This article was downloaded by:
On: *26 January 2011*
Access details: *Access Details: Free Access*
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

Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

On the interaction of the morphological structure and the LC behaviour of LC side group block copolymers

H. Fischer[a]; S. Poser[b]; M. Arnold[b]
[a] H. H. Wills Physics Laboratory, University of Bristol, Bristol, England [b] Institute for Technical Chemistry, Martin-Luther University Halle-Wittenberg, Halle-Saale, Germany

To cite this Article Fischer, H. , Poser, S. and Arnold, M.(1995) 'On the interaction of the morphological structure and the LC behaviour of LC side group block copolymers', Liquid Crystals, 18: 3, 503 — 509

To link to this Article: DOI: 10.1080/02678299508036651

URL: http://dx.doi.org/10.1080/02678299508036651

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or 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.

LIQUID CRYSTALS, 1995, VOL. 18, NO. 3, 503–509

On the interaction of the morphological structure and the LC behaviour of LC side group block copolymers

by H. FISCHER*, S. POSER† and M. ARNOLD†
H. H. Wills Physics Laboratory, University of Bristol, Tyndall Avenue, Royal Fort, Bristol, BS8 1TL, England

(*Received 26 June 1994; accepted 27 July 1994*)

The interaction between morphological structure and phase behaviour of a LC side group block copolymer has been investigated using DSC, TEM and small angle X-ray diffraction. All samples of Polystyrene-*block*-2-(3-cholesteryloxycarbonyloxy)ethyl methacrylate (PS-*b*-PChEMA) show a phase separation between the two blocks. It was found that in the case of those samples where the liquid crystalline sub-phase is not continuous (spheres), only a nematic phase is seen, whereas in all samples in which there is a continuous liquid crystalline sub-phase, the smectic A phase of the homopolymer is formed. On the other hand, the block copolymer seems to stabilize the LC phase; no dependency of the clearing temperatures on the molecular weight of the LC blocks has been observed.

1. Introduction

Block copolymers composed of incompatible block segments form in general a micro-domain morphology in the solid state. In this class of polymers it is possible to combine the properties of two completely different polymers with no macroscopic phase separation occurring. Owing to the chemical link between the non-compatible polymers, the phase separation is limited to a microscopic scale, and is dependent on the thermodynamic interaction parameter χ, on the temperature, on the molecular weights of the constituent block chains and on the volume fraction of the different blocks [1–7]. Several different morphologies have been predicted and observed. These morphologies are spheres in a cubic lattice or rods in a hexagonal lattice embedded in the matrix of the other component of the block copolymer or lamellae of both. Recently, ordered bicontinuous morphologies (OBDD) were also found [8–13]. It is even possible to observe other structures like catanoid lamellae and hollow cylinders [14].

A different way, to obtain structured non-crystalline materials, is by the synthesis of liquid crystalline polymers. Therefore, in the past 20 years a major interest has been in the synthesis of main chain or side group polymers and the understanding of the principles of their structuring with respect to the molecular shapes of the mesogenic units. If one of the blocks in a block copolymer is now a liquid crystalline (LC) side group polymer, the structures of the resulting polymers will be influenced by two different structuring effects. On the one hand, the immiscibility of the blocks should cause a phase separation, but on the other hand, the nematic director of the mesogenic units in the LC sub-phase should force a spontaneous orientation of the mesogenic groups. Adams *et al.*, first reported a synthesis of block copolymers with a LC side group polymer block, using a polymer analogous reaction [15]; meanwhile other synthetic methods such as group transfer polymerization [16], photopolymerization of LC methacrylates [17] and ring opening metathesis polymerization [18] have been reported. Also living cationic [19] and anionic polymerization [20] have been used successfully to synthesize this type of polymer.

