A Block Copolymer from Polystyrene and Columnar Liquid-Crystalline Poly(diethylsiloxane)

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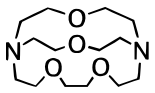
ABSTRACT: A block copolymer from polystyrene (PS) and poly(diethylsiloxane) (PDES) has been synthesized by sequential anionic polymerization. By DSC, the PDES block was shown to exist in the columnar mesophase at ambient temperatures. By transmission electron microscopy and scanning force microscopy on thin films, the block copolymer was shown to build regular structures, showing a large periodicity, which is unusual for relatively low molecular weight block copolymers and must be ascribed to the fact that the PDES block exists in the mesophase.

Introduction

Block copolymers from poly(dimethylsiloxane) (PDMS) and polystyrene are well-known.[1,2] Due to the incompatibility between the hydrocarbon and the siloxane chains, these polymers show microphase separation into glassy polystyrene and rubbery PDMS domains.[1,3]

Unlike PDMS, poly(di-*n*-alkylsiloxane)s with longer side chains are able to form a columnar mesophase, in which the molecules are positionally and orientationally ordered in a two-dimensional hexagonal lattice, but where along the chain no long range correlations exist.[3−5] The best known member of this series of polysiloxanes is poly(diethylsiloxane) (PDES). PDES with a molecular weight over ca. 30 000 g/mol exists in the mesophase at ambient temperatures.[6,7] Well-defined samples of this polymer can be synthesized by anionic ring opening polymerization of the cyclic trimer hexaethylcyclotrisiloxane (D_3^{Et}), initiated by an organolithium compound. In first instance, a nonreactive lithium silanolate results, which can be activated for polymerization by addition of a lithium complexing compound, e.g. the cryptand [211] (**1**).[8] The reaction is terminated by the addition of a chlorosilane.



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Block copolymers from PDES and polystyrene can be expected to segregate into glassy polystyrene domains, exhibiting mechanical strength and optical isotropy, and mesomorphic PDES domains, exhibiting plasticity and birefringence.

Experimental Section

Materials. Hexaethylcyclotrisiloxane (D_3^{Et}) was prepared as described before[9] and purified by distillation from CaH_2 on a high vacuum line. Styrene (Merck, >99%) was distilled from KOH and subsequently degassed and distilled from $Mg(C_4H_9)_2$ by means of a high vacuum line. Hexamethylcyclotrisiloxane (D_3^{Me}, Aldrich, 98%) and toluene (Merck, p.a.) were distilled from CaH_2 and sodium, respectively, and stored under argon. The cryptand [211] (Merck, 98%) was distilled under high vacuum conditions, using a quartz apparatus. The ligand was obtained as a colorless liquid, which was dried azeotropically with toluene/$Mg(C_4H_9)_2$, dissolved in toluene, and stored under argon in a quartz flask. Trimethylchlorosilane (ABCR, 99.9%) and *sec*-BuLi (Aldrich, 12% in 92/8 cyclohexane/hexane) were used as received.

Synthesis of the Block Copolymer. The AB block copolymer was synthesized by sequential polymerization of styrene and hexaethylcyclotrisiloxane, D_3^{Et} (where D^{Et} denotes a $-Si(Et_2)O-$ unit). The polymerization was carried out in a glovebox under a nitrogen atmosphere containing less than 1 ppm H_2O and O_2. It was started by the addition of *sec*-BuLi (0.14 mmol) to a solution of styrene (1.50 g) in toluene (15 mL) at −20 °C. After ca. 30 min, the solution was allowed to warm up to room temperature, and after a total reaction time of ca. 3 h, a sample (0.5 g of PS) was taken and terminated with methanol. Since the attack of the polystyryl anions on D_3^{Et} proceeds very slowly, a small amount of the more reactive hexamethylcyclotrisiloxane (D_3^{Me}, 0.13 mmol) was added first in slight excess with respect to the lithium carbanions and allowed to react overnight. The reaction could be monitored by the disappearance of the orange color. After the solution had turned colorless, a second sample (0.5 g of PS) was taken. Then, D_3^{Et} (5.0 g) and the cryptand [211] (0.10 mmol) were added, after which the reaction mixture turned opaque. With increasing viscosity, the reaction mixture became clear again. The reaction was terminated with trimethylchlorosilane at about 80% D_3^{Et} conversion. The block copolymer was isolated from the solution, purified by repeatedly precipitating in hot ethanol, and dried under vacuum at 80 °C.

