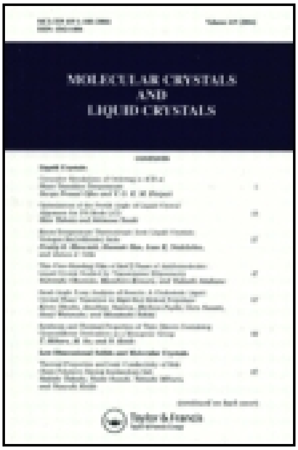
This article was downloaded by: [University of California, San Diego]
On: 16 August 2012, At: 02:43
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954
Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Phase Properties of Monomer/Liquid Crystal and Polymer/Liquid Crystal Mixtures

U. Maschke [a], F. Roussel [b], F. Benmouna [c], A. Daoudi [b], J.-M. Buisine [b], X. Coqueret [a] & M. Benmouna [c]

[a] Laboratoire de Chimie Macromoléculaire (UPRESA CNRS N° 8009), Bătiment C6, Université des Sciences et Technologies de Lille, F-59655, Villeneuve d'Ascq Cedex, France

[b] Laboratoire de Thermophysique de la Matière Condensée (Equipe de I'UPRESA N°8024 du CNRS), Université du Littoral, MREID, F-59140, Dunkerque, France

[c] Faculté des Sciences, Université Aboubakr Belkaïd, BP119, 13000, Tlemcen, Algeria

Version of record first published: 27 Oct 2006

To cite this article: U. Maschke, F. Roussel, F. Benmouna, A. Daoudi, J.-M. Buisine, X. Coqueret & M. Benmouna (2001): Phase Properties of Monomer/Liquid Crystal and Polymer/Liquid Crystal Mixtures, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 365:1, 287-295

To link to this article: http://dx.doi.org/10.1080/10587250108025306

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.tandfonline.com/page/terms-and-conditions

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae, and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand, or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Downloaded by [University of California, San Diego] at 02:43 16 August 2012

Mol. Cryst. and Liq. Cryst., 2001, Vol. 365, pp. 287-295
Reprints available directly from the publisher
Photocopying permitted by license only

© 2001 OPA (Overseas Publishers Association) N.V.
Published by license under the
Gordon and Breach Science Publishers imprint,
a member of the Taylor & Francis Group,
Printed in the USA

Downloaded by [University of California, San Diego] at 02:43 16 August 2012

Phase Properties of Monomer/Liquid Crystal and Polymer/Liquid Crystal Mixtures

U. MASCHKE[a], F. ROUSSEL[b], F. BENMOUNA[c], A. DAOUDI[b],
J.-M. BUISINE[b], X. COQUERET[a] and M. BENMOUNA[c]

[a]*Laboratoire de Chimie Macromoléculaire (UPRESA CNRS N° 8009), Bâtiment C6, Université des Sciences et Technologies de Lille, F-59655 Villeneuve d'Ascq Cedex, France,* [b]*Laboratoire de Thermophysique de la Matière Condensée (Equipe de l'UPRESA N°8024 du CNRS), Université du Littoral, MREID, F-59140 Dunkerque, France and* [c]*Faculté des Sciences, Université Aboubakr Belkaïd, BP119, 13000 Tlemcen, Algeria*

The phase diagrams of monomer and polymer/liquid crystal (LC) mixtures are investigated. Two LCs are used: one is the eutectic mixture of four cyanobiphenylene derivatives known as E7 and the other is 4-cyano-4'-*n*-pentyl-biphenyl or 5CB. The sensitivity of the phase behavior to the nature of monomer, the nature of LC and the UV polymerization is characterized. A single example of UV polymerized/LC system is considered for comparison. Experimental phase diagrams are established by polarized optical microscopy and analyzed with a formalism using mean field theories of Flory-Huggins and Maier-Saupe.

