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Liquid-Crystalline Diblock Copolymers Produced by Living Cationic and Anionic Polymerizations

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Two series of liquid-crystalline block copolymers have been synthesized. These polymeric systems consist of an amorphous block and a mesogenic side-chain block. The first system is formed by poly(*n*-butylvinyl ether) (poly(BVE)) as an amorphous block and poly(6-((4-cyano-4′-biphenyl)oxy)hexylvinyl ether) as the liquid-crystalline block. The second system is formed by poly(styrene) (PS) and poly(6-((4-cyano-4′-biphenyl)oxy)hexyl methacrylate). In both systems the mesogenic unit is the same but the polymeric main chains are different. The polymers were prepared by a living polymerization method, cationic in the case of vinyl ethers and anionic in the case of the styrene/methacrylate system, which resulted in materials with well-defined molecular weights and narrow molecular weight distributions. The block copolymers exhibit smectic polymorphism, which has been characterized by means of optical microscopy, DSC, and X-ray diffraction. The microphase-separated character of these block copolymers has been proved by means of small-angle X-ray scattering studies and transmission electron microscopy (TEM).

Introduction

Side-chain liquid-crystal polymers have been extensively investigated in recent years.[1,2] Many studies have been reported in which the relationship between the structure and the physical properties of the polymer was investigated. Polymers with different main-chain backbones, different mesogenic units, and variable flexible spacers have been synthesized. As far as the main-chain backbone is concerned, the most studied systems are poly(vinyl ethers), poly(meth)acrylates, and polysiloxanes. The variety in the mesogenic units is much greater.

The development of polymerization methods such as living polymerization, controlled polymerization, and group-transfer polymerization opens a huge field of new possibilities in the design and synthesis of liquid-crystalline polymeric systems (homopolymer and block and graft copolymers) with well-defined structures, controlled molecular weights and narrow molecular weight distributions. The study of these well-defined polymers provides the possibility of establishing a precise relationship between the structure and the properties of the mesogenic material.

As far as liquid-crystalline block copolymers are concerned, some systems have been described in which one of the blocks is a mesogenic polymer and the other is an amorphous polymer. These systems have been prepared by living cationic polymerization (vinyl ethers),[3−6] living anionic polymerization (polystyrene−polymethacrylate),[7,8] polymer analogous reactions,[9−11] group-transfer polymerization,[12] and living ring-opening metathesis polymerization.[13]

The interest of this type of materials consists of the combination of the properties of two completely different polymers, which are chemically bound to each other. This prevents the occurrence of macroscopic phase separation phenomena. At the same time, a microscopic phase separation takes place due to the segregation of the two (or more) different polymer chains. Ordered mesomorphic structures are obtained (lamellae, cylinders, spheres) in which one of the blocks presents its own order due to its liquid-crystalline nature.

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In this work, we present two new series of liquid-crystalline block copolymers. The amorphous blocks are poly(*n*-butylvinyl ether) and polystyrene and the mesogenic blocks are poly(6-((4-cyano-4′-biphenyl)oxy)-hexylvinyl ether) and poly(6-((4-cyano-4′-biphenyl)oxy)-hexyl methacrylate), respectively.

As has been previously mentioned, many different approaches are possible when pursuing the synthesis of liquid-crystalline block copolymers. We have chosen two different systems whose main chains require different polymer formation mechanisms: anionic polymerization of styrene and methacrylate comonomers and cationic polymerization of vinyl ethers. Moreover, the presence of these main chains give rise to polymers with different thermal behavior as they show glass transitions at high temperature (styrene/methacrylate system) or at low temperatures (vinyl ether systems). In the first place, we are looking for the most versatile, easy, and reproducible synthetic method to achieve block copolymers and in the second place, the study of the behavior of the polymers obtained will give us an idea of which are the most suitable materials from the point of view of technological applications. This comparative study is simplified by choosing the same mesogenic unit for both systems.

The mesomorphic properties of the polymers have been studied with the aid of optical microscopy, DSC, and X-ray diffraction. The microphase separation in the case of the block copolymers has been observed using DSC and small-angle X-ray diffraction methods and transmission electron microscopy.

