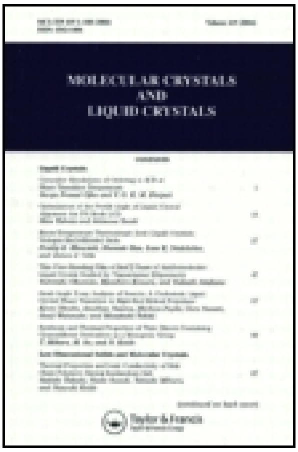


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

On the Isotropic-Anisotropic Biphasic Behavior of Two Side Chain Liquid-Crystalline Polyacrylates

M. Laus [a], A. S. Angeloni [a], G. Galli [b] & E. Chiellini [b]

[a] Dipartimento di Chimica Industriale e dei Materiali, Università di Bologna, Viale Risorgimento 4, 40136, Bologna, Italy

[b] Dipartimento di Chimica e Chimica Industriale, Università di Pisa, Via Risorgimento 35, 56126, Pisa, Italy

Version of record first published: 24 Sep 2006.

To cite this article: M. Laus , A. S. Angeloni , G. Galli & E. Chiellini (1994): On the Isotropic-Anisotropic Biphasic Behavior of Two Side Chain Liquid-Crystalline Polyacrylates, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 254:1, 241-250

To link to this article: http://dx.doi.org/10.1080/10587259408036079

Mol. Cryst. Liq. Cryst. 1994, Vol. 254, pp. 241–250
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

ON THE ISOTROPIC-ANISOTROPIC BIPHASIC BEHAVIOR OF TWO SIDE CHAIN LIQUID-CRYSTALLINE POLYACRYLATES

M.LAUS[1], A.S.ANGELONI[1], G.GALLI[2], and E.CHIELLINI[2]

[1]Dipartimento di Chimica Industriale e dei Materiali,
Università di Bologna, Viale Risorgimento 4, 40136 Bologna, Italy
[2]Dipartimento di Chimica e Chimica Industriale,
Università di Pisa, Via Risorgimento 35, 56126 Pisa, Italy

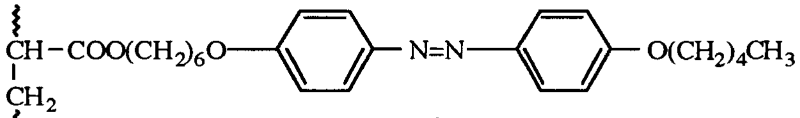
(Received: February 7, 1994)

Abstract The biphasic behavior was studied for two polyacrylates ***1*** and ***2***, by DSC by annealing the polymers inside the respective apparent biphasic gap associated with the nematic-isotropic transition (polymer ***1***) or to the smectic Ad-isotropic transition (polymer ***2***). A biphasic thermal range in which isotropic and smectic Ad phases or isotropic and nematic phases coexist at equilibrium was revealed. In both cases, the thermodynamic width of the biphasic region was estimated to be about 2.0 K.

