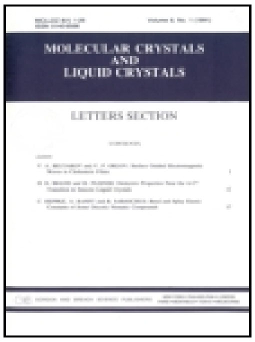


Molecular Crystals and Liquid Crystals

ISSN: 1542-1406 (Print) 1563-5287 (Online) Journal homepage: http://www.tandfonline.com/loi/gmcl20

Chemical-Physical Characterization of a Binary Mixture Made of a Photosensitive Azobenzene Derivative and a Smectogen

Eleonora Borello, Mario Cifelli, Celia Duce, Giancarlo Galli, Maria Rosaria Tine', Vera Hamplova, Gabriela Ambrozic & Valentina Domenici

To cite this article: Eleonora Borello, Mario Cifelli, Celia Duce, Giancarlo Galli, Maria Rosaria Tine', Vera Hamplova, Gabriela Ambrozic & Valentina Domenici (2015) Chemical-Physical Characterization of a Binary Mixture Made of a Photosensitive Azobenzene Derivative and a Smectogen, Molecular Crystals and Liquid Crystals, 614:1, 54-61, DOI: 10.1080/15421406.2015.1049908

To link to this article: http://dx.doi.org/10.1080/15421406.2015.1049908

Mol. Cryst. Liq. Cryst., Vol. 614: pp. 54–61, 2015
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2015.1049908

Chemical-Physical Characterization of a Binary Mixture Made of a Photosensitive Azobenzene Derivative and a Smectogen

ELEONORA BORELLO,[1] MARIO CIFELLI,[1] CELIA DUCE,[1]
GIANCARLO GALLI,[1] MARIA ROSARIA TINE',[1]
VERA HAMPLOVA,[2] GABRIELA AMBROZIC,[3]
AND VALENTINA DOMENICI[1,*]

[1]Dipartimento di Chimica e Chimica Industriale, Università di Pisa, Pisa, Italy
[2]Department of Dielectrics, Institute of Physics, Academy of Sciences of the Czech Republic, Prague, Czech Republic
[3]National Institute of Chemistry, Ljubljana, Slovenia

We present the characterization of new binary mixtures made of two rod-like molecules: a photosensitive azobenzene derivative (called J7*) and a smectogen (called* M11*). The interest in these two specific compounds is related to their use as basic constituents of photo-active liquid crystalline elastomers and their opto-mechanic applications. Differential scanning calorimetry and polarized optical microscopy were used to characterize the phase diagram of the binary system* J7-M11*. ^{2}H NMR spectroscopy of the ^{2}H-selectively labelled* M11*, either alone or as a probe in binary mixtures containing different ratios* J7/M11*, was applied to study the orientational ordering properties.*

Keywords liquid crystalline mixture; nematic; smectic A; photosensitive molecules; DSC; ^{2}H NMR

1. Introduction

Most of technological devices based on liquid crystals contain mixtures of different mesogens, and not pure compounds. As an example, liquid crystals used as solvents are made by two or more compounds in order to tune several physical properties or to widen the temperature range of mesophase stability. Commercial liquid crystals used in temperature sensors and optical devices are typically composed of binary or ternary mixtures [1]. This is also due to the aim to combine the properties of the different components, such as the occurrence of a nematic phase, the positive or negative magnetic susceptibility, the high conductivity, the photo-sensitivity and so on [2,3,4,5].

The response to visible light [6] is essential in many liquid crystal applications and among the most studied compounds, the azobenzene derivatives [7] are promising due to their *trans* to *cis* photoisomerization and consequent change of their molecular shape

---

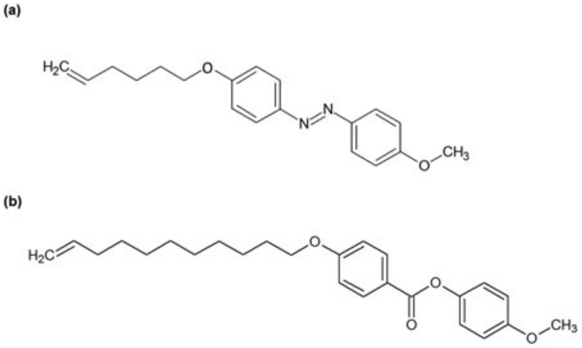
[*]Address correspondence to Valentina Domenici, Dipartimento di Chimica e Chimica Industriale, Università di Pisa, via Moruzzi 13, 56124, Pisa, Italy. E-mail: valentina.domenici@unipi.it

Color versions of one or more of the figures in the article can be found online at www.tandfonline.com/gmcl.