Experimental Section

Materials. 1,10-Phenanthroline and palladium(II) acetate from Acros Chimica, 1,6-chlorohexanol from Aldrich, and 4-cyano-4′-hydroxybiphenyl from Merck were used as received. All the solvents were obtained from Merck and were dried according to conventional methods. 1,10-Phenantrolinepalladium(II) diacetate, the catalyst for the synthesis of vinyl ethers, was prepared according to a literature procedure.[14]

For the cationic polymerization, *n*-butyl vinyl ether (BVE, Aldrich) was refluxed over calcium hydride and distilled twice under argon. Triflic acid (Acros Chimica) was distilled under argon and methyl sulfide (Aldrich) was refluxed over 9-borabicyclo[3.3.1]nonane and then distilled under argon. Methylene chloride (polymerization solvent) and *n*-hexane (solvent for **5**) were distilled twice over calcium hydride under argon into a flask containing 3 Å molecular sieves.

Methacryloyl chloride (Aldrich, 90%) was distilled under argon before use.

For the anionic polymerization, styrene (Aldrich, 99%+) was distilled over sodium before use. *sec*-Butyllithium (1.4 M solution in cyclohexane) from Aldrich was used as received. 1,1-Diphenylethylene (DPE, Aldrich, 97%) was degassed and distilled twice from calcium hydride under reduced pressure. Monomer **3** was repeatedly freeze-dried from its benzene solution. Tetrahydrofuran, the polymerization solvent, was distilled from sodium benzophenone under argon.

Techniques. ^{1}H NMR spectra were recorded using a Bruker DPX 300 spectrometer. TMS was used as an internal standard, and deuterated chloroform as a solvent.

A Perkin-Elmer DSC-7 differential scanning calorimeter was used to determine the temperatures and enthalpies of transition of the polymers. In all cases, the heating and cooling rates were 20 °C/min.

A Reichert optical microscope provided with a Mettler FP52 hot stage was used to observe the thermal transitions and to analyze the textures of the mesophases.

The molecular weights and polydispersities of the polymers were determined by means of GPC.

All the samples were dissolved in chloroform (Merck p.a.) in a concentration of 1 mg/mL. Of each sample an amount of 25 μL was injected into a couple of columns (PL−gel−5 μL−mixed C, with guard column μL−gel 5 μL−GUARD−linear at $M_w = (2-3) \times 10^6$) and was eluted with chloroform (Acros, LC-quality). The flow rate was 1 mL/min and the UV detector was set at 254 nm. The column was calibrated with the aid of polystyrene standards (Easy-cal).

The X-ray measurements were carried out using a home-built system consisting of a sealed X-ray tube (Cu Kα radiation), a graphite monochromator, a pinhole collimator, a sample stage. All the components were mounted on an optical bench to provide maximum flexibility and easy alignment. Wide-angle X-ray (WAXS) patterns were recorded at a sample-to-detector distance of 7.4 cm and small-angle X-ray (SAXS) patterns were recorded at a sample-to-detector distance of 31.2 cm. The pinholes of the collimator were 0.25 mm in diameter and lay 15 cm apart.

The sample preparation for transmission electron microscopy (TEM) is described elsewhere.[9] A JEOL 2000 FX operating at 80 keV was used for the TEM studies.

Synthesis of the Monomers (2 and 3) and Polymerization. *Synthesis of 4-Cyano-4′-(6-hydroxyhexan-1-yloxy)-biphenyl (**1**).* 4-Cyano-4-hydroxybiphenyl (19.5 g, 0.1 mol), potassium hydroxide (5.6 g, 0.1 mol), and a few crystals of potassium iodide were dissolved in a mixture of ethanol−water (4/1, 150 mL). 6-Chloro-1-hexanol (15 g, 0.22 mol) was added to the resulting solution, which was heated to reflux for 24 h. The ethanol was removed by rotary evaporation and the resulting solid was washed successively with water, dilute aqueous NaOH, and water. Recrystallization from 2-propanol yielded 21 g (70%) of white crystals.

^{1}H NMR (δ, ppm, CDCl$_3$) 7.72 (d, 2H), 7.65 (d, 2H), 7.55 (d, 2H), 7.00 (d, 2H), 4.00 (t, 2H), 3.70 (t, 2H), 1.85 (q, 2H), 1.70−1.40 (m, 6H), 1.30 (s,1H). Mp 95 °C (nematic phase). Clearing point: 115 °C.