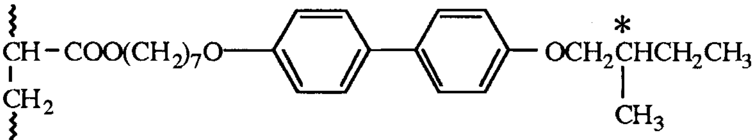
INTRODUCTION

Experimental and theoretical investigations of the thermodynamic and kinetic nature of the liquid-crystalline phase transitions in semiflexible polymeric systems have revealed peculiar physics that is not realized in low molar mass systems. The occurrence of a thermodynamically stable biphasic region located between the pure nematic phase and the pure isotropic phase has been reported in main chain polymers with regular[1-6] or statistical[7-10] distribution of rigid and flexible segments along the chain backbone. The coexistence of nematic and isotropic phases over a finite range of temperatures is unambiguously indicative of the multicomponent nature of the polymeric systems, as follows from the phase rule. However, the understanding of the structural and molecular factors conducive to incompatibility in the melt and of the driving force for macrophase segregation is just at the beginning. Several different segregation mechanisms have been proposed to account for the nematic-isotropic biphase separation process. The nematic-isotropic biphase behavior of main chain liquid-crystalline polymers with regular structure is primarily ascribed to the molecular weight polydispersity of the samples. This phase separation appears due to the effects of the molecular weight and molecular weight distribution of the polymer. In fact, for the nematic-isotropic biphase separation to be observed, the phase transition parameters of the individual species constituting the polymer sample should differ substantially, according to their distinct molecular weight dependences. In addition, the average molecular weight of the sample should be fairly high. These results led to the hypothesis[6] that the nematic-isotropic biphase segregation in main chain polymers with regular structure is mainly driven by a screening mechanism of entropic origin, in which the lower molar mass species segregate from the longer chain molecules. In addition, the chemical heterogeneity of main chain liquid-crystalline polymers with statistical distribution of comonomeric units is suggested to produce a distribution of persistence lengths, strictly connected to a distribution of chain flexibilities, so called polyflexibility, capable of promoting partitioning between the two liquid phases with the more rigid chain molecules being selectively incorporated into the anisotropic phase. Theoretical calculations[11,12] are in agreement with the above explanation of the biphasic behavior of liquid-crystalline statistical copolymers.

Very recently, the observation of the nematic-isotropic[13] and smectic-isotropic[14] biphasic behavior has been reported for side chain liquid-crystalline polymers containing different mesogenic moieties. In particular, two side chain polyacrylates *1* and *2* with the following structures:



1



2

have been studied in detail for their biphasic behavior. Polyacrylates *1* and *2* are based on the azobenzene and biphenyl mesogenic units respectively and present a very different mesomorphism, involving smectic C and nematic mesophases for the former and smectic A1 and Ad mesophases for the latter. Therefore, these polymers permitted to study the isotropic-anisotropic biphasic behavior either at the nematic-isotropic (polymer *1*) or at the smectic-isotropic transition (polymer *2*). This paper reviews our previous investigations and includes our latest results on the biphasic behavior of these polymers.

EXPERIMENTAL PART

The synthesis of polyacrylates *1* and *2* is reported in Refs. 15 and 16 respectively. The number average molecular weight (Mn) and first polydispersity index (Mw/Mn) were evaluated by SEC to be Mn=79000 and Mw/Mn= 2.93 for polymer *1* and Mn= 59000 and Mw/Mn=1.9 for polymer *2*, in terms of polystyrene standard.

The biphasic behavior of both polymer samples was studied by DSC (Perkin Elmer DSC-7) according to the following procedure. A polymer sample was heated for 20 min at a temperature 20 K higher than the isotropization one. Subsequently, the sample was cooled at 1 K min^{-1} to a selected temperature in the biphasic region, maintained at this temperature for several hours and then rapidly cooled to room temperature and finally subjected to several heating/cooling cycles at 10 K min^{-1}. For each annealing temperature a fresh polymer sample was employed. Optical microscopy observations were performed on polymer films between glass slides by means of a Reichert Polyvar microscope equipped with a programmable Mettler FP52 heating stage at a scanning rate of 10 K min^{-1}.

RESULTS AND DISCUSSION

Liquid-crystalline behavior

The mesomorphic properties of polyacrylate *1* were studied[17] by differential scanning calorimetry (DSC), observation of textures on the hot stage of a polarizing microscope and X-ray diffraction analysis. Polyacrylate *1* is semicrystalline and shows a bilayer smectic C and a nematic mesophase with the following phase sequence (the entropy changes associated to the relevant transitions are in brackets):

$$K \xrightarrow{378\ K} S_{Cd} \xrightarrow{402\ K\ (2.7\ Jmol^{-1}K^{-1})} N \xrightarrow{416\ K\ (1.9\ Jmol^{-1}K^{-1})} I$$

