Liquid Crystalline Side Group Block Copolymers with *n*-Butyl Methacrylate as an Amorphous A-Block: Synthesis and Characterization

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ABSTRACT: A second system of liquid crystalline (LC) side group block copolymers with *n*-butyl methacrylate as an amorphous A-block has been synthesized and characterized. The system poly(*n*-butyl methacrylate)/poly[2-((((3-cholesteryl)oxy)carbonyl)oxy)ethyl methacrylate] (PBMA/PChEMA) displays a similar phase diagram and macroscopic and microscopic interaction between the morphological structure and the LC behavior of LC side group block copolymers as the system polystyrene (PS)/PChEMA. A formation of a disordered (nematic) phase is also seen in those samples where the LC subphase is not continuous (spheres), whereas in all samples in which there is a continuous LC subphase, the smectic A phase of the homopolymer is formed. For volume fractions of PBMA (Φ_{PBMA}) $\approx$ 0.6–0.7, a cylindrical structure of the LC subphase was expected. The formation of the smectic A phase in the subphase like that displayed in the homopolymer PChEMA seems to be more favorable than the formation of an equilibrium morphology. The orientation of the LC subphase with respect to the orientation of the morphological elements is dependent on the morphological structure.

Introduction

A broad variety of liquid crystalline (LC) polymers with side group mesogens have been synthesized and studied over the last 15 years.[1–3] Also statistical and regular copolymers containing monomer(s) with LC side groups and nonmesogenic monomers have been prepared.[4–6] They show in general unexpected properties, such as displaying a strong stabilization of the LC phases instead of a gradual disappearance of the LC properties with the "dilution" of the mesogenic units by nonmesogenic compounds.[7,8]

The synthesis of block copolymers with one amorphous block and one block containing LC side groups is another possibility for modifying LC polymers and for studying the interaction between the morphological structure displayed due to the phase separation between two immiscible blocks and the LC behavior of the LC side group polymer block.

The preparation of such block copolymers was described only about 6 years ago. The first synthesis of AB diblock copolymers was carried out by Adams et al.[9] using an anionic step polymerization reaction with a subsequent polymer-analogous reaction. The products displayed both phase separation and LC behavior. A similar synthetic route was described by Zascke et al.,[10] Ober et al.,[11] and Poser et al.[12] for the synthesis of diblock copolymers. Other synthetic routes to such polymers are group transfer polymerization,[13] photopolymerization,[14] ring-opening polymerization,[15] and direct anionic[16] and cationic polymerization. Recently, the preparation of triblock copolymers with inner[18–20] and outer LC blocks[20–22] was also described.

Our investigations to elucidate the interaction between the morphological structure and the LC behavior of the block copolymers were carried out with an extended number of diblock and triblock samples varying in composition and block length. Phase separation within the two blocks was always found and four principal morphologies could be detected, *e.g.*, a tetragonal arrangement of rods.[23] It has been shown that the morphology present influences not only the type of the mesophase displayed by the LC subphase but also the orientation of the smectic layers in the subphase with respect to the orientation of the interface between the blocks.[12,18–21]

Since it was possible to detect in recent studies an influence of the nature of the amorphous A-block (*e.g.*, polystyrene and polybutadiene) on the LC behavior of polymers with a lamellar morphology,[10,24] it was the aim of this work to investigate this influence further by varying again the chemical nature of the amorphous A-block. It was especially of interest whether the change of the non-LC block from polystyrene to poly(*n*-butyl methacrylate) would change the influence of both parts and interaction between the morphology and LC phase behavior. Since the structure of the backbone chain is now unique for the whole block copolymer, new effects can be expected. This change of the chemical nature of block A will also change the interaction parameter χ of block A and therefore, besides influencing the phase diagram in general, also the interaction of the non-LC block A and the main chain of block B at the interface. The main chain of block B tends to separate from the cholesteryl side groups in the smectic phase.

A series of diblock copolymers with different compositions has been synthesized and characterized by means of DSC, X-ray diffraction, transmission electron microscopy, and optical microscopy.