Methods. Molecular weights and molecular weight distributions were obtained from GPC. The setup consisted of Waters μ-Styragel columns with pore sizes of 10^5, 10^4, 10^3, and 10^6 Å. Sample detection was performed by a Waters 410 differential refractometer and a Viscotek H502B differential viscometer, allowing universal calibration. Toluene was used as the eluent, and the setup was calibrated with narrow polystyrene samples.

DSC measurements were made with samples of about 10 mg on a Perkin Elmer DSC 7 system. Cooling and heating rates were 10 °C/min, except for the determination of the polystyrene T_g, where a heating rate of 30 °C/min was used.

Films for transmission electron microscopy were cast on a water surface from a 1 wt % solution of the block copolymer in toluene and transferred to copper grids. Transmission electron micrographs were recorded with a Philips EM 301 microscope operating at 80 kV in the bright field mode. No staining was necessary, because of the differences in electron absorption and scattering of the PS and PDES domains.

Thin block copolymer films for scanning force microscopy were cast from a 1 wt % solution in toluene on a mica substrate. A Nanoscope III (Digital Instruments) operating in the tapping mode[10] was employed to scan the surface of the dried films. The measurements were made at ambient conditions (in air) using a Si cantilever with a spring constant of about 50 N/m and a resonance frequency of about 360 kHz.

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Table 1. Molecular Weights and Molecular Weight Distributions from GPC

	calcd M_n	M_n	M_w	M_w/M_n
PS block	11 000	13 700	14 700	1.07
PS block[a]	11 000	13 400	14 600	1.09
block copolymer	124 000	94 400	116 000	1.2

[a] Control sample taken before addition of D_3^{Et}.

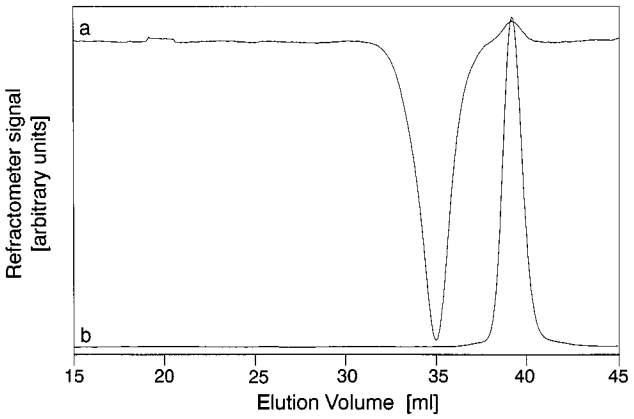

Figure 1. GPC chromatograms of (a) PS-*b*-PDES and (b) the PS block (signal from the refractometer, in toluene PDES, shows a negative and, in PS, a positive signal).

The radius of the tip was evaluated as being ca. 10 nm, using a calibration gauge for SFM tips.[11]

Results and Discussion

Molecular weights and molecular weight distribution of the block copolymer are listed in Table 1. End capping of the polystyryl anions with D_3^{Me} had no significant influence on the molecular weight. Figure 1 shows GPC chromatograms of the block copolymer and the polystyrene homopolymer. Analysis of these chromatograms revealed that the block copolymer sample contained some homopolystyrene. From PDES and PS homopolymer samples the concentration−peak area relationship was determined and the amount of homopolystyrene could be estimated to be about 1.3 wt %. The presence of this homopolymer may be caused by some side reactions during the initiation of the siloxane block. It is, however, not expected that this amount of homopolymer influences the sample's phase behavior.