Recently, we reported experiments concerning block copolymers with one or two amorphous block(s) involving polystyrene (PS) and a liquid crystalline block, poly-2-(3-cholesteryloxycarbonyloxy)ethyl methacrylate (PChEMA); PS-*b*-PChEMA as a diblock copolymer [21] is shown in figure 1 and PChEMA-*b*-PS-*b*-PChEMA) is a triblock copolymer [22]. There, phase separation has been proved using DSC, and the morphology displayed was investigated using small angle diffraction methods and transmission electron microscopy (TEM) [21–23]. The liquid crystalline behaviour has been evaluated with the help of X-ray diffraction, polarized optical microscopy (POM) and DSC. Initial investigations on the AB type copolymers Polystyrene-*b*-2-(3-cholesteryloxycarbonyloxy)ethyl methacrylates (PS-*b*-

---

*Author for correspondence. Centre for Polymers and Composites, University of Technology, Eindhoven, P.O. Box 513, Eindhoven, 5709 GR, The Netherlands.

†Institute for Technical Chemistry, Martin-Luther University Halle-Wittenberg, Neuwerk 7, Halle-Saale 06108, Germany.

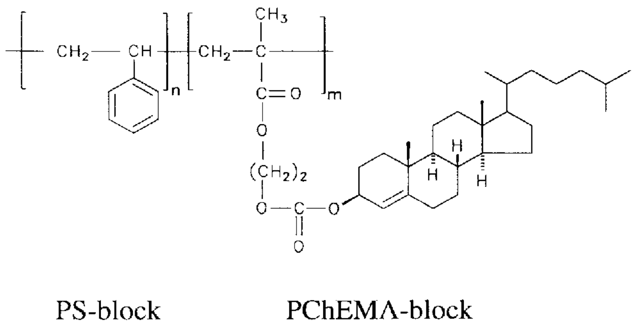


Figure 1. Structure of the block copolymers.

PChEMA) and Polybutadien-*b*-2-(3-cholesteryloxycarbonyloxy)ethyl methacrylates (PB-*b*-PChEMA) suggested an influence of the amorphous block on the phase structure of the LC-block, favouring lamellar structure [24]. It is the aim of this paper to study the influence of the morphology of the block copolymer on the phase structure of the LC-block. Questions of interest are also: is LC behaviour and phase separation observable in these block copolymers? Is there an interaction between the structure of the LC sub-phase and the morphology of the block copolymer? Are there new morphological structures due to the interaction between the block structure and the liquid crystalline structure present? We are interested further in the interaction between the block morphology displayed and the phase structure of the LC sub-phase. Also the orientation of the mesogenic units with respect to the orientation of the morphological structure will be studied.

2. Experimental

The synthesis of the diblock and triblock copolymers polystyrene-*block*-2-(3-cholesteryloxycarbonyloxy)ethyl methacrylates (PS-*b*-PChEMA and PChEMA-*b*-PS-*b*-PChEMA) has been described elsewhere [21, 22]. The polymers were freed from residual monomeric LC using HPLC equipment from Knauer. Thermal behaviour was observed using a Perkin-Elmer DSC 7 with heating and cooling rates of 10 K min^{-1}. X-ray studies were carried out using an Eliott GX 21 with copper target, combined with a Rigaku Denki small angle film camera and a Siemens Area Detector X-100 in conjunction with a PC for collecting, storing and analysing the images. For the TEM studies a Phillips EM 301 was used. The preparation techniques for the samples for the TEM, DSC and X-ray studies have been described previously [22].

3. Results and Discussion

The morphology displayed by block copolymers has been well studied in the system PS-*b*-PB and is mainly dependent upon the volume fraction of the two blocks. The scheme for the morphologies is, as described by Bates and Frederickson, a sequence of spherical, rodlike hexagonal, double diamond and lamellar phases [13]. The diblock and triblock copolymers described in our study display a significantly different scheme of morphologies (see figure 2 (*a*) and (*b*), and the table). The known