Synthesis of the LC Block Copolymers

The synthesis of the LC block copolymers was carried out in analogy to the system polystyrene/poly[2-((((3-cholesteryl)oxy)carbonyl)oxy)ethyl methacrylate] (PS/PChEMA).[12] In a first step, the starting block copolymers were prepared by a sequential anionic polymerization of *n*-butyl methacrylate (BMA) and 2-hydroxy-

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Scheme 1

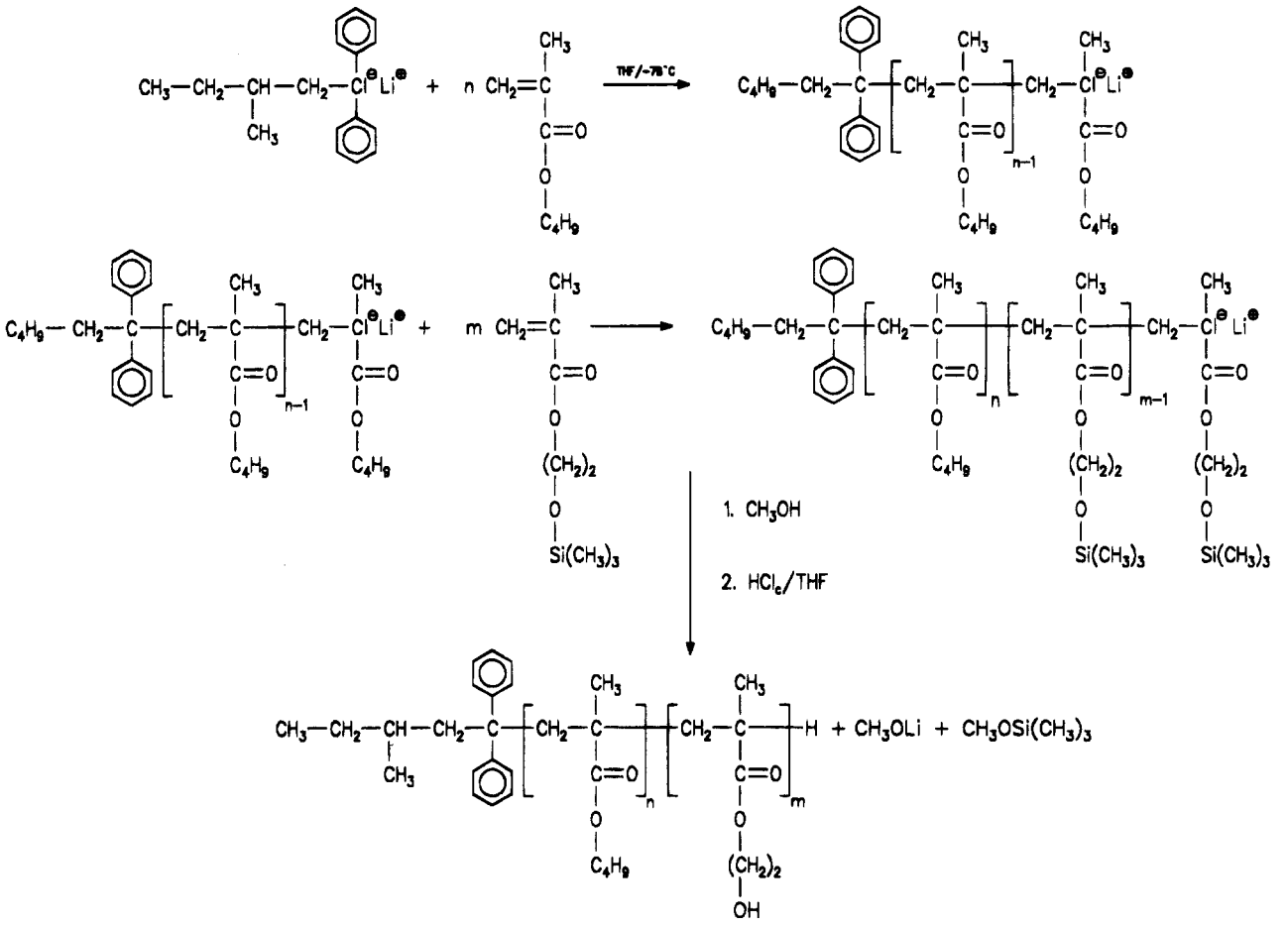


Table 1. Molecular Weights, Comonomer Ratios, and Molecular Weight Distributions of the BMA/HEMA Diblock Copolymers