Figure 2a shows a DSC diagram of the sample. Due to the low polystyrene content (ca. 11 wt %), only a small ΔC_p effect was monitored for the polystyrene T_g.

Poly(diethylsiloxane) is known to crystallize in two different modifications: a chain folded α modification, which is kinetically favored, and an extended chain β modification, which is thermodynamically more stable.[12] α-PDES and β-PDES are characterized by thermal transition to the mesophase (μ) at ca. 7 and 15 °C, respectively. Both transitions, as well as the transition of the mesophase to the isotropic melt, have been monitored. Figure 2b shows a DSC diagram of a PDES sample of about the same molecular weight as the length of the copolymer's PDES block, and Table 2 compares transition temperatures and compositions of the crystalline phases. The block copolymer's transition temperatures are, within experimental error, equal to those of the homopolymer. It can be concluded that the formation of the mesophase is not hindered by the presence of the polystyrene block. From Table 2 it becomes clear that the amount of crystalline material in the extended chain β modification, as calculated from the peak ratios at 7 and 16 °C, is much smaller for the block copolymer than for the homopoly(diethylsiloxane) sample. A similar effect has been observed in PDES networks, where the fraction of β-crystalline material was much lower in the network than in the precursor polymer.[13]

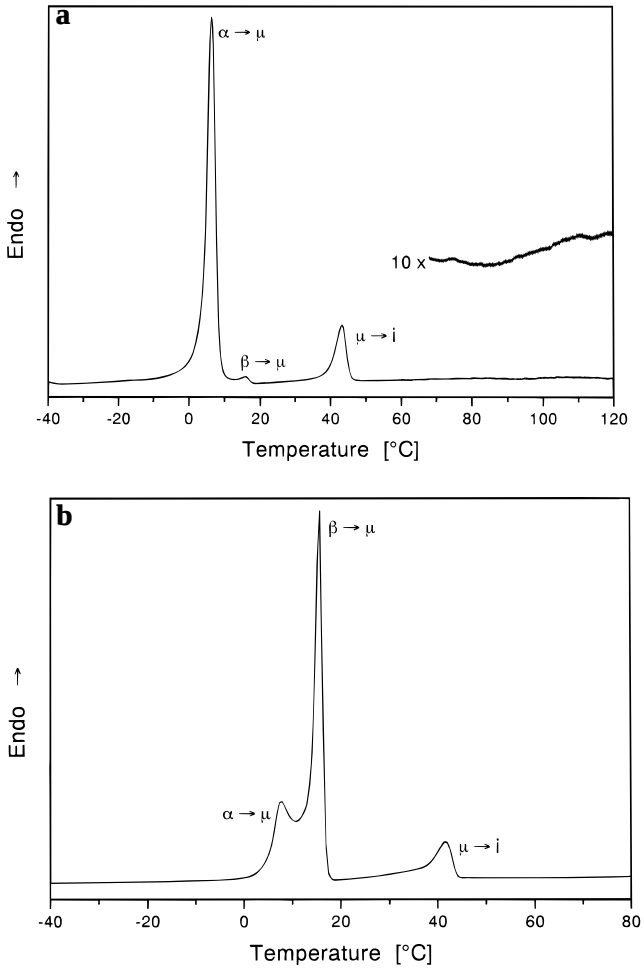

Figure 2. Heating thermograms of (a) PS-*b*-PDES and (b) PDES (M_w = 89 000, M_w/M_n = 1.12) after cooling from 80 °C with 10 °C/min, heating rate 10 °C/min, heating rate for T_g determination 30 °C/min.