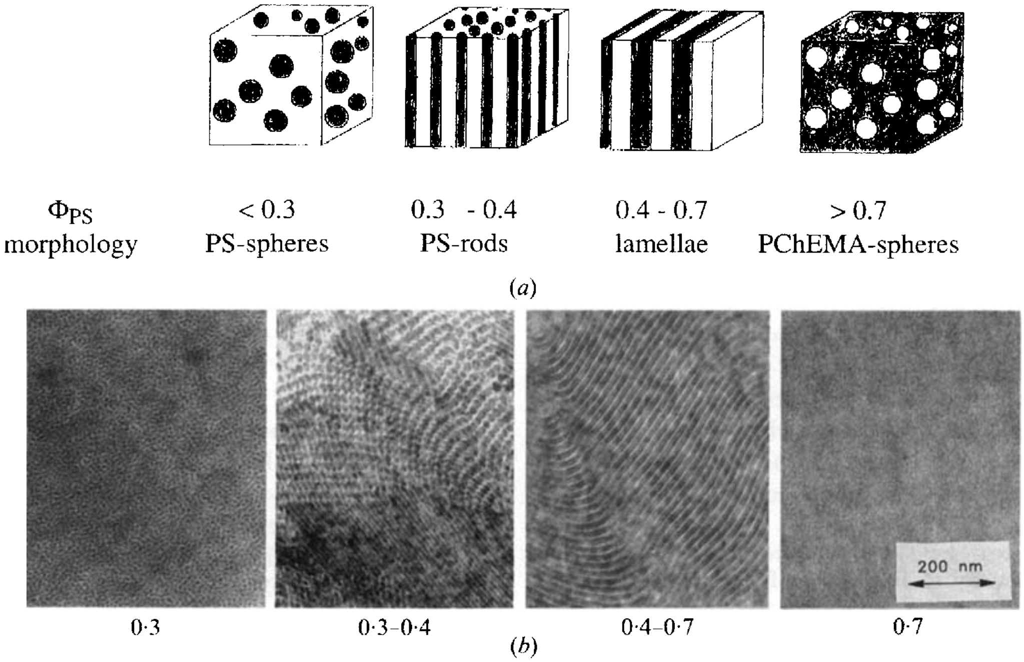


Figure 2. (*a*) Schematical representations, (*b*) TEM photographs of the observed morphologies.

Molecular weight, PS volume fraction, molecular weight distribution and thermal data for the block copolymers synthesized.

Sample	M_n PS	M_n Copol.	Φ_{PS}	D	Phase behaviour/°C	Morph. (TEM)
PS			1·00		g 102 I	
		Homopolymerers			PChEMA	
PChEMA1	14700		0·00	1·00	g 93 S_A 125 I	
PChEMA2	19500		0·00	1·07	g 98 S_A 145 I	
PChEMA3	61000		0·00	1·05	g 109 S_A 194 I	
PChEMA4	86000		0·00	1·12	g 113 S_A 204 I	
PChEMA5	250000		0·00	1·90	g 126 S_A 213 I	
		Diblock copolymerers			PS-PChEMA	
53	57500	73200	0·78	1·07	g 105 g 126 N 188 I	PChEMA-spheres
55	48300	71000	0·67	1·07	g 101 g 126 S_A187 I	lamellae
57	62200	109000	0·56	1·11	g 103 S_A 197 I	lamellae
59	51000	133000	0·37	1·11	g 103 g 126 S_A 202 I	PS-rods
78	20400	64000	0·30	1·03	g 91 g 120 S_A 189 I	PS-spheres
82	18400	111000	0·16	1·11	g 100 g 127 S_A 200 I	PS-spheres
75	10100	63000	0·15	1·18	g 91 g 123 S_A 198 I	PS-spheres
61	25000	202000	0·11	1·10	g 102 g 125 S_A 199 I	PS-spheres
		Triblock copolymers			PChEMA-PS-PChEMA	
DB 2	29100	54300	0·53	1·15	g 100 g 119 S_A 190 I	lamellae
DB 4	22200	77300	0·29	1·15	g 101 g 117 S_A 184 I	PS-rods
DB 7	25600	75000	0·33	1·20	g 102 g 118 S_A 199 I	PS-rods
DB 5	22600	64000	0·35	1·15	g 98 g 118 S_A 186 I	PS-rods
DB 6	24000	43000	0·55	1·20	g 101 g 118 S_A 183 I	lamellae
DB 8	21000	29000	0·70	1·05	g 98 g 118 N 193 I	PChEMA-spheres
DB 9	26000	29000	0·88	1·04	g 98 g N 194 I	PChEMA-spheres
DB10	20000	87000	0·22	1·47	g 103 g 118 S_A 201 I	PS-spheres
DB11	34000	57000	0·59	1·25	g 99 g 120 S_A 194 I	lamellae
DB12	52000	78000	0·66	1·12	g 95 g 119 S_A 180 I	lamellae
DB14	26000	45000	0·57	1·13	g 93 g 118 S_A 197 I	lamellae
DB15	37700	53500	0·70	1·09	g 103 g 116 S_A 200 I	lamellae
DB16	54400	68000	0·77	1·09	g 93 g N 194 I	PChEMA-spheres
DB17	21000	23000	0·90	1·10	g 98 g N 184 I	PChEMA-spheres
DB18	37000	42000	0·88	1·26	g 92 g N 195 I	PChEMA-spheres
DB19	51200	53000	0·96	1·08	g 98 g I	PChEMA-spheres
DB20	22700	26700	0·84	1·06	g 96 g N 186 I	PChEMA-spheres
DB21	34700	37000	0·93	1·07	g 98 g N 194 I	PChEMA-spheres