sample	BMA/HEMA mole ratio	$M_{n,cal}$ 1st block	M_n 1st block[a] (m_w/M_n)	M_n PHEMA block[b]	M_n block copolymer[c]	M_w/M_n
BMA		49 000	50 000 (1.04)			
BMA/HEMA						
BH 18	1:1.43	23 000	25 100 (1.15)	33 000	58 100	1.12
BH 11	1:0.81	29 000	30 300 (1.20)	22 700	53 000	1.05
BH 12	1:0.37	45 000	45 600 (1.04)	15 500	61 100	1.14
BH 17	1:0.30	35 000	37 500 (1.16)	10 300	47 800	1.25
BH 13	1:0.19	32 000	31 800 (1.21)	5 500	37 300	1.11
BH 14	1:0.10	40 000	43 400 (1.08)	4 000	47 400	1.44
BH 15	1:0.04	50 000	52 800 (1.22)	1 800	54 600	1.09

[a] All molecular weights in g/mol, determined by size exclusion chromatography. [b] Calculated from the difference between the molecular weight of the first block and that of the copolymer. [c] SEC of the block copolymers was carried out on samples esterified with benzoyl chloride.

ethyl methacrylate (HEMA). Therefore, a protected form of HEMA (2-((trimethylsilyl)oxy)ethyl methacrylate) was used. The trimethylsilyl group was split off completely by a reaction with concentrated hydrochloric acid (HCl) dissolved in tetrahydrofuran (THF) (Scheme 1). Polymers with different block ratios and block lengths were obtained by variation of the initiator/monomer/comonomer ratios (see Table 1).

The block copolymers were prepared in high yield (>95%) and narrow molecular weight distribution, as is typical for an anionic polymerization process. The block copolymers with free OH groups were converted to the final products using an esterification reaction with cholesteryl chloroformate (see Scheme 2).

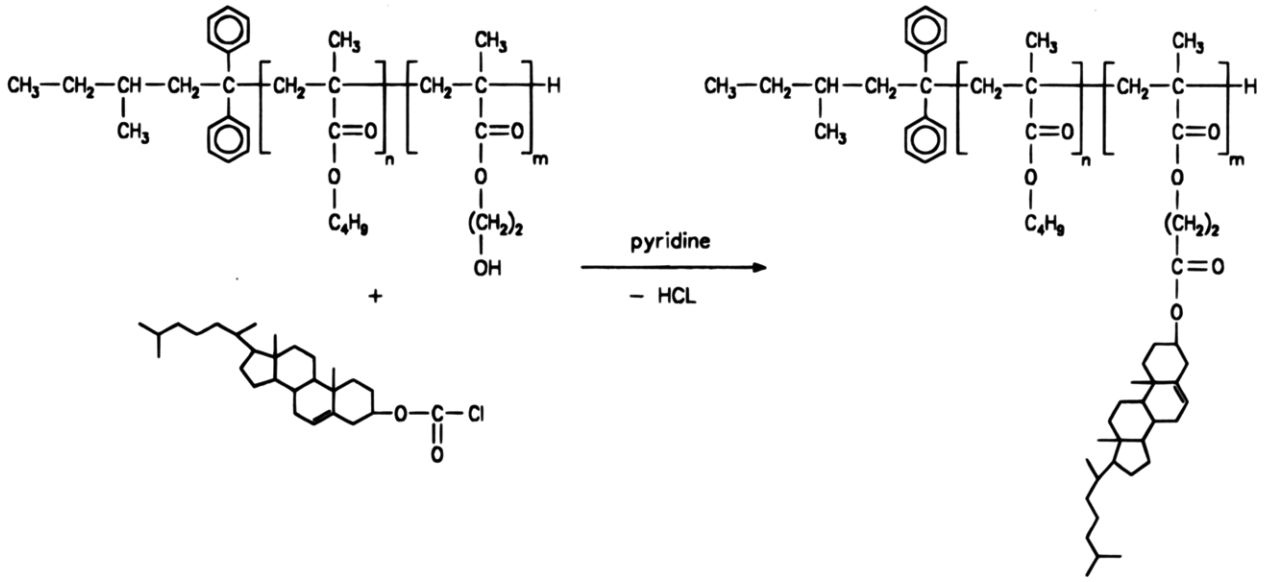
Complete conversion of the OH groups was verified by IR and ^{1}H NMR spectroscopy. Due to the very similar dissolving behaviors of the final block copolymer and the unreacted excess cholesteryl compound, it was difficult to separate them and to obtain the pure polymers as required for a careful characterization. The final separations were carried by preparative HPLC (see Figure 1).