$$K \xleftarrow{365\ K} S_{Cd} \xleftarrow{400\ K} N \xleftarrow{414\ K} I$$

Polyacrylate *2* is amorphous and presents a smectic Ad and a smectic A1 mesophase occurring within a few degree temperature range. The investigation into the transition temperature dependence on the DSC scanning rate showed[14] that the former mesophase is enantiotropic whereas the latter is monotropic in character. The mesophase sequence of polyacrylate *2*, including also the entropy changes associated with the relevant transitions, can be summarized as follows:

$$g \xrightarrow{360\ K} S_{Ad} \xrightarrow{407\ K\ (30.2\ Jmol^{-1}K^{-1})} I$$

$$g \xleftarrow{358\ K} S_{Ad} \xleftarrow{389\ K\ (16.1\ Jmol^{-1}K^{-1})} S_{A1} \xleftarrow{414\ K\ (14.5\ Jmol^{-1}K^{-1})} I$$

Biphasic behavior

The biphasic behavior of polyacrylates *1* and *2* was delineated by differential scanning calorimetry according to the following thermal procedure. The samples were heated to a temperature 20 K higher than the isotropization, slowly cooled to the predetermined annealing temperature Ta, maintained at this temperature for several hours and then rapidly cooled to room temperature. Annealing times of 10 hours for polymer *1* and 15 hours for polymer *2* were found suitable to achieve the best macroscopic separation without any concomitant degradation phenomena. The samples were then subjected to one heating/cooling cycle. In the DSC heating curves of both polymers *1* and *2*, following annealing at

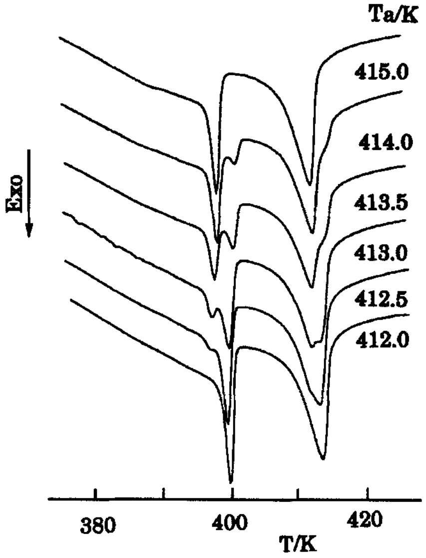


FIGURE 1 DSC cooling curves (10 $Kmin^{-1}$) for polymer *1* following annealing at different temperatures Ta (annealing time= 10 h).

various temperatures Ta, the broad endothermic peaks corresponding to the smectic Cd-nematic and nematic-isotropic transitions for the former, and to the smectic Ad-isotropic transition for the latter, were structured into several strongly overlapping components and no unequivocal conclusions could be drawn on the biphasic behavior. On the contrary, in the DSC cooling curves the exothermic peaks corresponding to the isotropic-nematic and nematic-smectic Cd transitions of polymer *1*, and to the isotropic-smectic A1 and smectic A1-smectic Ad transitions of polymer *2* appear well resolved and, accordingly, the biphasic behavior of both polymer samples was clearly delineated considering the DSC cooling curves alone. Figure 1 illustrates the DSC cooling curves of polymer *1* following annealing at temperatures Ta inside the nematic-isotropic biphasic region. When the annealing temperature ranged between 414 and 412.5 K, the isotropic-nematic and nematic-smectic Cd transition profiles appear structured into two fairly well resolved components, whose peak temperatures and relative magnitudes depend on Ta. The trends of the isotropic-nematic and the nematic-smectic Cd peak temperatures as a function of Ta are illustrated in Figure 2. The peak temperatures of both isotropic-nematic transition exotherms and of both nematic-smectic Cd