morphologies are observed in copolymers with small volume fractions of polystyrene ϕ_{PS}. However, if the volume fractions of polystyrene increase to $0{\cdot}6<\phi_{PS}<0{\cdot}8$, no cylindrical phase has been observed. We have found rather a direct transition from a lamellar to a spherical morphology (see figure 3). It appears that the dividing lines of the areas with spherical morphologies are very well defined due to the fact that on both lines there are two data points for samples showing both morphologies. Considering a symmetric phase diagram, the area of the hexagonal phase of PChEMA is obviously occupied by the lamellar phase (see figure 3). This is understandable if one takes the structure of the sub-phase into account. The open circles represent a nematic structure of the sub-phase, whereas the filled symbols represent the smectic A phase of the sub-phase. There is obviously an interaction between the phase formation of the LC sub-phase and the morphology. It seems that the LC-spheres embedded in the PS matrix are too small to realise a smectic layered structure. The dimensions of the sub-phases, being only 200 Å in a spherical sub-phase, mean that only a few layers of the liquid crystalline structure (45 Å thick) should be present. This is clearly not enough for a smectic phase to form. Curvature of the spheres may also play an important part in this effect. Therefore, a new structure—*chiral nematic*—of the LC sub-phase is introduced due to the morphology.

With a volume fraction of $\phi_{PS}\approx 0{\cdot}6$–$0{\cdot}7$ a cylindrical structure of the LC sub-phase may be expected. It may well be that the energetic differences between lamellar and hexagonal phases is smaller than the difference in energy terms between a nematic and a smectic structure. On the other hand, the formation of the thermodynamically stable smectic A phase in the sub-phase is ener-

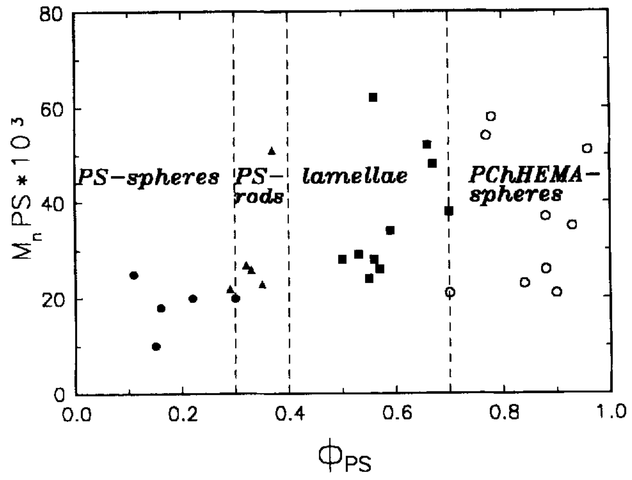
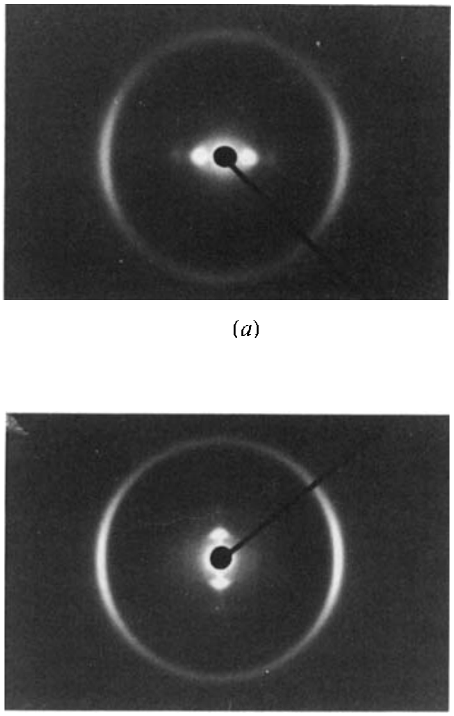