Table 2. Transition Temperatures[a] and Compositions[b] of the Crystalline Phases from DSC

	M_n (PDES)	$T_{\alpha-\mu}$ (°C)	$T_{\beta-\mu}$ (°C)	$T_{\mu-i}$ (°C)	T_g (°C)	x_α (wt %)	x_β (wt %)
PS-*b*-PDES	81 000	6.5	15.9	43	98	98.5	1.5
PDES	80 000	7.6	15.9	42		40	60

[a] Peak maxima are taken as transition temperatures. [b] Estimated from the DSC peak areas, using $\Delta H_{\alpha-\mu}$ = 17 and $\Delta H_{\beta-\mu}$ = 21 J/g, respectively.[12]

The structure of the PS-PDES block copolymer was examined by scanning force microscopy (SFM) and transmission electron microscopy. Linear patterns, or stripes, were observed by SFM at the free surface of the cast films as shown in Figure 3. Most of the stripes are organized periodically with a period of 120 nm.

The observed structure can be assigned to micro domains which result because the constituent blocks segregate into different phases, i.e., the stripes consist of alternating PS and PDES domains. At room temperature PS exists in the amorphous glassy state and PDES in the columnar mesophase. These states differ from each other not only by molecular order, but show

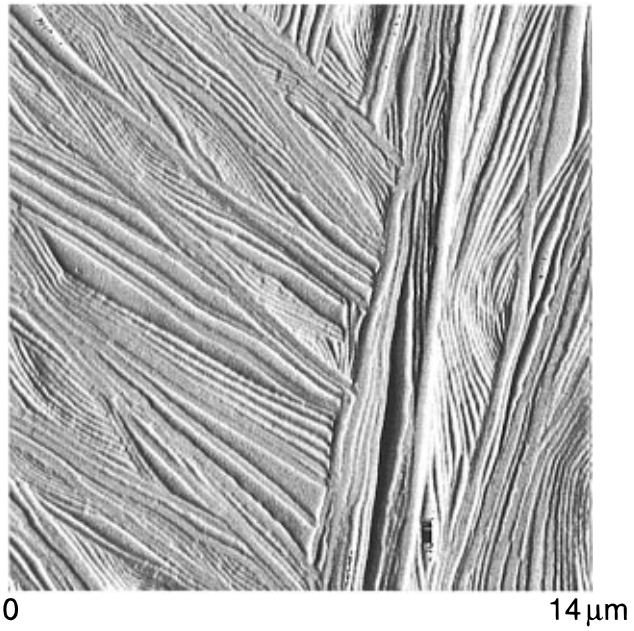

Figure 3. SFM micrograph of the surface of the PS-PDES block copolymer, cast on a mica substrate from a 1% solution in toluene.

different mechanical properties as well; e.g., the elastic modulus for amorphous PS is about 3200 MPa, while for PDES this value is less than 1 MPa.[14]

In order to discriminate between the components in the SFM experiment, the sample was scanned with different forces. The force value was varied either by changing the set point of the feedback system or by a frequency shift. Absolute values of the forces affecting the sample depend on many parameters, e.g., frequency, amplitude, mechanical characteristics of sample and cantilever, or tip geometry. However, a peak value was estimated to lie between 10^{-9} and 10^{-6} nN, which corresponds to a surface deformation of 0.8−2 nm.[15]

Variations of the structure depending on the force value are shown in Figure 4. Increasing the force caused deformation of the surface. The convex elevated stripes in the low force image are modified to grooves, bordered with linear protrusions of 20 nm in width and ca. 1.4 nm in height. The indentation of the tip into the surface by taking the height of the protrusion is in agreement with the calculated values for the surface deformation. The deformation was reversible, and the stripes recovered to their original shape upon decreasing the force. Thus, the experiment revealed two components with different strength. Upon increasing the force, the minor PS phase gets visualized as protrusions while the softer PDES phase experiences larger deformations and appears as grooves.

Transmission electron microscopy on thin films (Figure 5a) revealed structures similar to those found in the SFM experiment. In this case, the periodicity is about 100−125 nm, which is consistent with that observed by SFM. If the film was annealed at 130 °C, a structure as depicted in Figure 5b was found.