[8,9]. For instance, the incorporation of azobenzene derivatives as dopants [10], chemically bonded pendant units [11], as well as photo-crosslinkers [12,13] into liquid crystalline polymers [14] and elastomers [15] has been widely explored with the purpose to enhance existing material properties or to enable new effects. Examples include the photo-induced alignment [16] and photo-induced optical anisotropy [17], the light-induced nanopatterning and nanowriting [18] and various properties related to optical and holographic applications [19,20,21,22].

In all these photo-active liquid crystalline systems, the azobenzene derivatives are present in low percentage, to avoid too high absorbance and to maintain a relative good transparency of the matrix. They are usually mixed with other mesogens, nematic or smectic ones, depending on the final desired mesomorphic properties. The characterization of the chemical-physical properties of the resulting binary or ternary mixture is in order to assess the potential for practical application.

In this work, a binary system made of an azomesogen, (E)-4,4′-(hex-5-en-1-yloxy)-4′-methoxyazobenzene (namely **J7**), and a smectogen, 4-methoxyphenyl 4-(undec-10-en-1-yloxy) benzoate (namely **M11**), is investigated (see **Scheme 1**). These two molecules are basic components of liquid crystalline elastomers having optical properties [19–22,23].



Scheme 1. Molecular structure of the molecules used to prepare the liquid crystalline mixture: (a) the azomesogen, **J7**; (b) the smectogen, **M11**.

The mesomorphic behaviour and self-assembling properties of the binary system, by varying the relative percentage of the two compounds, **J7** and **M11**, were studied by differential scanning calorimetry (DSC) and polarized optical microscopy (POM). By varying the ratio between the two molecules, we obtained liquid crystalline systems exhibiting a nematic or both nematic and smectic A phases. The orientational ordering properties of some of these mixtures were also investigated by means of ^{2}H NMR spectroscopy.

2. Experimental Section

The syntheses of the azobenzene derivative **J7** and the smectogen **M11** are reported in Ref.s [23,24,25,26]. The binary mixtures were prepared by mixing and then heating/cooling several times the weighed exact amounts of the two compounds in order to obtain a homogeneous mixture.

Sequence of phases and phase transition temperatures of the investigated binary mixtures (see **Table 1**) were determined on heating/cooling to/from the isotropic phase by identification of characteristic textures and their changes observed in a polarizing optical

Table 1. Sequence of phases and phase transition temperatures (°C) as obtained by DSC for the liquid crystalline binary mixtures investigated in this work (the weight percentage of J7 is indicated to specify the mixture). Details of DSC measurements are reported in the text.

wt% J7	phase	*T(°C)*	phase	*T(°C)*	phase	*T(°C)*	Phase
0	**Cr**	30.7	**SmA**	43.0	**N**	71.2	**Iso**
9.9	**Cr**	20.3	**SmA**	32.5	**N**	70.8	**Iso**
18.5	**Cr**	18.2	**SmA**	29.0	**N**	71.2	**Iso**
29.5	**Cr**	22.0	/		**N**	71.7	**Iso**
41.7	**Cr**	15.2	/		**N**	72.0	**Iso**
50.8	**Cr**	33.2	/		**N**	73.5	**Iso**
60.2	**Cr**	41.8	/		**N**	74.0	**Iso**
69.5	**Cr**	48.8	/		**N**	74.7	**Iso**
79.1	**Cr**	54.8	/		**N**	75.5	**Iso**
90.1	**Cr**	59.8	/		**N**	77.8	**Iso**
100	**Cr**	60.5	/		**N**	71.7	**Iso**

microscope (**POM**) (Reichert-Jung Polyvar). A heating stage with a temperature programmer was used for the temperature control, which enabled temperature stabilization within 0.1°C.