Figure 3. Phase diagram of the observed block copolymers.

getically more favourable than the formation of an equilibrium morphology. In those samples, where the liquid crystalline sub-phase is not continuous (spheres), only a nematic phase is seen, whereas in all samples, in which there is a continuous liquid crystalline sub-phase, the smectic A phase of the homopolymer is formed. A smectic phase can only be realised in continuous sub-phases like the lamellar or matric phases, not in rods or spheres of the LC sub-phase with a very small diameter compared to the layer spacing. Therefore lamellar morphology will be displayed. The influence of the sub-phase on the morphology is stronger. A similar picture was observed with respect to the morphology consisting of PS-rods embedded in a PChEMA-matrix. Here a tetragonal arrangement of the rods has been found instead of the hexagonal structure known from the system PS-*b*-PB [23]. This structural change may also be produced due to the interaction between morphological structure and phase behaviour of a LC side group block copolymer.

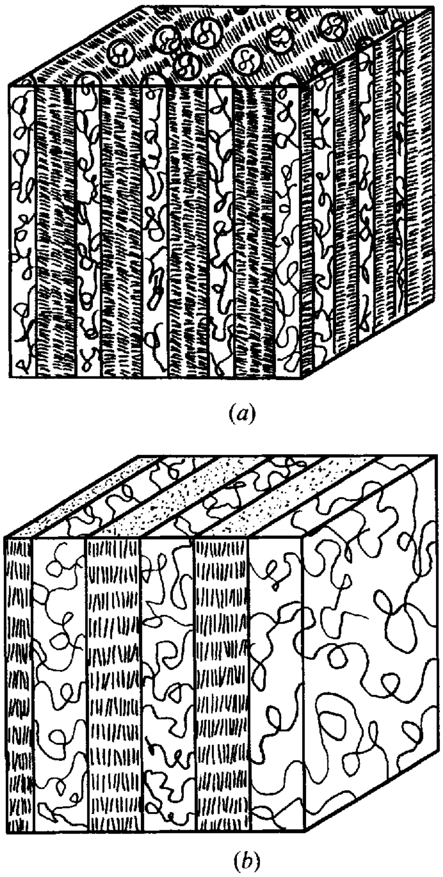
Small angle X-ray studies of oriented samples should provide some information about the orientation of the smectic layers in the sub-phase with respect to the morphology. The results are shown in figure 4. The inner reflections are caused by the phase separation of the two blocks and indicate the orientation of the morphological structure. The outer reflections show the orientation of the smectic layers, where the orientation of the mesogenic units is perpendicular to the layer orientation [21]. Two principal pictures have been observed. In the case of PS-spheres and PS-rods embedded in the LC side group polymer matrix, the orientation of the morphology is parallel to the orientation of the smectic layers of the matrix; in other words, the LC side group polymer is orienting like a homopolymer; the element which responses to the shear is the liquid crystalline matrix. The mesogenic groups are perpendicular to the morphological elements and a deformation of the PS-spheres into ellipsoids occurs. A completely different behaviour was observed for samples with lamellar morphology. Here the orientation of the smectic layers is perpendicular, as already described previously [25]. We believe that here the element of the structure which responds to the shear field is the morphological element, contrary to that for the samples described before (see figure 5).


(*a*)

(*b*)

Figure 4. Small angle X-ray diffraction pattern of (*a*) sample DB 7 (PS-rods), (*b*) sample DB11 (lamellar morphology).