Keywords: Monomer; polymer; liquid crystal; phase diagram; optical microscopy; Flory-Huggins; Maier-Saupe

INTRODUCTION

Blends of linear polymers and low molecular weight liquid crystals (LCs) are the subject of a particular attention due to potential applications in display technologies, privacy windows, light shutters

Downloaded by [University of California, San Diego] at 02:43 16 August 2012

and others[1-5]. Their ability to respond in a controlled fashion to an external excitation such as a laser pulse, an electric or a magnetic field, a pressure or a shear stress gives them a spectrum of applications that generate a great deal of research efforts in various laboratories around the world. These applications gather a synergy of interesting properties characterizing different constituents in the compound. The phase behavior of these systems is important to know for a better understanding of their performance in practical applications. Recently, systematic investigations of the phase properties of various mixtures involving different polymers and LCs[6-8] were reported. This work goes along the same lines and considers mixtures of low molecular weight monomers and LCs. An attempt is made to characterize the effects of the nature of molecular species on their miscibility. An example of a high molecular weight polymer and a LC system is considered to identify the loss of miscibility subsequent to an increase in the polymer mass. The present study allows us to gather the fundamental information on the miscibility of monomers and LCs leading to an indirect measure of the Flory-Huggins interaction parameter χ. This is a fundamental parameter depending on the chemical nature and specific interactions of the molecular species of the mixture. The estimate of χ is free from unknown effects related with the size and polymer architecture that are unavoidable in dealing with linear and crosslinked polymer networks. An example of a polymer/LC system is given to illustrate the increase of χ with the polymer molecular weight. While monomers considered here have different functionalities (i.e. mono-, di- and trifunctional monomers), since we are investigating the phase behavior of uncured systems, this functionality is not really relevent.

More important is the fact that two different LCs are considered. One is the eutectic mixture of four cyanobiphenyl-paraphenylenes known as E7 and the other is the single component 4-cyano-4′-*n*-pentyl-biphenyl or 5CB.

THEORETICAL BACKGROUND

Experimental phase diagrams are analyzed using a theoretical formalism that combines the Flory-Huggins[9] theory of isotropic mixing and the Maier-Saupe[10,11] theory of nematic order. The starting point is the free energy $f=f^{(i)}+f^{(n)}$ where $f^{(i)}$ is the Flory-Huggins free energy and $f^{(n)}$ is the Maier-Saupe free energy

$$\frac{f^{(i)}}{k_B T}=\frac{\varphi_1}{N_1}\ln\varphi_1+\frac{\varphi_2}{N_2}\ln\varphi_2+\chi\varphi_1\varphi_2 \tag{1}$$

and

$$\frac{f^{(n)}}{k_B T}=\frac{\varphi_1}{N_1}\left[-\ln Z+\frac{\nu\varphi_1 s^2}{2}\right] \tag{2}$$

where k_BT is the thermal energy, $\varphi_1=1-\varphi_2$ the volume fraction of LC with one repeat unit ($N_1=1$) and N_2 is the number of repeat units of the second component, Z is the nematic partition function, $\nu=4.54T_{NI}/T$, T_{NI} being the nematic-isotropic transition temperature of the LC, s is the nematic order parameter. Both quantities s and Z depend on temperature and composition while χ is function of temperature. The binodal is calculated following the standard procedure[6-8,12,13] of equating the chemical potential of both constituents 1 and 2 in coexisting phases (α) and (β) $\Delta\mu_1^{(\alpha)}=\Delta\mu_1^{(\beta)}$ and $\Delta\mu_2^{(\alpha)}=\Delta\mu_2^{(\beta)}$ with $\Delta\mu_1=(\delta\Delta F/\delta n_1)_{T,\,n2}$, ΔF being the total free energy of the blend, n_1 and n_2 are the numbers of molecules 1 and 2. A similar definition holds for $\Delta\mu_2$ and the quantities

Downloaded by [University of California, San Diego] at 02:43 16 August 2012

Downloaded by [University of California, San Diego] at 02:43 16 August 2012

in subscript remain fixed when performing derivatives. Resolution of these sets of equations leads to the coexistence curves represented by continuous lines in the figures below.