*Synthesis of Monomer **2**.* Compound **1** (11.8 g, 0.04 mol) was added to a mixture of 1,10-phenanthrolinepalladium(II) diacetate (1.62 g, 4.0 mmol), *n*-butyl vinyl ether (220 mL), and dry chloroform (200 mL). The mixture was heated at 60 °C for 6 h. After cooling and filtration through Celite to remove the catalyst, the solvent was distilled in a rotary evaporator, and the product was purified by recrystallization from ethanol 96% to yield 9.5 g (75%) of white crystals.

^{1}H NMR (δ ppm, CDCl$_3$) 7.75 (d, 2H), 7.65 (d, 2H), 7.50 (d, 2H), 7.00 (d, 2H), 6.50 (dd, 1H), 4.20 (dd, 1H), 4.00 (t, 2H + dd, 1H), 3.70 (t, 2H), 1.85 (q, 2H), 1.75 (q, 2H), 1.60−1.40 (m, 4H). Mp 75 °C (monotropic nematic phase).

*Synthesis of Monomer **3**.* Compound **1** (8.85 g, 0.03 mol) was dissolved in a mixture of dry tetrahydrofuran (250 mL) and triethylamine (3.33 g, 0.033 mol). To this mixture a solution of methacryloyl chloride (3.13 g, 0.03 mol) in 50 mL of dry THF was added dropwise. The reaction mixture was stirred at room temperature overnight. The white solid which precipitated was removed through filtration and the solution evaporated at reduced pressure. The residue obtained was recrystallized from 96% ethanol to yield 8.1 g (74%) of white crystals.

^{1}H NMR (δ ppm, CDCl$_3$) 7.75 (d, 2H), 7.60 (d, 2H), 7.55 (d, 2H), 7.00 (d, 2H), 6.10 (s, 1H), 5.55 (s, 1H), 4.20 (t, 2H), 4.00 (t, 2H), 2.00 (s, 3H), 1.85 (q, 2H), 1.75 (q, 2H), 1.55 (m, 4H). Mp 77 °C.

Polymerizations. *Series I. Vinyl Ethers.* Polymerizations were carried out in glass flasks equipped with glass stopcocks and rubber septa under an argon atmosphere at 0 °C for 1 h. All glassware was dried overnight at 150 °C.

Monomer **2** was further dried under vacuum overnight in the polymerization flask. Then the flask was filled with argon and cooled to 0 °C, and the methylene chloride, dimethyl sulfide, and triflic acid were added via a syringe.

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Table 1. Molecular Weights, Polydispersities, and Thermal and Thermodynamical Properties of Polymers of Series I

						thermal behavior (T (°C), ΔH (J/g))^d	
polymer	[Mo]/[I]^a	[**2**]/[BVE]	M_n^b	wt % poly(**2**)^c	D^b	heating	cooling
Ia	15		4400	100	1.18	g 24 S_X 44 (1.6) S_A 109 (2.0) I g 15 S_A 102 (2.1) I	I 103 (−1.9) S_A 3 g
Ib	25	0.6	7500	70	1.20	g 23 S_X 48 (2.4) S_A 109 (1.4) I g 21 S_X 46 (2.7) S_A 102 (1.4) I	I 98 (−1.3) S_A 45 (−2.6) S_X 18 g
Ic	35	1.2	16700	80	1.08	g 34 S_X71 (3.7) S_A 121 (1.6) I g 32 S_X72 (3.3) S_A 121 (1.6) I	I 117(−1.4) S_A 69 (−3.6) S_X 29 g
Id	15	3.0	15100	90	1.30	g 30 S_X 69 (5.0) S_A 119 (1.7) I g 20 S_X 57 (4.1) S_A 115 (1.7) I	I 113(−1.7) S_A 51 (−3.6) S_X 15 g