Studies have been carried out to obtain information about the width of the interface. It was found previously, that the thickness of the interface between the phase separated blocks of polystyrene-*b*-isoprene block copolymers (about 2 nm) is independent of the molecular weight of the block components [26] and of the volume fraction of both block components [27]. Anastasiadis *et al.* [28], described the system polystyrene-*b*-methyl methacrylate, and they also found that the interfacial thickness (5 nm) was not dependent on the molecular weight of the block copolymers. Similar results have been found in our system (see figure 6). It was possible to stain the interface selectively using very short staining times (5 min) [29]. The thickness of the interface (2·5 ± 1 nm) was found to be independent of the morphology and of the molecular weight of both blocks. This small value for


(a)

(b)

Figure 5. Schematic representation of the orientation of the morphology and the smectic layers in the sub-phase for (*a*) PS spheres or PS rods embedded in a PChEMA matrix and (*b*) lamellar morphology.

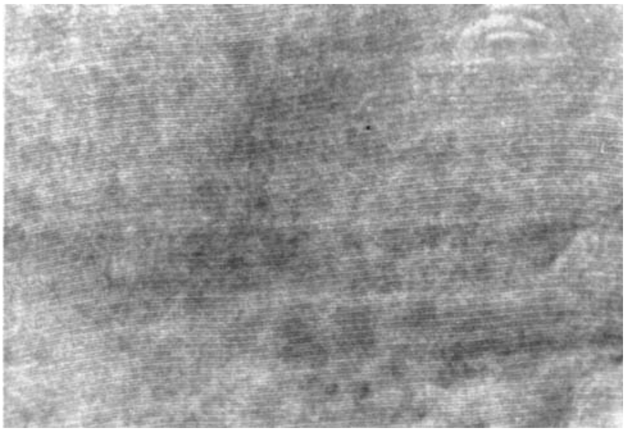


Figure 6. TEM picture of sample 72; lamellar morphology.

the interface agrees with the observations obtained from the oriented samples. A much larger interface should be expected for a parallel orientation of the smectic layers to the lamellae in the samples with lamellar morphology. This is because of back folding of the polystyrene blocks from the chains coming from middle of the 200 Å thick lamellae, which clearly occurs. Also, it would be hard to realise a smectic structure with only 4–5 layers in the case of a parallel orientation of smectic layers and lamellae. Different again is the case for PS-spheres and PS-rods; the distance between them is only about 100 Å, therefore a back folding may occur with no significant increase of the interfacial thickness.

It is now obvious that the polymers described in this study provide a good opportunity to study size effects on the stability of microphases. Also the influence of stability is of interest. Adams *et al.*, reported for their block copolymers a quite substantial decrease of the transition enthalpy at the clearing temperature of the LC sub-phase compared with the homopolymers [15]. This was attributed to a rather thick interface. With the small interface observed in our system, a different behaviour should be expected. Indeed, only a minor decrease of the transition enthalpy at the clearing point has been registered for the block copolymers with a smectic sub-phase (see figure 7). The clearing enthalpy seems to be independent of the molecular weight of the blocks and of the morphology. The plot in figure 7 enables us now to distinguish between the different structures of the sub-phase; a significantly smaller transition enthalpy has been recorded for the samples with a $\phi_{PS} > 0{\cdot}7$ due to the lower order in the nematic sub-phase [22].

A plot of the clearing temperatures against the molecular weight of the LC block provides a surprising picture (see figure 8). Contrary to the known behaviour of the homopolymers [30], which show a strong depen-

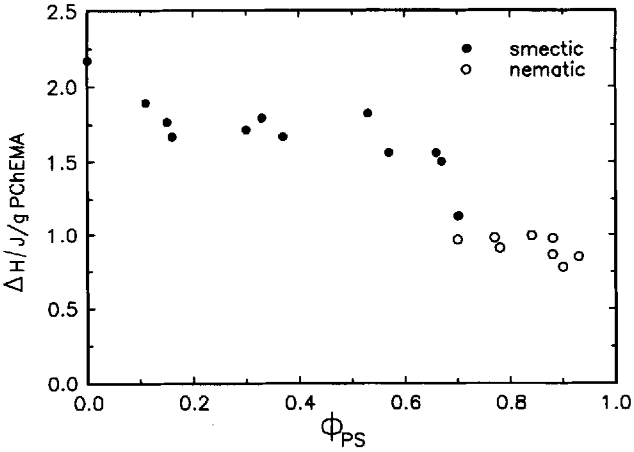


Figure 7. Transition enthalpies of the block copolymers at the clearing point.