Phase transition temperatures of these mixtures were also evaluated from Differential Scanning Calorimeter (**DSC**) (Pyris Diamond DSC by Perkin Elmer) on cooling and heating the sample at rates of 3 and 10°C min^{-1}. Several cycles were performed to check the reproducibility of the mesophase transitions. The sample (about 3 mg) hermetically sealed in aluminium pan was placed in a nitrogen atmosphere. The temperature was calibrated on extrapolated onsets of melting points of water, indium and zinc.

^{2}H NMR spectra were acquired by means of a 400 MHz Bruker Avance I spectrometer, with a Deuterium Larmor frequency of 61.4MHz. A solid echo pulse sequence was used with a 90° pulse of 15 μs, echo delay of 40 μs, 128 scans, 0.5s of recycle delay and proton decoupling. To acquire ^{2}H NMR spectra of the mixtures, a small percentage (less than 5%) of M11 ^{2}H-labelled on the first aromatic ring was used.

Data analysis was performed by using Excel and home-made package working with Mathematica 5.2.

3. Results and Discussions

Pure compounds, J7 and M11, and several mixtures of J7/M11, as indicated in ***Table 1***, were investigated in order to characterize their mesomorphic properties. POM and DSC measurements confirmed that pure compounds are both mesogens: The azobenzene derivative J7 has a nematic phase stable in a short temperature range (about 11 degrees), while the mesogen M11 shows a nematic and a smectic A phases. For both compounds, the mesophases are stable at temperature higher than room temperature, thus hampering their use in most of technological applications.

The different J7/M11 mixtures were also investigated by means of DSC as described in the previous section. DSC curves recorded at the third cooling cycle are reported in **Figure 1**. In all DSC curves, it is possible to note the presence of a small peak at high temperatures (in the range 70–80°C), indicating a transition between the isotropic and the

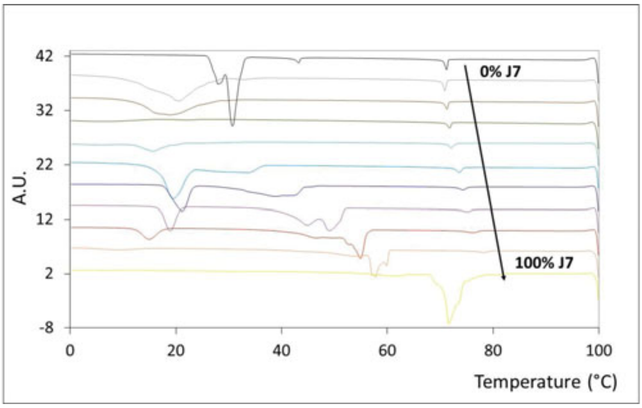
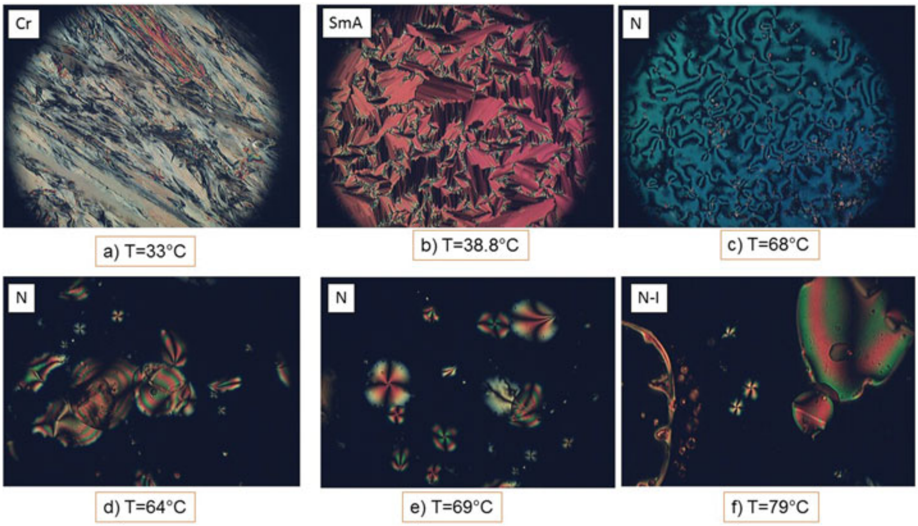


Figure 1. DSC curves of the third cooling cycle at 10°C/min of different J7/M11 binary mixtures containing a percentage of J7 ranging from 0% (top) to 100% (bottom).