EXPERIMENTAL PART

Materials

Propoxylated glyceroltriacrylate (GPTA) and tripropylene glyceroldiacrylate (TPGDA) as monomers were obtained from Cray Valley (France). The monomer 2-ethylhexylacrylate (2-EHA) was supplied from Aldrich (France). The LC 5CB and E7 were purchased from Merck Encolab GmbH (Germany). 5CB can be characterized by the following characteristic transition temperatures: T_{KN}=23°C, and T_{NI}=35.3°C.[14] E7 exhibits a single nematic-isotropic transition temperature at T_{NI}=61°C.

Sample preparation

x weight-percent (wt%) of LC (x=10, 20, ..., 90) and (100-x) wt% of the monomer were mixed together at room temperature for several hours. Samples for optical microscopy were prepared by sandwiching a drop of the mixture between two round glass slides.

The UV-polymerization was performed at room temperature under nitrogen atmosphere using a Seiko-UV 1 Unit. The polymerization of 2-EHA was induced by 2wt% (with respect to 2-EHA) of Darocur 1173 (Ciba, France) applying an UV intensity of 17.5mW/cm^2 at λ=365nm, and an irradiation time of 3min.

POM measurements

The samples prepared as mentioned earlier were submitted to a heating

Downloaded by [University of California, San Diego] at 02:43 16 August 2012

rate of 2°C/min from room temperature to 15 degrees above the transition temperature leading to the isotropic phase. Then samples were left approximately 5min in the isotropic state. The samples corresponding to approximately 30wt% LMWLC or higher were then cooled to room temperature at a rate of -2°C/min. The same rate was used for samples with lower concentration of LMWLC but cooling was performed to lower temperatures. This procedure was followed after 5min by a heating ramp at a rate of 2°C/min. Transition temperatures were recorded during this heating ramp.

RESULTS AND DISCUSSION

Figure 1 collects the phase diagrams of three selected monomer/E7 mixtures obtained under similar conditions in the (T,φ_1) coordinate system. The symbols represent POM data recorded following the procedure described in the experimental section. Solid lines represent the theoretical binodals for different monomers. The nematic+isotropic/isotropic (N+I)/(I) transition temperature ($T_{(N+I)/(I)}$) decreases sharply upon adding monomer to the LC E7. This is found in the range of LC weight fraction φ_1 between 1 to 0.55. The depression of $T_{(N+I)/(I)}$ follows a similar trend for the three monomers. Below $\varphi_1=0.55$, the transition temperature decreases more or less rapidly depending upon the monomer. 2-EHA shows the highest miscibility with E7 since $T_{(N+I)/(I)}$ continues to decrease rapidly for φ_1 below 0.55 while the other two systems exhibit a slower decrease. The GPTA-TPGDA(1:1) /E7 mixture shows the lowest miscibility with E7. As an illustration, when φ_1 goes from 1 to 0.55, $T_{(N+I)/(I)}$ drops sharply from 61°C to less than 10°C but when φ_1 varies from 0.55 to 0.3, this temperature remains

Downloaded by [University of California, San Diego] at 02:43 16 August 2012

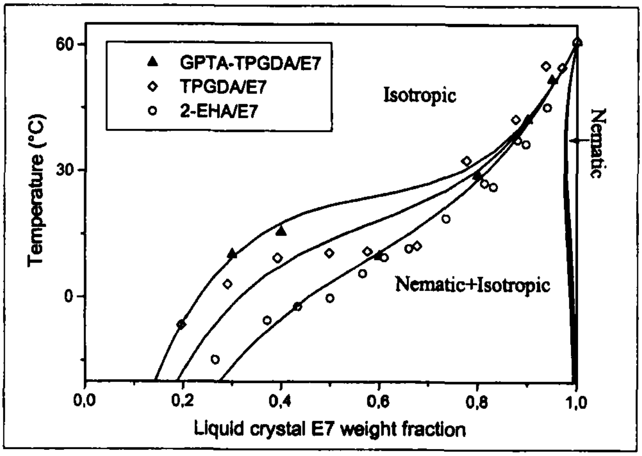


FIGURE 1 Phase diagrams of monomer/E7 systems. The symbols represent POM data for 2-EHA, TPGDA, and TPGDA-GPTA (1:1). The solid lines are the calculated binodals using $N_1=1$, $N_2=2$, $T_{NI}=61°C$ and 2-EHA $\chi=-0.4+400/T$; TPGDA $\chi=-0.4+468/T$; TPGDA-GPTA $\chi=-0.4+518/T$

essentially constant for GPTA-TPGDA/E7 system.