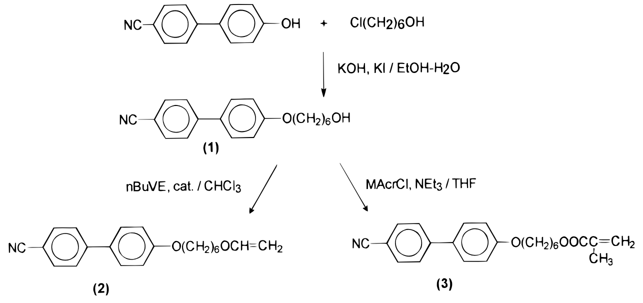
[a] [Mo]: initial concentration of BVE or of **2** (in the case of polymer **Ia**). [I]: initial concentration of initiator. [b] M_n = polystyrene equivalent molecular weight, $D = M_w/M_n$. Determined by GPC. [c] Determined by ^{1}H NMR. [d] DSC data corresponding to the first and second heating scans and to the first cooling scan (g: glass transition, S_X: unidentified smectic phase S_A: smectic A phase, I: isotropic liquid).

Table 2. Molecular Weights, Polydispersities, Thermal and Thermodynamical Properties of Polymers of Series II

						thermal behavior (T (°C))^d		
polymer	[Mo]/[I]^a	[S]/[**3**]	M_n^b	wt % PS^c	D^b	heating	cooling	$\Delta H(S_A{-}I)^e$ (J/g)
IIa	20		6100		1.30	g 53 S_A 91 I g 48 S_A 90 I	I 87 S_A 47 g	4.2
IIb	10	0.25	16000	6	1.12	g 68 g′ 71 S_A 101 I g 59 S_A 100 I	I 97 S_A 61 g	3.5
IIc	50	2	12600	37	1.28	g 52 g′ 77 S_A 99 I g 64 S_A 98 I	I 97 S_A 57 g	1.9
IId	40	3	9000	42	1.30	g 52 g′ 76 S_A 98 I g 64 S_A 98 I	I 95 S_A 56 g	1.3
IIe	30	3	7000	46	1.28	g 48 g′ 75 S_A 91 I g 57 S_A 91 I	I 89 S_A 51 g	1.2

[a] [Mo]: initial concentration of styrene or of **3** (in the case of polymer **IIa**). [I]: initial concentration of initiator. [b] M_n = polystyrene equivalent molecular weight, $D = M_w/M_n$. Determined by GPC. [c] Determined by ^{1}H NMR. [d] DSC data corresponding to the first and second heating scans and to the first cooling scan. (g, g′: glass transition, S_A: smectic A phase, I: isotropic liquid). [e] DSC data from the second heating scan.

Scheme 1. Synthetic Route to Monomers 2 and 3



The monomer concentration was about 10 wt % of the solvent volume, and the dimethyl sulfide concentration was 10 times that of the initiator.

The polymer molecular weight was controlled via the monomer/initiator ratio.

The block copolymers were obtained in sequential polymerization. A prechilled solution of monomer **2** in methylene chloride was added via syringe to the polymerization flask in which the living poly(BVE) chain had been formed.

At the end of the polymerization the reaction mixtures were precipitated into methanol containing a few drops of NH_4OH. The filtered polymers were dried and precipitated from methylene chloride solutions into methanol.

Table 1 summarizes the polymerization results. Although the polymer yields are lower than expected due to losses during the purification process, the conversions were almost quantitative in all cases.

Series 2. Styrene/Methacrylate. Homopolymerization. To a solution of monomer **1** (1 g, 2.7 mmol) in THF was added the corresponding amount of initiator initiator 3-methyl-1,1-diphenylpentyllithium (DPPL). The reaction was stirred at −78 °C under argon for 1 h. The polymerization was quenched by adding 5 mL of methanol. The polymer was repeatedly precipitated into methanol and further purified by means of column chromatography (silicagel, CH_2Cl_2).

Sequential Polymerization. THF (40 mL) and two drops of styrene were introduced into a 250 mL three-necked round flask under argon via a syringe. The solution was cooled to −78 °C. *sec*-Butyllithium (1.4 M solution in cyclohexane) was added until the solution was slightly yellow. The corresponding amounts of styrene and *sec*-butyllithium were added via syringe. After 5 min, 0.03 mL of DPE was added. The orange solution turned immediately deep red, and monomer **1** was added dissolved in 5 mL of THF. The reaction mixture was stirred at −78 °C for 30 min and then quenched by adding 5 mL of methanol. The block copolymers were repeatedly precipitated into methanol and further purified by means of column chromatography (silicagel, CH_2Cl_2).