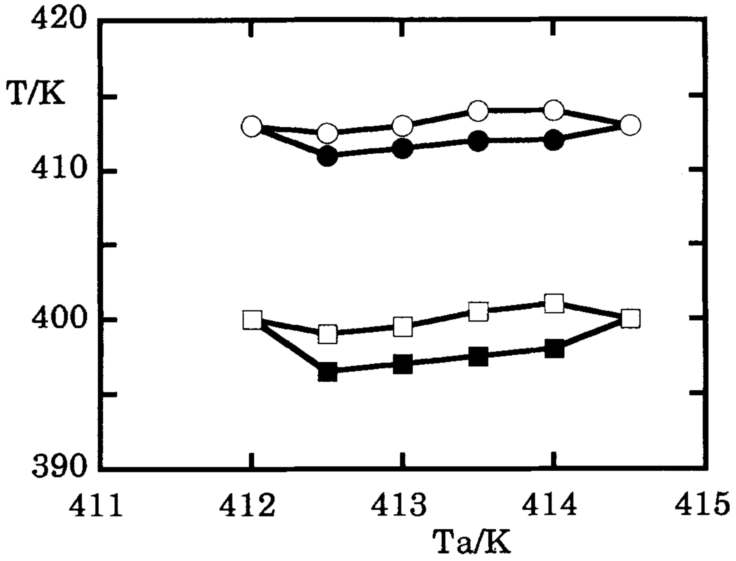


FIGURE 2 Isotropic-nematic (○, ●) and nematic-smectic Cd (□, ■) transition temperatures for the higher temperature component (open symbol) and lower temperature component in the biphase (full symbol) for polymer *1* following demixing (annealing time= 10 h) as functions of the annealing temperature Ta.

transition exotherms regularly increase with increasing annealing temperature. Although the strong overlap of the signals prevents accurate determination of the respective enthalpies, for both phase transitions the area of the lower temperature exothermic component increases with Ta, whereas the area of the higher-temperature exothermic component decreases. This trend is reproducible in successive cycles and can be reversed by changing the thermal treatment in the biphasic region.

Figure 3 collects the DSC cooling curves of polyacrylate *2* following annealing at different temperatures inside the smectic Ad-isotropic biphasic region. The isotropic-smectic A1 and smectic A1-smectic Ad transitions are structured into two well resolved components. The thermal evolution of the isotropic-smectic A1 components closely parallels the one of the smectic A1-smectic Ad components. For both phase transitions the area of the higher temperature exothermic components increases regularly with decreasing annealing temperature. The peak temperature trends of both the isotropic-smectic A1 and smectic A1-smectic Ad exothermic

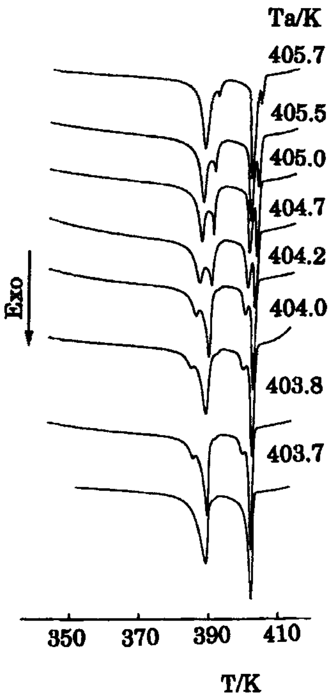


FIGURE 3 DSC cooling curves (10 $Kmin^{-1}$) for polymer *2* following annealing at different temperatures Ta (annealing time= 15 h).

components as functions of the annealing temperature are illustrated in Figure 4. The peak temperatures of both the isotropic-smectic A1 and smectic A1-smectic Ad components increase regularly with increasing Ta. The dual behavior observed at the isotropic-nematic and nematic-smectic Cd transitions of polymer *1* and at the isotropic-smectic A1 and smectic A1-smectic Ad transitions of polymer *2* reflects the distinct transitional processes of two polymer fractions with different average molecular weights which phase-separated during annealing inside the biphasic gap associated with the nematic-isotropic transition for the former and with the smectic Ad-isotropic transition for the latter polymer sample. The regular increase of the transition temperatures of both the demixed components with increasing Ta (Figures 2 and 4) indicates a parallel increase of the average molecular weight of the two polymer fractions undergoing these transitions. Correspondingly, the biphase fractionation process implies a substantial partitioning phenomenon with the longer