Figure 2 shows the phase diagrams of mixtures of the same monomers with 5CB. Unlike Figure 1, data for the three systems are different in the whole frame (T,φ_1). Consistent with the systems involving E7, depression of $T_{(N+I)/(I)}$ is more pronounced for 2-EHA/5CB than other mixtures. The general tendencies for the high miscibility of 2-EHA in LC and the largest gap in the system containing GPTA are consistent with Figure 1. The solid, dashed and dotted lines in Figure 2 represent the calculated curves using $\chi(T)=A+B/T$ where A and B are fit parameters. From the ratio of molecular weights of the monomers and LCs considered, one expects N_2 to be either 1 or 2. The

Downloaded by [University of California, San Diego] at 02:43 16 August 2012

choice of N_2 is dictated by the best fit between experimental data and theoretical curves. It should be pointed out that 5CB presents a crystalline/nematic transition at 23°C which complicates the phase behavior. The emergence of such a crystalline phase depends on the thermal treatment prior to the POM observations. If the system is kept long enough at low temperatures and the crystallization takes place, then melting of the crystalline phase may be quite slow depending on the viscosity and interaction parameter χ. The choice of thermal treatment is made here to avoid crystallization. To see how the diagrams are modified for high molecular weight polymers, Figure 3 shows the results of Poly(2-ethyl-hexylacrylate) (PEHA)/E7 and 2-EHA/E7 systems[15]. The solubility of the polymerized system in E7 at

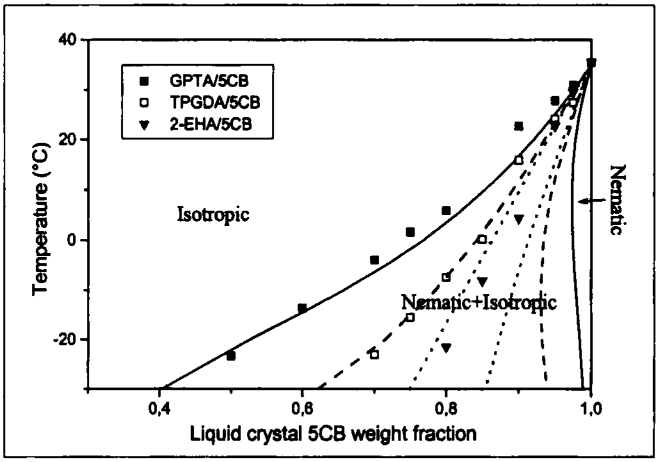


FIGURE 2 The same as Figure 1 for mixtures with 5CB. The calculated curves are obtained using N_1=1 and T_{NI}=35.3°C and 2-EHA N_2=1, χ= -2.34+277/T; GPTA N_2=2, χ=-0.596+ 392/T ; TPGDA N_2=1, χ=-0.63+464/T

Downloaded by [University of California, San Diego] at 02:43 16 August 2012

30°C is 20wt% and if this volume fraction of LC is exceeded, the system separates into a polymer rich isotropic phase and a pure E7