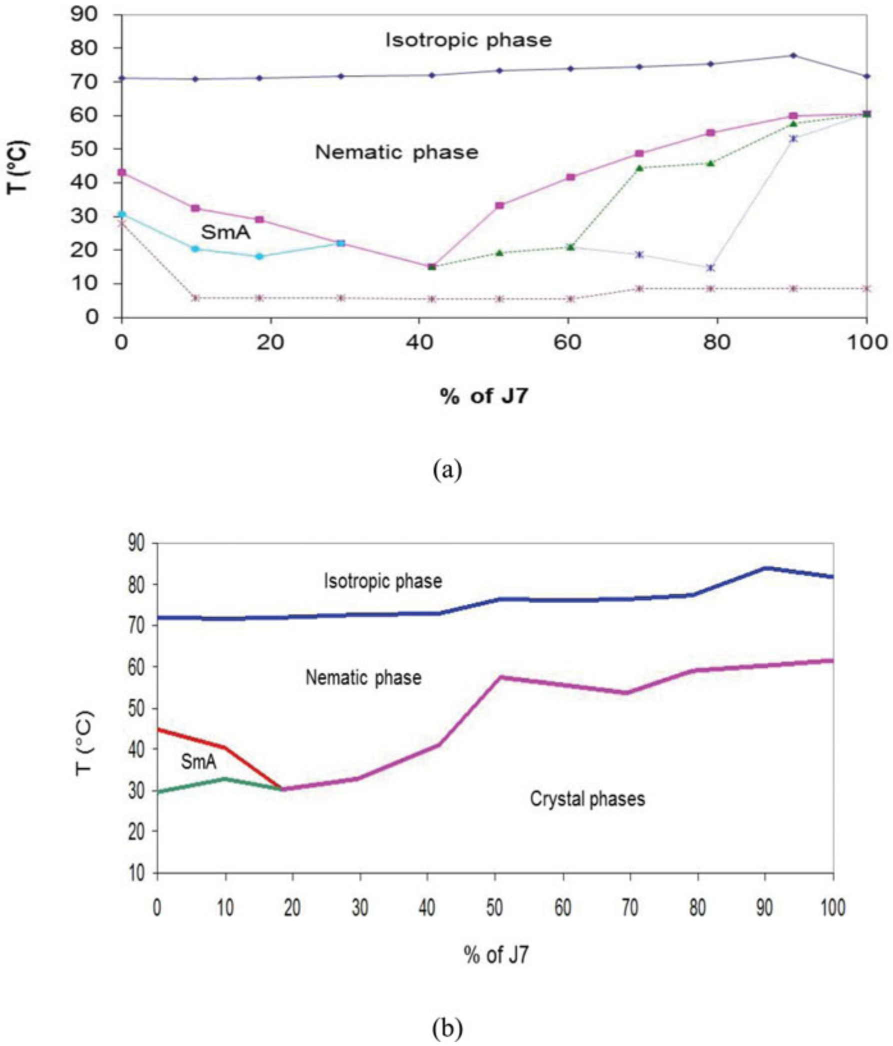
nematic phases. At weight percentage of J7 lower than 30%, an additional small peak is observed at lower temperatures (in the range 30–40°C), revealing a further transition between the nematic and the smectic A phase (identified by POM). The transition to the crystal phase (in the range 20–60°C), is characterized by one or more quite broad peaks, which can be attributed to the crystallization of the eutectic and/or pure components. These crystallization transitions are sensitive to the cooling/heating rate, as typically observed in liquid crystals [27].

The clear identification of the mesophases, as reported in **Table 1**, bases on POM observations. In **Figure 2** typical images obtained for two mixtures having different percentages of J7 and M11 are reported. **Figures 2a, 2b** and **2c** show the typical crystal, smectic A



a) T=33°C
b) T=38.8°C
c) T=68°C
d) T=64°C
e) T=69°C
f) T=79°C

Figure 2. (a), (b) and (c): images obtained by POM at different temperatures of the binary mixture formed by 9.9wt% J7; (d), (e) and (f): images obtained by POM at different temperatures of the binary mixture formed by 90.1wt% J7.