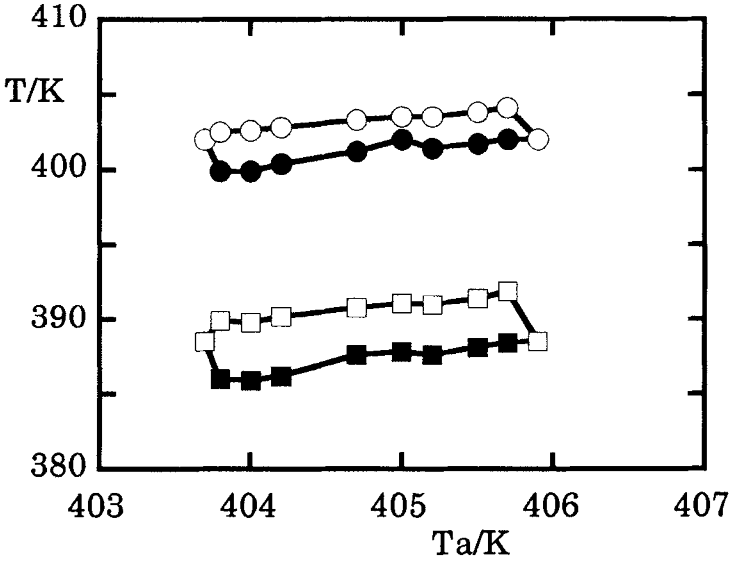


FIGURE 4 Isotropic-smectic A1 (○, ●) and smectic A1-smectic Ad (□, ■) transition temperatures for the higher temperature component (open symbol) and lower temperature component in the biphase (full symbol) for polymer *2* following demixing (annealing time= 15 h) as functions of the annealing temperature Ta.

chain molecules selectively incorporated into the anisotropic phase and the low molecular weight fractions preferentially segregated into the isotropic component. Accordingly, the described thermal treatment allows delineation of the coexistence of isotropic and anisotropic phases and evaluation of the thermodynamic width of the isotropic-nematic biphasic region of polymer *1* as well as the isotropic- smectic Ad biphasic region of polymer *2* which is about 2.0 K in both cases.

From a phenomenological standpoint, the behavior of polymers *1* and *2* subjected to the above thermal treatment, is very similar, although they were annealed inside the biphasic regions associated with the very distinct nematic-isotropic and smectic Ad-isotropic transitions. It has to be noted however that the efficiency of the phase separation, as reflected by the resolution of the relevant peaks in the DSC curves, is definitely greater for the sample annealed inside to the isotropic-smectic Ad biphasic region.

CONCLUSIONS

The biphasic behavior of two side chain liquid-crystalline polymers *1* and *2*, based on the azobenzene and biphenyl mesogenic units respectively, was studied by DSC. The samples, after annealing inside the apparent biphasic gap of their nematic-isotropic and smectic Ad-isotropic transitions respectively, showed a biphasic thermal range in which isotropic and nematic phases for polymer *1* and isotropic and smectic Ad phases for polymer *2* coexist at equilibrium and segregate. Once segregated, the two polymer fractions undergo distinct and independent transitions. The evolution of the transition temperatures of both segregated components as a function of the annealing temperature indicates that the biphase segregation is driven by the molecular weight differences within the macromolecular species of the polymer samples and is accompanied by a partitioning phenomenon in which the longer chain molecules are selectively incorporated into the anisotropic phase. This was verified for the nematic phase of polymer *1* and for the smectic Ad phase of polymer *2*. By the employed annealing procedure, the width of the isotropic-nematic and isotropic-smectic Ad biphasic regions was estimated under conditions approaching thermodynamic equilibrium and results in both cases to be about 2.0 K. However, a better segregation efficiency is observed at the isotropic-smectic Ad transition of polymer *2*.