Characterization of the LC Block Copolymers

A closer characterization of the block copolymers was performed by GPC, DSC, optical microscopy (POM), transmission electron microscopy (TEM), and X-ray diffraction techniques. Nearly all of the block copolymers showed two glass transition temperatures. Both corresponded to the glass transition temperatures of the pure homopolymers, indicating a phase separation between the two blocks (see Figure 2).

Obviously, the current system behaves similarly to the already investigated system PS/PChEMA.[12,19-21] The phase separation between the two blocks was also detected using small-angle X-ray diffraction (see Figure

Scheme 2



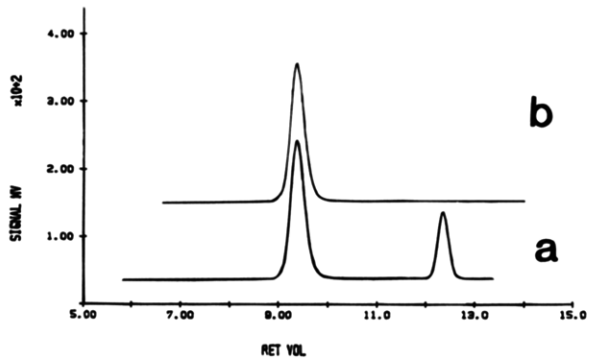


Figure 1. GPC traces for the sample BMA/CH 13 after reaction with cholesteryl chloroformate: (a) without purification; (b) with purification by preparative HPLC.

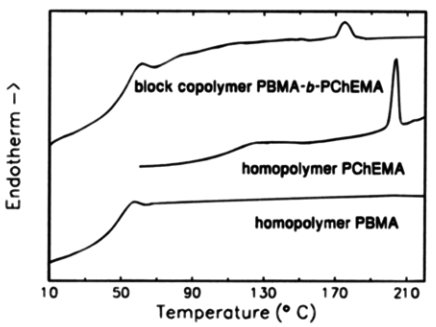


Figure 2. DSC traces of the homopolymers PBMA and PChEMA and of the block copolymer BMA/CH 14 (10 K/min, second heating scan).

3). Figure 3 shows the small-angle diffraction pattern of an oriented sample (pulled fiber) of polymer BMA/CH 14. Clearly visible is the reflection at small angles corresponding to a *d*-spacing of about 166 Å and indicating the phase separation of the blocks. No higher order reflections are observable while using this instrumentation. The diffraction peak width is only limited by instrumental broadening and not by the size of the structures observed. Another sharp and intense reflection is also present in Figure 3 perpendicular to the reflection described above. The second reflection corresponds to a *d*-spacing of 45 Å and reflects the presence of a smectic A-phase in analogy to the polymers of the system PS/PChEMA.[12] The orientation of the layers in

