matrices,⁷ we found an increase of the clearing temperature of up to 30 K in composite films fabricated from different commercial LC mixtures and a series of poly(methacrylates) bearing alkyl or cycloalkyl substituents. To elucidate these comparatively large shifts of T_{cr} , the impact of real conditions for manufacturing and treatment of LC/polymer composites, namely thermal stress, storage under vacuum, and storage under UV irradiation, on the n-i phase transition temperature of commercial nematic mixtures was investigated.

The most striking result is that the observed shift of the n-i phase transition temperature can be as much as 88 K. Besides shifts of T_{cr} , in one case a phase transition from nematic to smectic A has been observed after cooling the thermally stressed material to room temperature. Annealing or vacuum treatment causes partial evaporation of the more volatile components accompanied by enrichment of components having lower vapor pressures and higher clearing temperatures in the residue. Finally, UV irradiation may induce partial photochemical degradation and discoloration. Using a particularly sensitive LC mixture, composition changes were recorded by GC studies and structurally interpreted by simulation of associated mass spectra. Obviously, annealing of LC mixtures containing components with strongly different volatility may cause a considerably widening of the LC phase region toward higher temperatures.

In summary, among the LC mixtures investigated in this study, E7, MLC-6650, and L101 showed the highest stability. Consequently, to avoid difficulties during fabrication and operation of devices based on LC/polymer composites, the initial LC material must be subjected to corresponding tests with respect to the compositional and phase stability. The more the LC material is exposed to extreme conditions (temperature, vacuum, UV irradiation), the more important are such preliminary tests.

The selection of the commercial LC mixtures used in this study is not representative for the actual offer of the respective suppliers.

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References

1. Craighead, H. G.; Cheng, J.; Hackwood, S. *Appl Phys Lett* 1982, 40, 22.
2. Doane, J. W.; Vaz, N. A.; Wu, B.-G.; Žumer, S. *Appl Phys Lett* 1986, 48, 269.
3. Drzaic, P. S. *Liquid Crystal Dispersions*; World Scientific: Singapore, 1995.
4. Doane, J. W. *Liq Cryst* 2006, 33, 1313.
5. Shiyonovskaya, I.; Khan, A.; Green, S.; Magyar, G.; Pishnyak, O.; Marhefka, D.; Doane, J. W. *J Soc Inf Display* 2006, 14, 181.
6. Chari, K.; Kowalczyk, J.; Rankin, C. M.; Johnson, D. M.; Blanton, T. N.; Capurso, R. G. *Digest Tech Pap Soc Inf Display Int Symp*, 2006, 37, 1741.
7. Bauer, M.; Hartmann, L.; Kuschel, F.; Seiler, B.; Noack, E. *J Appl Polym Sci*, accepted for publication.
8. Nolan, P.; Tillin, M.; Coates, D. *Mol Cryst Liq Cryst Lett* 1992, 8, 129.
9. Nwabunma, D.; Kyu, T. *Polymer* 2001, 42, 801.
10. Bouchaour, T.; Benmouna, F.; Leclercq, L.; Ewen, B.; Coqueret, X.; Benmouna, M.; Maschke, U. *Liq Cryst* 2000, 27, 413.
11. Gigobus, N.; Benmouna, F.; Ewen, B.; Pakula, T.; Coqueret, X.; Benmouna, M.; Maschke, U. *J Polym Sci Part B Polym Phys* 2003, 41, 39.
12. Bedjaoui, L.; Bouchaour, T.; Benmouna, M.; Coqueret, X.; Maschke, U. *Mol Cryst Liq Cryst* 2004, 411, 537.
13. Gigobus, N.; Maschke, U.; Benmouna, F.; Ewen, B.; Coqueret, X.; Benmouna, M. *J Polym Sci Part B Polym Phys* 2001, 39, 581.
14. Gigobus, N.; Maschke, U.; Benmouna, F.; Ewen, B.; Coqueret, X.; Benmouna, M. *Eur Polym J* 2001, 37, 1079.
15. Bedjaoui, L.; Gigobus, N.; Ewen, B.; Pakula, T.; Coqueret, X.; Benmouna, M.; Maschke, U. *Polymer* 2004, 43, 6555.
16. Deshmukh, R. R.; Malik, M. K. *J Appl Polym Sci* 2008, 109, 627.
17. Mitrokhin, M. V.; Johnsen, L.; Fagerberg, R.; Holter, B.; Arisov, V. L. *Liq Cryst* 2004, 31, 317.
18. Crooker, P. P.; Yang, D. K. *Appl Phys Lett* 1990, 57, 2529.
19. Kyu, T.; Shen, C.; Chiu, H.-W. *Mol Cryst Liq Cryst* 1996, 287, 27.
20. Chisso Petrochemical Corporation; personal information: Tokyo/Japan, 2008;
21. Demus, D. *Fascinating Liquid Crystals; Books on Demand GmbH: Norderstedt/Germany*, 2007; p 32.
22. Demus, D.; Goodby, J.; Gray, G. W.; Spiess, H.-W.; Vill, V., Eds. *Handbook of Liquid Crystals*; Wiley-VCH: Weinheim, 1998.