Table 2 summarizes the polymerization results.

Results and Discussion

Synthesis. The syntheses of monomers **2** and **3** are shown in Scheme 1. They involve well-known procedures.

The method used to prepare the homopolymer and block copolymers of series I consists of a living cationic polymerization using the system triflic acid−methyl sulfide as an initiator (Scheme 2). This polymerization method has been extensively used and described by Percec and co-workers.[3] It has proved to yield good results in producing liquid-crystalline block copolymers with narrow molecular weight distribution.

Anionic polymerization using the *sec*-BuLi/DPE system as an initiator has been widely used to obtain poly(styrenes) and poly(methacrylates) with narrow molecular weight distributions.[7,8,17]

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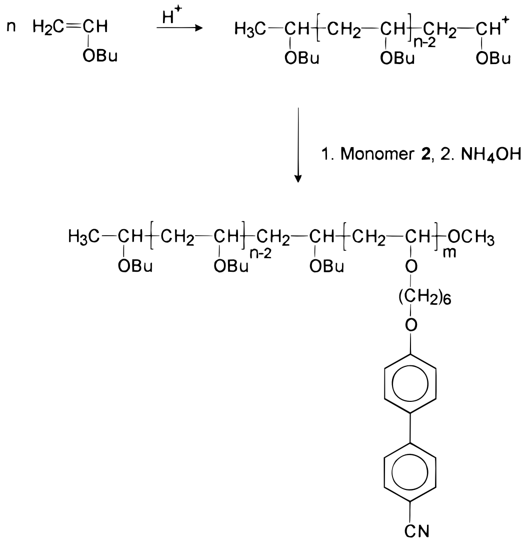
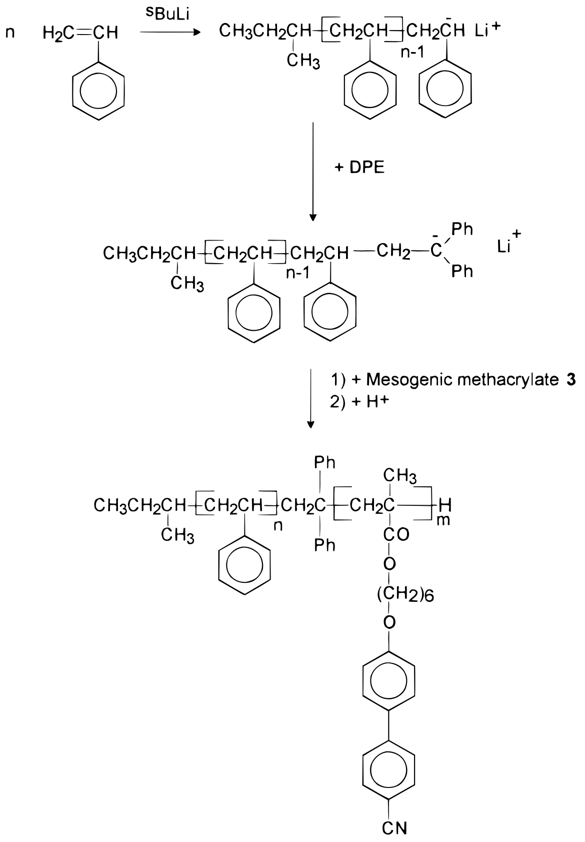
Scheme 2. Polymerization Method for Polymers of Series I



Scheme 3. Polymerization Method for Polymers of Series II



The poly(styrene-*co*-methacrylate) block copolymers (series II) were prepared by polymerizing styrene (initiator: *sec*-butyllithium), adding the living styrene polymer to DPE, and polymerizing with the aid of the mesogenic methacrylate **3** (Scheme 3). The liquid-crystalline homopolymer was synthesized using the initiator 3-methyl-1,1-diphenylpentyllithium (DPPL) which was prepared in a stoichiometric reaction of *sec*-butyllithium and DPE according to a method previously described.[15]

In our case, the presence of a cyano group in the mesogenic methacrylate **3** gives rise to undesirable reactions due to its reactivity with anions. However, the homopolymer and block copolymers described in this work were obtained in reasonable yields (about 50%). Their structures have been confirmed by means of ^{1}H NMR, and the properties of these materials also confirm their block copolymer nature.