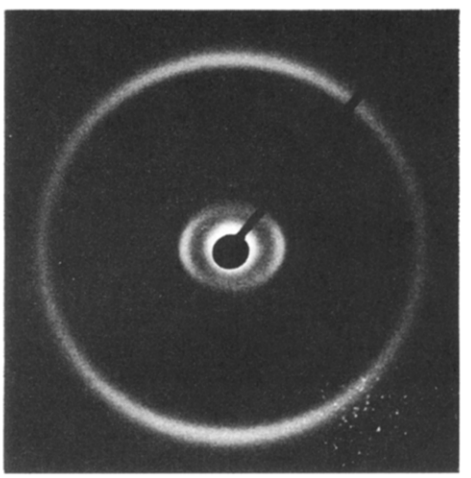


Figure 3. Small-angle X-ray diffraction pattern of sample BMA/CH 14 (oriented fiber, arrow indicates orientation direction, lamellar morphology).

the LC subphase is again perpendicular to the orientation of the lamellae as described extensively in ref 18 and below. The interface between the two blocks might be considered to be very narrow as observed in the system PS/PChEMA.[25]

The presence of a LC subphase can also be concluded from the appearance of clearing peaks in the DSC traces of the block copolymers (Figure 2), from POM studies, and from the wide-angle X-ray diffraction pattern (Figure 4). Figure 4 shows the X-ray diffraction pattern of an oriented sample (pulled fiber, same sample as in Figure 3) of polymer BMA/CH 14. Again, a small-angle reflection indicating the layer distances of the liquid crystalline phase at an angle corresponding to 45 Å is observable. Only this small-angle reflection displays an orientation, the other reflections at wide angles indicating the lateral distance of the mesogenic units. The two other reflections at 13.5 and 5.67 Å arise from the amorphous PBMA fraction and are overlapped with the lateral reflection of the mesogenic unit. Since the BMA chain remains unoriented, no orientation of those reflections can be observed.

An exception was the sample with the smallest content of LC side group polymer (BMA/CH 15, $\Phi_{PBMA} = 0.86$). Only one glass transition temperature (PBMA

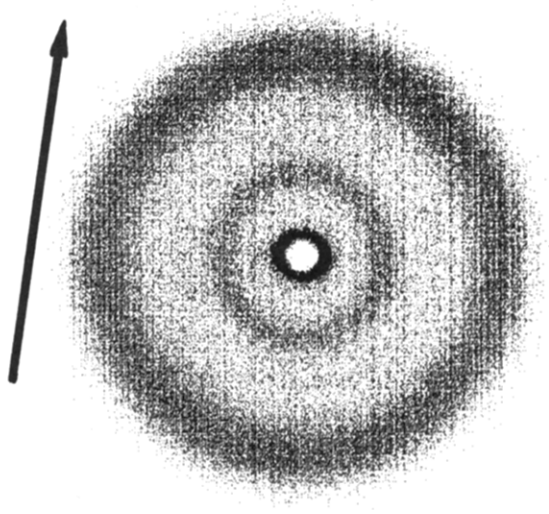


Figure 4. X-ray diffraction pattern of the smectic A phase of sample BMA/CH 14 (oriented fiber, arrow indicates orientation direction, 25 °C).

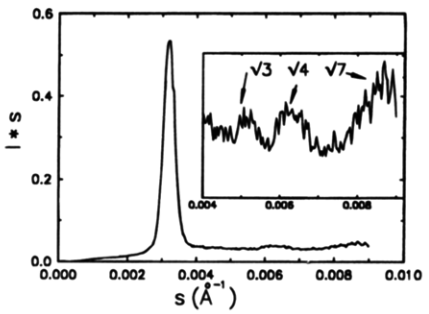


Figure 5. Small-angle X-ray diffractogram of sample BMA/CH 12 (hexagonal rodlike morphology).

block) could be detected by DSC. However, a clearing peak at 143 °C indicates still the presence of a liquid crystalline phase since both backbone homopolymers do not display a liquid crystalline or a crystalline phase. The liquid crystalline domains are perhaps so small that a glass transition temperature can be detected. The quite low clearing temperature compared to the homopolymer PChEMA and the other block copolymers suggests that only a disordered liquid crystalline phase (*nematic*) can be present, presumably due to the low molecular weight of the LC block or due to a morphological influence as explained below. This is supported by the fact that the wide-angle X-ray diffraction pattern no longer shows a reflection at small angles (45 Å) indicating a layered order of the liquid crystalline phase.