It must be noted that the textures found by TEM and SFM deviate, probably considerably, from the equilibrium bulk structure. Both SFM on surfaces as well as TEM were performed on cast thin films. The domain structure and orientation has been shown to depend on the thickness of such ultrathin films.[16,17] The transformation of the structure upon annealing (Figure 5a to 5b) demonstrates that the as cast film is a metastable

Figure 4. Lamellar structure of the block copolymer, measured by SFM at different forces: (a) amplitude (A) = 36.14 nm, (b) A = 30.58 nm, (c) A = 23.63 nm. Smaller amplitudes correspond to higher indentation of the surface.[14]

structure controlled by the casting conditions. However, also in the case of the annealed film, the domain structure may be notably influenced by the interface to the substrate or air.[18,19] Up to now we have not been able to do TEM on ultrathin sections from the bulk material. Further research must be also directed toward understanding of the actual equilibrium structure of this block copolymer as a function of the block lengths.

However, two conclusions may be drawn from the textures shown in Figures 3−5: (i) the regular domain structure confirms the preparation of a well-defined block copolymer and (ii) the periodicity of more than 100 nm is remarkable for a block copolymer with a molecular weight around 100 000. We ascribe the formation of such large domains to the stretched conformation of the mesomorphic PDES block.

Based on small angle neutron scattering experiments, a "hairpin" model has been developed, in which the PDES chains are assumed to be folded in two parallel stretched sequences.[20] If the length of two monomer units in an extended siloxane chain is taken as 5.1 Å,[21] the length of an extended PDES chain with a number

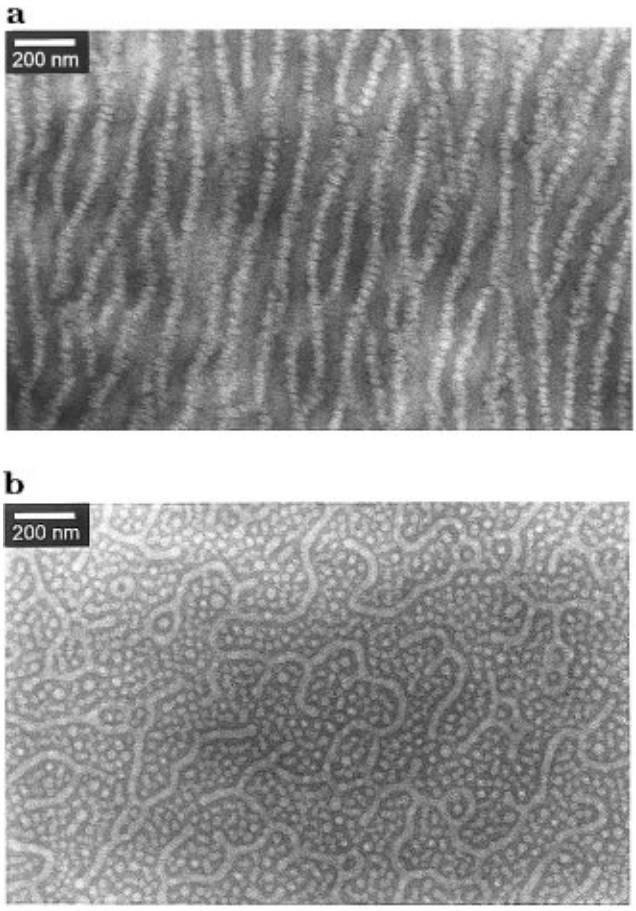

Figure 5. (a) TEM micrograph of a block copolymer thin film, cast from toluene solution, (b) after annealing at 130 °C.

average molecular weight of ca. 81 000 can be calculated to be ca. 200 nm. Half of this length correlates very well with the values for the width of the PDES stripes.

The large periodicity of this block copolymer allows us to enable domain sizes in the order of $\lambda/4$ (where λ is the wavelength of visible light). This is supported by the fact that the polymer in the bulk shows a yellowish to bluish tinge.

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