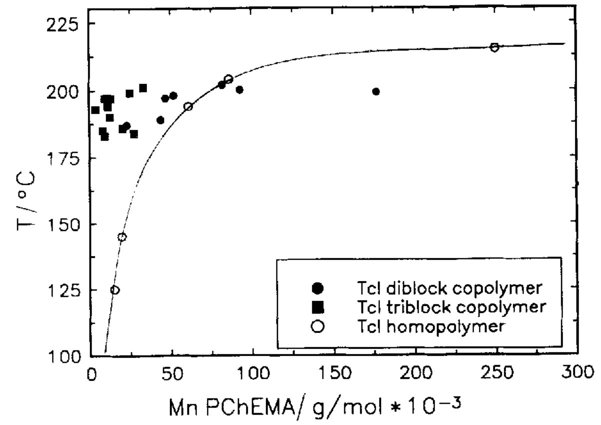


Figure 8. Dependency of the clearing temperatures of the homopolymers and block copolymers on the molecular weight of the LC side group polymer block.

dency of the clearing temperatures on the molecular weight, virtually no change in the clearing temperatures for the block copolymers was observable. This result is different from the findings of Bohnert *et al.* [20], who reported a similar relationship for block copolymers as for homopolymers. However, a difference might be that Bohnert *et al.*, used in their study block copolymers which displayed only a nematic phase, and hence there would not be such a strong interaction between morphology and LC sub-phase as in our system. The stabilization effect on the clearing temperature, and hence on the phase stability in our system may arise due to the interaction between the interfaces formed by the phase separation of the blocks and the LC sub-phase. It seems that the morphological structure enhances the stability of the LC sub-phase as long as this phase is able to form a continuum.

4. Conclusions

The interaction between morphological structure and phase behaviour of a LC side group block copolymer has been investigated. It was found that in the case of those samples where the liquid crystalline sub-phase is not continuous (spheres), only a nematic phase is seen, whereas in all samples in which there is a continuous liquid crystalline sub-phase, the smectic A phase of the homopolymer is formed. LC-spheres embedded in the PS matrix are too small to realise a smectic layered structure. A new structure—*nematic*—of the LC sub-phase is introduced due to the morphology. For volume fractions of PS, $\phi_{PS} \approx 0{\cdot}6$–$0{\cdot}7$, a cylindrical structure of the LC sub-phase was expected. The formation of the thermodynamically stable smectic A phase in the sub-phase seems to be energetically more favourable than the formation of an equilibrium morphology. A smectic phase can only be realised in continuous subphases like the lamellar or matrix phases, and not in rods or spheres of the LC sub-phase with a very small diameter compared to the layer spacing. Therefore a lamellar morphology was found for the samples with $\phi_{PS} \approx 0{\cdot}6$–$0{\cdot}7$. No change of the clearing temperature with molecular weight of the LC blocks for the block copolymers was observable, contrary to the known behaviour of homopolymers. It seems, that the morphological structure enhances the stability of the LC sub-phase as long as this phase is able to form a continuum.

Note added in proof—We became aware of a communication describing a diblock copolymer and a triblock copolymer with one liquid crystalline block (cf. Adams, J., Sänger, J., Tefehne, C., and Gronski, W., 1994, *Macromolec. rap. Commun.*, **15**, 879) in which the diblock copolymer displays a lamellar morphology. For this polymer the same characteristics were found as in our systems (transition temperatures independent from the molecular weight of the LC block, orientation behaviour of LC sub-phase and morphological element). However, the triblock copolymer with PS spheres embedded in a LC-matrix does not display as expected the equilibrium structure of the LC sub-phase (smectic) but a nematic phase, possibly due to impurities of the triblock copolymer.