Especially difficult was a direct imaging by TEM of the morphologies formed since due to the similar chemical nature no selective staining of one of the blocks could be achieved. TEM pictures were finally obtained from very thin cuts without staining using the decomposing effect of the electron beam. This is especially true for the sample with the largest volume fraction of BMA (BMA/CH 15, $\Phi_{PBMA} = 0.86$) where no sufficient contrast could be achieved and no specific morphology was found. Unfortunately, large deformations were recorded during the decomposition by the electron beam, so that the pictures have only a qualitative meaning with respect to the morphology displayed and no quantitative meaning in terms of distances. Samples with small volume fractions of BMA did show a morphology of highly regularly ordered spheres (see Figure 6), perhaps an influence of the ordered continuous phase of PChEMA. However, small-angle diffraction experiments were performed at a high-resolution X-ray diffraction station (Beamline 4, ESRF, Grenoble) in order to confirm the morphological structures as found by TEM by analyzing higher order reflections of the diffraction signal corresponding to the morphological structure. Figure 5 shows the observed reflection for sample BMA/CH 12. The reflections could be attributed to a hexagonal rodlike morphology (Table 2) and match the values $1:\sqrt{3}:\sqrt{4}:\sqrt{7}$. In principle, the expected morphologies were found and vary with the volume ratios of the different blocks in the copolymers.

The morphologies displayed by block copolymers are well studied in the system PS-*b*-PB and mainly depend on the volume fraction of the two blocks. The scheme for the morphologies is as described by Bates and Fredrickson, a sequence of spherical, rodlike hexagonal, double diamond, and lamellar phases.[27] Nevertheless, a phase sequence similar to that of the system PS/PChEMA[18,19] was obtained from the diblock copolymers described in our study (Figure 6). However, the known morphological sequence is observed for copolymers with small volume fractions of poly(butyl methacrylate) (Φ_{PBMA}). If the volume fraction of poly(butyl methacrylate) increases to a value of $0.6 < \Phi_{PBMA} < 0.8$, no cylindrical phase is observed. We have found a rather direct transition from a lamellar to a spherical morphology. Considering a symmetric phase diagram, the area of the hexagonal phase of PChEMA is again occupied by the lamellar phase. This is probably due to the structure of the subphase. In those samples where the LC subphase is not continuous (spheres), only a disordered phase is seen, whereas in all samples in which there is a continuous LC subphase, the smectic A phase of the homopolymer is formed. A smectic phase can only be realized in continuous subphases like the lamellar or matrix phases, not in rods or spheres of the LC subphase with a very small diameter compared to the layer spacing of the smectic layers (45 Å). The dimen-

Table 2. Molecular Weight, Thermal, and Morphological Data of the PBMA-*b*-PChEMA Block Copolymers[a]

sample	M_n PBMA	M_n copolymer	Φ_{PBMA}	phase behavior (°C)	morph (TEM)
PBMA	50 000		1.00	g 48 i	
		PBMA-*b*-PChEMA Diblock Copolymers			
BMA/CH 18	25 100	162 200	0.13	g 56 g 121 S_A 194 i	PBMA spheres
BMA/CH 11	30 300	125 000	0.21	g 54 g 112 S_A 182 i	PBMA spheres
BMA/CH 12	62 200	120 000	0.34	g 53 g 115 S_A 198 i	PBMA rods
BMA/CH 17	51 000	80 300	0.39	g 56 g 116 S_A 170 i	PBMA rods
BMA/CH 13	20 400	54 400	0.54	g 53 g 116 S_A 174 i	lamellae
BMA/CH 14	18 400	62 000	0.66	g 52 g 112 S_A 175 i	lamellae
BMA/CH 15	10 100	60 000	0.86	g51 g n 143 i	PChEMA spheres
PChEMA	86 000		0.00	g 113 S_A 194 i	

[a] All M_n values are in g/mol as derived by GPC; Φ_{PBMA} = volume fraction of PBMA, calculated using the densities for PBMA ($\varrho = 1.15$ g/cm^3) and PChEMA ($\varrho = 0.99$ g/cm^3).