(a)

(b)

Figure 3. Phase diagrams of the binary mixtures J7/M11 as obtained by DSC (a) and by POM (b) measurements. Solid lines refer to mesophase transitions, while dotted lines (a) correspond to crystallization of segregated portions of the samples and not reproducible crystal-crystal transitions, as discussed in the text.

and nematic textures, respectively, for a mixture containing more than 90% in weight of the smectogen M11. **Figures 2d, 2e** and **2f** show the POM images recorded at different temperatures in the nematic phase of a mixture containing more than 90% in weight of the azomesogen J7. Schlieren textures (**Fig. 2b**), fan-shaped textures (**Fig. 2c**) and Maltese cross textures (**Fig. 2e**) are indeed specific for the above mesophases.

On the basis of both DSC and POM investigations, a phase diagram of the binary system was obtained. The phase diagrams (temperature vs weight percentage of the azomesogen J7) obtained from DSC and POM studies are reported in **Figures 3a** and **3b**, respectively.

Except for the presence of different crystallization temperatures (dotted curves in **Figure 3a**), the two phase diagrams are very similar and they clearly show a quite wide

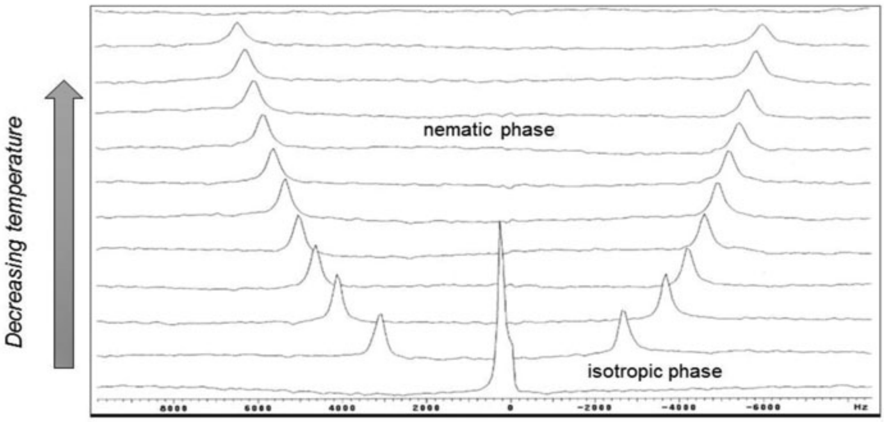


Figure 4. Stackplot of ^{2}H NMR spectra of a binary mixture containing 26.5wt% J7 and 4.6wt% ^{2}H-labelled **M11**). Spectra are recorded by cooling the sample from the isotropic phase to the crystal one, from 75°C to 30°C.

range of stability of the nematic phase, independent of the percentage of azomesogen J7, and the occurrence of a smectic A phase at percentage of J7 less than 30%.

There exists also a eutectic point at intermediate percentage of azomesogen (from 30 to 40% by DSC and from 20 to 30% by POM). This fact is interesting from an applicative point of view, since the crystallization temperature is below room temperature, indicating that this specific relative ratio of J7/M11 shows a nematic phase at room temperature.

The homogeneity of the liquid crystalline mixtures and their orientational properties can be investigated by means of ^{2}H NMR spectroscopy [28, 29]. To this purpose several binary mixtures were prepared by using small percentage of ^{2}H-selectively labelled M11 on the first phenyl ring (close to the long chain, see **Scheme 1b**) in the positions 3,3′. A selection of ^{2}H NMR, ^{1}H decoupled, spectra recorded on cooling the sample from the isotropic phase to the crystal one for a mixture containing 26.5wt% J7 is shown in **Figure 4**. The presence of sharp peaks and a single doublet in the mesophase range confirms the homogeneity of the mixture.