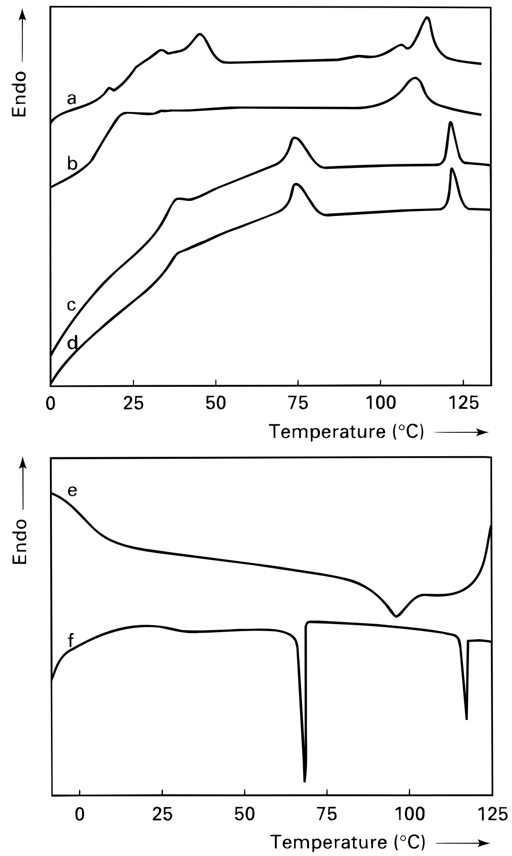


Figure 1. (A) (a) First heating scan of homopolymer Ia. (b) Second heating scan of homopolymer Ia. (c) First heating scan of block copolymer Ic. (d) Second heating scan of block copolymer Ic. (B) (e). First cooling scan of homopolymer Ia. (f) First cooling scan of block copolymer Ic.

By using a sequential living polymerization method, it is possible to synthesize block copolymers with controlled molecular weights, controlled relative compositions of the different blocks, and narrow molecular weight distributions. We are, thus, able to synthesize tailor-made polymeric materials in a reproducible way by adjusting the monomer/initiator concentration ratio. Both synthetic methods give rise to the desired liquid-crystalline block materials as it is described in the present work. However, the cationic polymerization of vinyl ethers appeared to be an easier and more reproducible synthetic method compared to the anionic polymerization of the styrene/methacrylate system. In our case, this fact is clearly influenced by the presence of a cyano group in the mesogenic units.

Characterization of the Polymers. The investigated polymers (homopolymers and block copolymers) were characterized using ^{1}H NMR, GPC, DSC, and polarizing optical microscopy. Their molecular weights, polydispersities and thermal properties are shown in Tables 1 and 2.

Series I. Vinyl Ethers. As an example, Figure 1a shows the thermograms obtained for homopolymer **Ia** and block copolymer **Ic** in the first and second heating scans. Figure 1b shows the first cooling scans of the same polymers.

All the polymers of series I show an unidentified smectic phase (S_X) at room temperature and a smectic A mesophase at higher temperatures.

The homopolymer **Ia** exhibited the S_X phase only in the first heating scan. This behavior was also reported by Percec et al.[16] for homopolymers poly(**2**) with molecular weights in the range 3000−4500, and the authors named this phase "inverse" monotropic.

For the block copolymers **Ib**, **Ic**, and **Id**, with higher degrees of polymerization, the S_X mesophase is enantiotropic and its appearance does not depend on the sample's thermal history.

The smectic A mesophase is enantiotropic in all the cases, and it is present in a wide range of temperatures.

From the DSC data only the T_g corresponding to the liquid-crystalline block can be observed.

The glass and phase transition temperatures depend mainly on the molecular weight of the liquid-crystalline chain. The values obtained for the enthalpy of the transition smectic A to isotropic liquid are in agreement with the occurrence of a phase separation, as they do not differ much from the expected values with due allowance for the weight fraction of the liquid crystalline block in the copolymer.

Series II. Styrene/Methacrylate. The thermal behavior of the polymers of series II is shown in Table 2. During the first heating scan, the untreated block copolymers **IIb**−**e** showed two glass transitions and a smectic A mesophase before becoming an isotropic liquid.