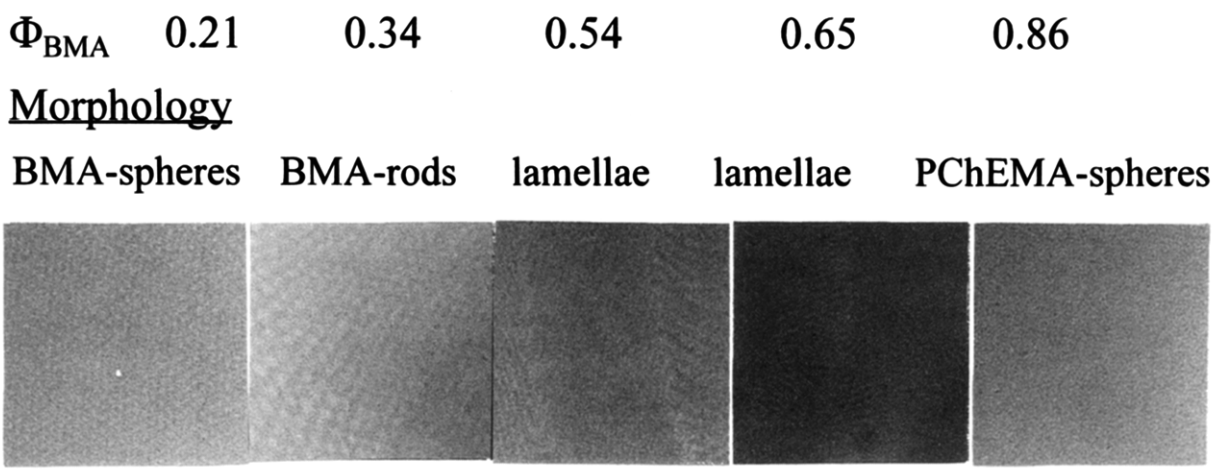


Figure 6. Volume fractions Φ_{PBMA} and TEM pictures (morphologies) of the block copolymers.

sions of the subphases, being only about 200 Å in a spherical subphase, mean that only a few layers of the liquid crystalline structure should be present. This is clearly not enough for a smectic phase to form. Curvature of the spheres may also play an important role in this effect. Therefore, a more disordered structure—*nematic*—of the LC subphase is presumably introduced due to the morphology. With a volume fraction of $\Phi_{PBMA} \approx 0.6-0.7$ a cylindrical structure of the LC subphase may be expected. It may well be that the energetic differences between lamellar and hexagonal phases are smaller than the differences in energy terms between a nematic and a smectic structure. On the other side is the formation of the thermodynamically stable smectic A phase in the subphase, energetically more favorable than the formation of an equilibrium morphology. So a lamellar morphology will be displayed.

Small-angle X-ray studies of shear-oriented samples (see Figure 3) should provide some information about the orientation of the smectic layers in the subphase with respect to the morphology. As already explained, 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; the mesogen orientation is perpendicular to the layer orientation. Two principal pictures have been observed similar to the PS/PChEMA system.[18] In the case of PBMA spheres and PBMA 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 responds to the shear is the liquid crystalline matrix. The mesogens are perpendicular to the morphological elements and a deformation of the PBMA spheres into ellipsoids occurs. A completely different behavior could be observed for samples with lamellar morphology (Figure 3). Here, the orientation of the smectic layers is perpendicular, as described previously.[18,28] We believe that the element of the structure which responds to the shear field is the morphological element, contrary to the samples described before where the bulk liquid crystalline phase reacts to the shear field.