References

[1] Tsukahara, Y., Izumi, A., Hashimoto, T., and Kawai, H., 1982, *Polymer J.*, **14,** 878.
[2] Gouin, J. P., Bosse, F., Nguyen, D., Williams, C. E., and Eisenberg, A., 1993, *Macromolecules*, **26,** 7250.
[3] Jiang, M., Cao, X., and Yu, T., 1986, *Polymer*, **27,** 1923.
[4] Nakazawa, H., and Ohta, T., 1993, *Macromolecules*, **26,** 5503.
[5] Beckman, J., Auschra, C., and Stadler, R., 1994, *Macromolek, Chem. rap. Commun.*, **15,** 67.
[6] Möller, M., and Lenz, R. W., 1989, *Macromolek. Chem.*, **190,** 1153.
[7] Richards, R. W., and Thomason, J. L., 1983, *Macromolecules*, **16,** 982.
[8] Alward, D. B., Kinning, D. J., Thomas E. L., and Fetters, L. J., 1986, *Macromolecules*, **19,** 215.
[9] Kinning, D. J., Thomas, E. L., Alward D. B., Fetters, L. J., and Handlin, D. L., Jr., 1986, *Macromolecules*, **19,** 1288.
[10] Thomas, E. L., Alward, D. B., Kinning, D. J., Martin, D. C., Handlin, D. L., Jr., and Fetters, L. J., 1986, *Macromolecules*, **19,** 2197.
[11] Hasegawa, H., Tanaka, H., Yamasaki, K., and Hashimoto, T., 1987, *Macromolecules*, **20,** 1651.
[12] Spontak, R. J., Smith, S. D., and Ashraf, A., 1993, *Macromolecules*, **26,** 956.
[13] Bates, F. S., and Frederickson, G. H., 1990, *Ann. Rev. Phys. Chem.*, **41,** 525.
[14] Disko, M. M., Liang, K. S., Behal, S. K., Roe, R. J., and Jeon, K. J., 1993, *Macromolecules*, **26,** 2983.
[15] Adams, J., and Gronski, W., 1989, *Macromolek, Chem. rap. Commun.*, **10,** 553.

[16] Hefft, M., and Springer, J., 1990, *Macromolek, Chem. rap. Commun.*, **11,** 397.

[17] Kodaira, T., and Mori, K., 1992, *Macromolek. Chem.*, **193,** 1331.

[18] Komiya, Z., and Schrock, R. R., *Macromolecules*, **26,** 1387.

[19] Percec, V., and Lee, M., 1992, *J. Macromolek. Sci. Chem.*, **29,** 723.

[20] Bohnert, R., and Finkelmann, H., 1994, *Macromolek. Chem.*, **195,** 689.

[21] Arnold, M., Poser, S., Fischer, H., Frank, W., and Utschick, H., 1994, *Macromol. Rap. Commun.*, **15,** 487.

[22] Fischer, H., Poser, S., Frank, W., and Arnold, M., *Macromolecules*, (submitted).

[23] Fischer, H., 1994, *Polymer*, **35,** 3786.

[24] Zaschke, B., Frank, W., Fischer, H., and Arnold, M., 1991, *Polymer Bull.*, **27,** 1.

[25] Adams, J., and Gronski, W., 1990, *Liquid Crystal Polymers*, edited by D. A. Wein and C. K. Ober (A.C.S. Symposium Series, Vol. 433), p. 174.

[26] Hashimoto, T., Shibayama, M., and Kawai, H., 1980, *Macromolecules*, **13,** 1237.

[27] Hashimoto, T., Fujimura, M., and Kawai, H., 1997, *Macromolecules*, **10,** 1661.

[28] Anastasiadis, S. H., Russel, T. P., Satija, S. K., and Majkrzak, C. F., 1990, *J. chem. Phys.*, **92,** 5677.

[29] Fischer, H., 1994, *Macromolec. rap. Commun.*, **15**.

[30] Finkelmann, H., and Rehage, G., 1984, *Adv. Polym. Sci.*, **60/61,** 113.