These data are in agreement with the occurrence of a phase separation phenomenon: the block copolymers show the same transitions as their constituent polymeric blocks, the glass transition and smectic A phase as the mesogenic polymer **IIa** and the glass transition corresponding to a low molecular weight polystyrene chain.

The clearing points measured for the block copolymers are in accordance with those of the homopolymer. Only slight differences due to different molecular weights of the mesogenic chain involved in the block copolymers can be observed.

The two glass transitions observed during the first heating scans were not observed in the same way in the first cooling and second heating scans. A jump in the specific heat of the samples was observed in the range of temperatures in which the two glass transitions were previously found.

However, the isotropic transition occurred at the same temperature, indicating that the two blocks are still segregated to a certain extent.

With respect to the S_A−I transition enthalpies it is noteworthy that the values obtained are much lower than those that can be calculated taking into account the block composition and the enthalpy value obtained for homopolymer **IIa**. The higher the content of polystyrene in the block copolymer, the greater the deviation of the value obtained from the calculated one (Figure 2). This can be explained by assuming the existence of an interphase between the two segregated phases near the isotropic transition. The mesogenic chains in such an interphase show no transition when the seggregated chains do, resulting in a decrease in the transition enthalpy with respect to the calculated value. This effect may be the result of the relatively low molecular weight of the two blocks in the polymers. Such an interphase is not to be expected at lower temperatures because the X-ray data clearly indicate phase separations (see below).

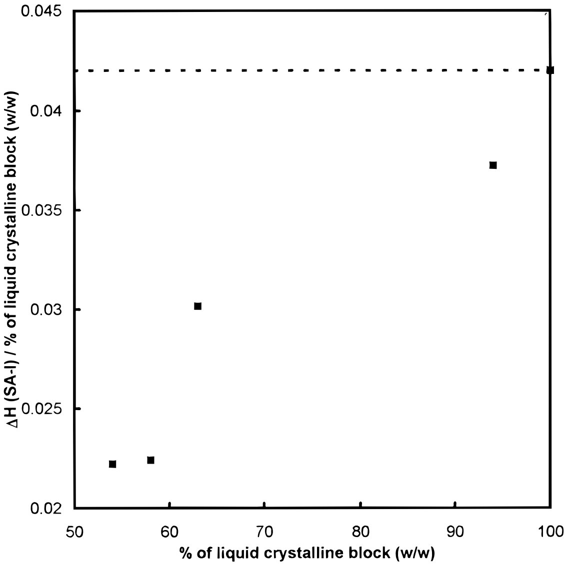


Figure 2. Enthalpy of transition S_A−I divided by the weight percentage of poly(**3**) as a function of this weight percentage for polymers of series II.

X-ray diffraction measurements. *Series I. Vinyl Ethers.* Block copolymers **Ib** and **Ic** were studied by means of X-ray diffraction at room temperature. The samples were oriented films made at room temperature by shearing the polymers on a glass surface.

WAXS studies revealed a reflection at ~4.3 Å, corresponding to the spacing between the mesogens. This reflection showed four peaks of maximum intensity, indicating a tilted arrangement of the molecules in the smectic layers. The calculated tilt angle from the X-ray diffraction pattern is ~45°.

Intense reflections were also observed at ~25 Å. They corresponded to the spacing of the smectic layers. This value is in agreement with a tilted structure of the molecules in the partially interdigitated bilayer, which is typical of polymers containing the cyanobiphenyl moiety as a mesogenic group.[18,19]

In an orthogonal arrangement a bilayer with a thickness of ~35 Å can be expected. Considering a molecular tilt angle of ~45°, we found a *d* spacing of ~25 Å for the smectic bilayer.

SAXS showed intense reflections at ~200 Å due to the phase separation of the blocks.