To visualize the segregation phenomenon in side chain liquid-crystalline polymers, let us imagine that at the segregation initial stage the various polymer molecules are strongly interpenetrated in the melt with the higher molecular weight species possessing an oblate shape[18,19], resulting from the coupling of the backbone with the anisotropic field generated by the mesogenic groups, and the lower molecular weight species being in the random coil configuration with the relevant mesogenic groups placed isotropic-wise. Since the most favourable steric-packing interactions are established among the mesogenic groups belonging to the higher molecular weight species, incompatibility phenomena may arise at the local scale. These in turn would drive the overall polymer molecules to disorient and equilibrate through giant collective motions, ultimately leading to migrations at the molecular level. This results in a segregation of the various macromolecules with different molecular weight into distinct anisotropic and isotropic domains of macroscopic size.

This idealized mechanism suggests that the efficiency of the segregation depends on the differences between the local scale interactions of the mesogenic groups in the isotropic and anisotropic state. Accordingly, a better biphase separation efficiency should be expected at the smectic-isotropic transition rather than at the nematic-isotropic one, in possible agreement with the discussed experimental findings.

Financial supports from Ministero dell'Università e della Ricerca Scientifica e Tecnologica and CNR of Italy are acknowledged.

REFERENCES

1. J. F. D'Allest, P.P. Wu, A. Blumstein and R. B. Blumstein, Mol. Cryst. Liq.Cryst. Lett., 3, 103 (1986).
2. J. F. D' Allest, P. Sixou, A. Blumstein and R. B. Blumstein, Mol. Cryst. Liq. Cryst., 157, 229 (1988).
3. D. Y. Kim, J. F. D' Allest, A. Blumstein and R. B. Blumstein, Mol. Cryst. Liq. Cryst., 157, 253 (1988).
4. M. Laus, D. Caretti, A. S. Angeloni, G. Galli and E. Chiellini, Macromolecules, 24, 1459 (1991).
5. E Chiellini, G. Galli, M. Laus, A. S. Angeloni, and D. Caretti, Mol. Cryst. Liq. Cryst., 215, 101 (1991).
6. M. Laus, A. S. Angeloni, G. Galli and E. Chiellini, Macromolecules, 25, 5901 (1992).
7. S. J. Moore and S. I. Stupp, Macromolecules, 20, 273, 282 (1987).
8. S. J. Moore and S. I. Stupp, Macromolecules, 21, 1217 (1988).
9. P. G. Martin and S.I. Stupp, Macromolecules, 21, 1222 (1988).
10. S. I. Stupp, J. S. Moore and P. G. Martin, Macromolecules, 21, 1228 (1988).
11. G. H. Fredrickson, Macromolecules, 22, 2746 (1989).
12. G. H. Fredrickson and L. Leibler, Macromolecules, 23, 531 (1990).
13. G. Galli, E. Chiellini, M. Laus, D. Caretti and A. S. Angeloni, Makromol. Chem., Rapid Commun., 12, 43 (1991).
14. M. Laus, A. S. Angeloni, G. Galli and E. Chiellini, Thermochim. Acta, in press.
15. A. S. Angeloni, D. Caretti, C. Carlini, E. Chiellini, G. Galli, A. Altomare, R. Solaro, and M. Laus, Liq. Crys., 5, 513 (1989).
16. M. Laus, A. S. Angeloni, G. Galli, and E. Chiellini, J. Polym. Sci., Polym. Phys., in preparation.
17. O. Francescangeli, B. Yang, E. Chiellini, G. Galli, A. S. Angeloni, and M. Laus, Liq. Cryst., 3, 353 (1993).
18. G. Pépi, L. Noirez, P. Keller, M. Lambert, F. Moussa, J. P. Cotton, C. Strazielle, A. Lapp, F. Hardouin, M. Mauzac, and H. Richard, Makromol. Chem., 191, 1383 (1990).
19. M. Warner in Side Chain Liquid Crystalline Polymers, C. B. McArdle ed., Blackie, Glasgow, 1989.