As shown in the phase diagrams (**Fig. 3**), this percentage of J7 corresponds to the occurrence of a nematic phase stable in a wide temperature range and this is confirmed by the observed quadrupolar splitting shown in **Fig. 4**. The quadrupolar splitting ($\Delta\nu_q$) is temperature-dependent and, in principle, it can be analyzed in order to get information about the molecular orientational order parameters, S_{zz} and Δ_{biax} ($= S_{xx}$-S_{yy}), by using the following equation [30]:

$$\Delta\nu_q = \frac{3}{2}q_{aa}\left\{S_{zz}\left(\cos^2\phi - \frac{1}{2}\sin^2\phi - \frac{\eta}{6}\cos^2\phi + \frac{\eta}{6} + \frac{\eta}{3}\sin^2\phi\right)\right.$$
$$\left. + \ \Delta_{biax}\left(\frac{1}{2}\sin^2\phi + \frac{\eta}{6}\cos^2\phi + \frac{\eta}{6}\right)\right\} \tag{1}$$

In our case, the molecular biaxiality is neglected, thus reducing the complexity of the equation. The parameterη is fixed to 0.04 and q_{aa} to 185 kHz, according to the literature [30]. The angle φ between the C-D bond and the *para* axis of the phenyl ring has been

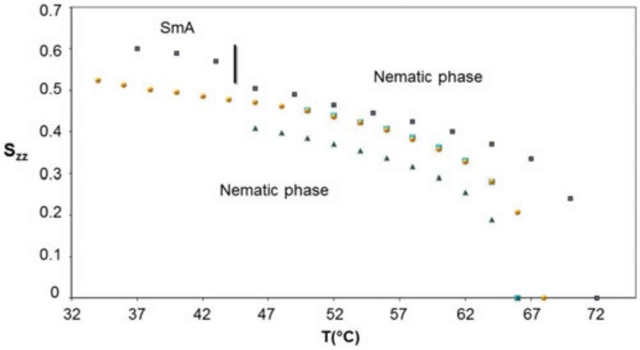


Figure 5. Orientational order parameter (S_{zz}) as a function of temperature, obtained by analysing ^{2}H NMR spectra as described in the text, of the smectogen M11 (■) and of several binary mixtures: 30.7wt% J7 (▲), 46.7 wt% J7 (●) and 88.7 wt% J7 (■).

assumed equal to 60° for M11 as typical of rod-like smectogens [28]. The trend of the orientational order parameter S_{zz} as a function of temperature has been obtained in several mixtures having different weight percentages of J7, as reported in **Figure 5**.

The main orientational order, S_{zz}, of the pure M11 is also reported for comparison. As expected, the orientational order of the pure smectogen M11 is higher than all other cases. The presence of additional mesogen J7, which is shorter than M11 and forms a nematic phase only, decreases the orientational ordering properties. However, the values of S_{zz} at saturation, i.e. at lower temperatures, are quite high in all cases, even for the mixture closest to the eutectic one (namely the mixture containing 46.7 wt% J7 in **Figure 5**). This is quite promising from the applicative point of view.

Conclusions

In this work, we present the preparation and chemical-physical characterization of several binary mixtures composed of an azomesogen and a smectogen, in different percentages. These compounds are of interest due to their use as basic components of photosensitive liquid crystal elastomers. Here, the mesophase diagram of this binary system has been investigated based on POM and DSC analysis. Moreover, the orientational order of these mixtures has been determined by means of ^{2}H NMR studies. Further steps of this research are related to the investigation of the optical properties of these binary mixtures related to the *trans-cis* isomerization and back relaxation process.

Funding

V. D. thanks the Centre of Excellence NAMASTE (Ljubljana) for the financial support as Visitor Professor (2013). This work was also supported by the projects ASCR M100101204, ASCR M100101211, 7AMB14PLO35, CSF 13-14133S and PRIN 2010-2011 (n. 2010C4R8M8).

References

[1] Bahadur, B. (1991) In *Liquid crystal: applications and uses*, Singapore: World Scientific.

[2] Chaturvedi, S., Chaturvedi, N., Verma, R., Pandey, A. S., Tiwari, S. N., & Dhar, R. (2013) *J. Therm. Anal. Calorim.*, *112*, 767–775.

[3] Govindaiah, T. N., Sreepad, H. R., & Nagapp, X. (2013) *Mol. Cryst. Liq. Cryst.*, *574*, 101–108.

[4] Hori, R., Miwa, Y., Yamamoto, K., & Kutsumizu, S. (2014) *J. Phys. Chem. B*, *118*, 3743–3749.

[5] Magdi, M., Abdelgawad, N., Fahmi, A., Alaasar, M. A., Salem, R. A. (2011) *Thermochim. Acta*, *517*, 63–73.

[6] Jin, O., Fu, D., Wei, J., Yang, H., & Guo, J. (2014) *RSC Adv.*, *4*, 28597–28600.