In the case of block copolymer **Ib**, these reflections are perpendicular to those attributable to the smectic layers when the film is positioned edge-on with respect to the X-ray beam. When the film is positioned flat-on, no small-angle reflections attributable to the separation

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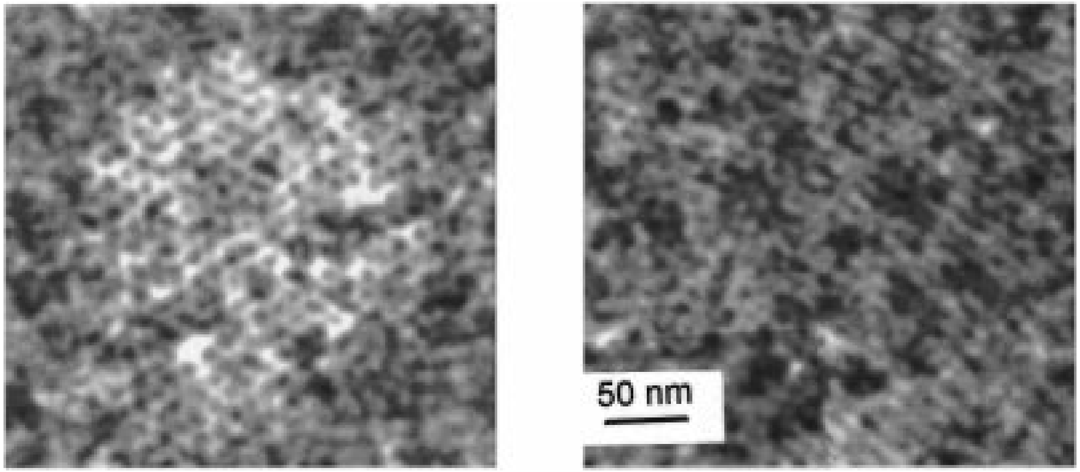

Figure 3. TEM microphotographs of block copolymer IIc.

of the blocks are observed. These results suggest the existence of a lamellar structure.[20]

The patterns obtained for block copolymer **Ic**, on the contrary, show a parallel orientation of the blocks with respect to the smectic layers. These patterns have been found for cylindrical or spherical structures.[20] Thus, in the case of block copolymer **Ic**, a morphology consisting of cylinders or spheres of poly(BVE) in a matrix of poly(**2**) can be expected.

No TEM studies of these materials have yet been carried out, because a distortion of the cuts due to the low glass transition temperatures during cutting was always observable. In the future research will be carried out into cryogenically cut samples to confirm the interpretations of the X-ray data obtained.

Series II. Styrene/Methacrylate. X-ray diffraction experiments were carried out at room temperature using oriented samples of block copolymers **IIb**−**e**. The samples were fibers drawn from the S_A melt.

Reflections were observed at ~4.3 Å, which correspond to the spacing between the mesogens. In this case only two intensity maxima were observed, perpendicular to the reflections attributable to the smectic layers for an orthogonal S_A mesophase. The *d* spacing obtained for the smectic interdigitated bilayer[18] is ~36 Å.

SAXS studies showed intense reflections in the 130−160 Å range attributable to the phase separation of the constituent blocks.

In the case of block copolymers **IIc**−**e** these reflections were found to be parallel to those corresponding to the smectic layers, suggesting a cylindrical or spherical morphology of polystyrene in a matrix of poly(**3**).

The polymers of series II could be studied using the TEM. No deformation of the samples occurred during the cutting procedure because the T_g of the polystyrene block was higher than that of the poly(*n*-butylvinyl ether) blocks of the samples of series I. As an example a TEM picture of a thin cut of sample **IId** is shown in Figure 3. A cylindrical morphology is visible. Figure 3a shows a view of the cylinders side-on and Figure 3b a view of an area of a cut through the cylinders. Here too, an approximately hexagonal arrangement of the cylinders can be seen. The morphologies found in the TEM investigation confirm the results of the X-ray investigations of the polymers of series II.

Conclusions

Two series of liquid-crystalline block copolymers have been synthesized and their thermal and structural properties have been investigated. The chemical composition of the polymeric main chain and the non-liquid-crystalline polymeric block influences their microphase separation. The use of poly(vinyl ether) as main chain provides materials with low glass transition temperatures, that are easy to process and with highly phase-separated microstructures. The polystyrene − liquid-crystalline poly(methacrylate) system results in brittle materials that are much more difficult to process. Calorimetric studies have shown that the interphase region between the two segregated blocks is larger than in the poly(vinyl ether) system. From all these results, it can be concluded that the liquid-crystalline vinyl ether block copolymers are suitable materials to be used for application purposes.

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