Conclusions

The system PBMA/PChEMA displays a similar phase diagram and macroscopic and microscopic interaction between the morphological structure and the LC behavior of LC side group block copolymers as the system PS/PChEMA. A formation of a disordered (nematic) phase is also seen in those samples where the LC subphase is not continuous (spheres), whereas in all samples in which there is a continuous LC subphase, the smectic A phase of the homopolymer is formed. For volume fractions of PBMA (Φ_{PBMA}) $\approx 0.6-0.7$, a cylindrical structure of the LC subphase was expected. The formation of the smectic A phase in the subphase seems to be more favorable than the formation of an equilibrium morphology. A smectic phase can only be realized in continuous subphases like the lamellar or matrix phases, not in rods or spheres of the LC subphase with a very small diameter compared to the layer spacing. Therefore a lamellar morphology was found for the samples with $\Phi_{PBMA} \approx 0.6-0.7$. The orientation of the LC subphase with respect to the orientation of the morphological elements is dependent on the morphological structure.

Experimental Section

The anionic polymerization was carried out under an argon atmosphere. Tetrahydrofuran (THF) distilled over freshly pressed sodium was used as solvent. The reaction of the OH groups of the second monomer (2-hydroxyethyl methacrylate (HEMA)) with trimethylchlorosilane was carried out according to the procedure described by Zaschke et al.[24] Shortly before the polymerization, both monomers were purified from the remaining water and alcohol by reacting with aluminum triisobutyl after McGrath et al.[26] The initiator ((1,1-diphenyl-3-methylpentyl)lithium) was prepared before the polymerization by a reaction between *sec*-butyllithium and 1,1-diphenylethylene (ratio 1:2). The insertion of the second monomer was carried out after taking a sample of the first block for analysis. After the polymerization, the trimethylsilyl groups were split off by reaction with concentrated hydrochloric acid dissolved in THF, and the block copolymers were precipitated in water. The reaction of the BMA/HEMA block copolymers with cholesteryl chloroformate was carried out at 0 °C by dissolving 1 g of the polymer in 70 mL of dry pyridine and subsequently adding the reaction solution of the chloroformate dissolved in THF in 100% excess. The reaction mixture was stirred for 4 days and precipitated in methanol, washed, and dried. A final purificiation was carried out by preparative HPLC (column PSS, SDV linear, 10 μm, RI detector) to separate the excess of the mesogenic substance.

The molecular weights of the homopolymers and block copolymers were analyzed using a Knauer HPLC apparatus (column PSS, SDV linear, 5 μm, RI/Viscodetector) by using a universal calibration curve. In order to detect the molecular weight of the BMA/HEMA block copolymers, it was necessary to esterify the samples with benzoyl chloride.

Samples for transmission electron microscopy (TEM) and differential scanning calorimetry (DSC) were prepared by casting approximately 1 mm thick films from dilute solutions of the polymers in toluene over a period of about 10 days at 25 °C and annealing them afterward at 130 °C for 24 h under vacuum. The samples were cut using a diamond knife at room temperature, and the thin films (approximately 100 nm thick) were transferred onto copper grids. A Philips EM 301 was used for the TEM studies. DSC traces were obtained using a Perkin-Elmer DSC 7 with heating and cooling rates of 10 K/min. Optical microscopy (POM) was performed using a Zeiss Ultraphot combined with a Linkam THM 600 hot stage. X-ray studies were carried out using an Eliott GX 21 with a copper target combined with a Siemens X-1000 area detector and a Rigaku Denki small-angle film camera. Therefore oriented samples were prepared by pulling fibers out of a melt of the block copolymers. More precise small-angle measurements were performed at the synchrotron facility ESRF in Grenoble, Beamline 4, with a camera length of 9.5 m. The wavelength used was 1 Å and the detection device was a gas-filled multiwire area detector. The accumulation time was 5 min. One-dimensional plots were obtained by radial intensity integration followed by a Lorenz correction of the data.

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