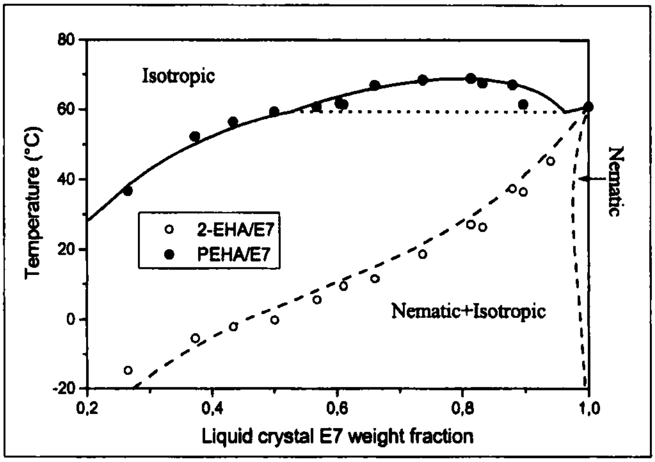


FIGURE 3 Phase diagram of 2-EHA/E7 (lower diagram) and PEHA/E7 (upper diagram) mixtures. The symbols are POM data. The solid lines represent the calculated curves using, $N_1=1$, $T_{NI}=61°C$ and a) 2-EHA/E7 $N_2=2$, $\chi=-0.4+400/T$, b) PEHA/E7 $N_2=16$, $\chi=-2.49+1123/T$

nematic phase. In the monomeric 2-EHA/E7 system, the miscibility limit in E7 at the same temperature exceeds 90wt-% LC. Therefore, a significant loss of miscibility results from the UV- polymerization process.

CONCLUSIONS

The phase diagram of uncured monomer/LC systems depends crucially upon the type of monomer and LC under consideration. The transition temperature from (N+I) to (I) decreases sharply upon adding a small amount of monomer to the LC. In the case of E7, the $T_{(N+I)/(I)}$ depression

Downloaded by [University of California, San Diego] at 02:43 16 August 2012

is sensitive to the nature of monomer only after a certain concentration while for 5CB, this depression is significant after a trace amount of monomer is added to the LC.

Acknowledgement
This work has been accomplished during a stay of F.B. at the "Université du Littoral - Côte d'Opale" of Dunkerque (France) as a guest professor. The authors gratefully acknowledge the support of the CNRS, the EU programme FEDER, the Région Nord-Pas de Calais, and the Ministère de l'Enseignement Supérieur et de la Recherche.

References

[1] J.W. Doane, in *Liquid Crystals – Applications and Uses*, edited by B. Bahadur, World Scientific, Singapore, (1990).
[2] P. S. Drzaic, *Liquid Crystal Dispersions*, World Scientific, Singapore (1995).
[3] S. Chandrasekhar, *Liquid Crystals*, 2nd ed. Cambridge, University Press (1992).
[4] P.G. de Gennes, J. Prost *The Physics of Liquid Crystals*, 2nd ed., Oxford: Oxford Science Publications, Clarendon Press, 1993.
[5] U. Maschke, X. Coqueret, C. Loucheux, *J. Appl. Polym. Sci.* 56, 1547 (1995).
[6] T. Bouchaour, F. Benmouna, L. Leclercq, B. Ewen, X. Coqueret, M. Benmouna, U. Maschke *Liq. Cryst.* 27, 413 (2000).
[7] F. Benmouna, A. Daoudi, F. Roussel, J.-M. Buisine, X. Coqueret, U. Maschke, a) *J. Polym. Sci., Part B: Polym. Phys.* 37, 1841 (1999) and b) *Macromolecules* 33, 960 (2000).
[8] T. Bouchaour, F. Benmouna, F. Roussel, J.-M. Buisine, X. Coqueret, M. Benmouna, U. Maschke, *Polymer*, accepted for publication.
[9] P. J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, Ithaca (1965).
[10] W. Maier, A. Saupe, *Z. Naturforschung* 14a, 882 (1959).
[11] W. Maier, A. Saupe, *Z. Naturforschung* 15a, 287 (1960).
[12] C. Shen, T. Kyu, *J. Chem. Phys.* 102, 556 (1995).
[13] W.-K. Kim, T. Kyu, *Mol. Cryst. Liq. Cryst.* 250 131 (1994).
[14] Values given by Merck Encolab GmbH (Germany).
[15] F. Roussel, J.-M. Buisine, U. Maschke, X. Coqueret, F. Benmouna, *Phys. Rev. E*, in press.