[7] Yu, Y., Ikeda, T. (2004) *J. Photochem. Photobiol. C*, *5*, 247–265.

[8] Marini, A., Zupancic, B., Domenici, V., Mennucci, B., Zalar, B., Veracini, C. A. (2012) *Chem. Phys. Chem*, *13*, 3958–3965.

[9] Camacho-Lopez, M., Finkelmann, H., Palffy-Muhoray, P., & Shelley, M. (2004) *Nat Mater.*, *3*, 307–310.

[10] Lee, C. R., Fu, T. L., Cheng, K. T., Mo, T. S., Fuh, A. Y. G. (2004) *Phys Rev E*, *69*, 031704.

[11] Gimenez, R., Millaruelo, M., Pinol, M., Serrano, J. L., Vinuales, A., Rosenhauer, R., (2005) *Polymer*, *46*, 9230–9242.

[12] Takase, H., Natansohn, A., & Rochon, P. (2003) *Polymer*, *44*, 7345–7351.

[13] Kawatsuki, N., Uchida, E. (2007) *Polymer*, *48*, 3066–3073.

[14] Galli, G., Chiellini, E. (2006) *Liq Cryst*, *33*, 1297–1301.

[15] Yu, Y., Nakano, M., & Ikeda, T. (2003) *Nature*, *425*, 145.

[16] Barrett, C. J., Mamiya, J. I., Yager, K. G., & Ikeda, T. (2007) *Soft Matter*, *3*, 1249–1261.

[17] Schab-Balcerzak, E., Sapich, B., & Stumpe, J. (2005) *Polymer*, *46*, 49–59.

[18] Menghetti, S., Alderighi, M., Galli, G., Tantussi, F., Morandini, M., Fuso, F., & Allegrini, M. (2012). *J. Mater. Chem.*, *22*, 14510–14517.

[19] Devetak, M., Zupancic, B., Lebar, A., Umek, P., Zalar, B., Domenici, V., Ambrozic, G., Zigon, M., Copic, M., & Drevensek-Olenik, I. (2009) *Phys. Rev. E*, *80*, 050701.

[20] Gregorc, M., Zalar, B., Domenici, V., Ambrozic, G., Drevensek-Olenik, I., Fally, M., & Copic, M. (2011) *Phys. Rev. E*, *84*, 031707.

[21] Gregorc, M., Li, H., Domenici, V., Ambrozic, G., Copic, M., & Drevensek-Olenik, I. (2012) *Materials*, *5*, 741–753.

[22] Gregorc, M., Li, H., Domenici, V., Ambrozic, G., Copic, M., & Drevensek-Olenik, I. (2013) *Phys. Rev. E*, *87*, 022507.

[23] Domenici, V., Milavec, J., Bubnov, A., Pociecha, D., Zupančič, B., Rešetič, A., Hamplová, V., Gorecka, E., & Zalar, B. (2014) *RSC Adv.*, *4*, 44056–44064.

[24] Marini, A., Domenici, A., Malanga, C., Menicagli, R., & Veracini, C. A. (2010) *Tetrahedron*, *66*, 3472–3477.

[25] Finkelmann, H., Kiechle, U., & Rehage, G. (1983) *Mol. Cryst. Liq. Cryst.*, *94*, 343–358.

[26] Domenici, V., Ambrozic, G., Copic, M., Lebar, A., Drevensek-Olenik, I., Umek, P., Zalar, B., Zupancic, B., & Zigon, M. (2009) *Polymer*, *50*, 4837–4844.

[27] Kumar, S. (2011) In *Liquid Crystals: Experimental Study of Physical Properties and Phase Transitions*, Cambridge University Press, Cambridge.

[28] Cifelli, M., Domenici, V., Veracini, C. A. (2013) *Curr. Opin. Colloid Interface Sci.*, *18*, 190–200.

[29] Domenici, V. (2012). *Prog. Nucl. Magn. Reson. Spectrosc.*, *63*, 1–32.

[30] Veracini, C. A. (1985) "NMR Spectra in Liquid Crystals the Partially Averaged Spin Hamiltonian." In *Nuclear Magnetic Resonance of Liquid Crystals*; Emsley, J. W., Ed.; Reidel: Dordrecht, Netherlands; Vol. 141, Chapter 5.