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Liquid Crystalline Triblock Copolymers. Mechanical Behaviour and Orientation under Uniaxial Strain

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SUMMARY: The stress-strain and orientation behaviour of side-chain liquid crystalline(SLCP) ABA triblock copolymers with a backbone of polystyrene-*block*-1,2-polybutadiene-*block*-polystyrene and a cyanobiphenyl mesogen in the side chain was investigated in dependence of molecular weight. The polymer shows the behaviour of a thermoplastic liquid crystalline elastomer(TPLCE) in the nematic phase in a region between the glass transitions of the polystyrene block and the SLCP. The ultimate properties and E-modulus is lower than for conventional thermoplastic elastomers. Under uniaxial strain liquid crystalline order perpendicular to the direction of strain is induced.

Introduction

ABA LC triblock copolymers with a low content of amorphous hard A-blocks and a soft LC center block represent a novel type of block copolymers that can be regarded as thermoplastic liquid crystalline elastomers (TPLCE). A TPLCE represents an anisotropic network and the question arises how the elastic properties of a TPLCE compare with those of conventional TPE's as well as with those of liquid crystalline elastomers (LCE). The synthesis and the morphological behaviour of TPLCE's based on polystyrene-b-1,2-polybutadiene-b-polystyrene triblocks has been reported in previous papers[1-2]. It has also been reported that the the TPLCE transforms to an optically transparent single-crystal-like material under large oscillatory shear[3]. In this paper the mechanical and orientational behaviour under uniaxial strain is reported.

Materials

The materials studied in the present work are ABA triblock copolymers with polystyrene A-blocks and a side chain liquid crystalline polymer(SLCP) B-block of the following structure

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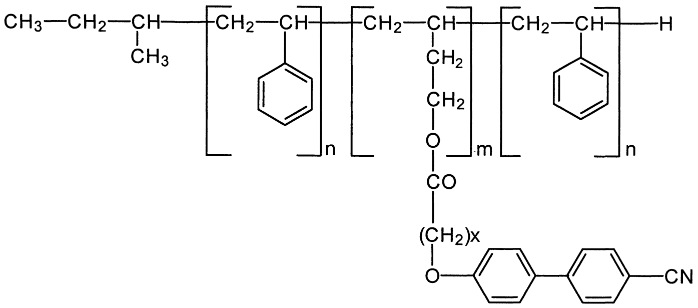

where x = 4 in the present case. Synthesis and characterization are have been described in a previous paper¹⁾. The phase transitions of the SLCP block are g/34°C/n/122°C/i. Triblocks of molecular weights 411000 g/mol (sample A) and 84000 g/mol (sample B) are investigated having a PS content of 10.5 wt% and 11.9 wt%, respectively. The block copolymers possess spherical bcc morphology in the isotropic melt²⁾ and the transition to the nematic phase induces a morphological transition into a hcp cylindrical morphology²⁾.

Experimental

Block copolymers were melt pressed at 160°C for 20 min and cooled slowly to room temperature during 12h. After cooling the samples were annealed at 160°c for at least 24h. For stress-strain measurements standard samples according to DIN 53 455, form 4, were prepared. The measurements were carried out with a computer-controlled INSTRON 4204 testing machine at a stretching rate of 2 mm/s. Dynamic mechanical analysis (DMA) was carried out with a Rheometrix solid analyser RSAII in shear sandwhich geometry. 2D WAXS measurements were performed with a Kiessig camera and an image-plate detector system.

Mechanical properties

In Fig. 1 stress-strain curves up to strain at break are shown for two molecular weights of the triblock copolymers. The materials exhibit rubber-like elasticity in a certain temperature range between Tg of the nematic center block and Tg of the PS domains. The typical plateau region of isotropic thermoplastic elastomers (TPE) as SIS block copolymers⁴⁾ is less developed and maximal strain and stress values are lower in the LC triblock copolymers. For the lower molecular weight material the tear strength decreases with increasing temperature until flow starts at about 64° C. In contrast the ultimate properties of the higher molecular weight material are almost independent of temperature up to 80°C and also the form of the

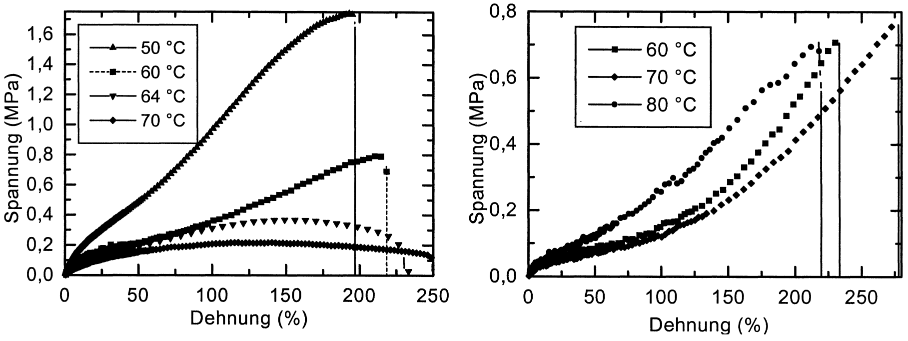

Figure 1: Stress-strain curves of triblock copolymer with Mn = 84 000 g/mol (left) and with Mn = 411 000 g/mol (right)

curves does not change and shows TPE-like behaviour. Within the limitation of the temperature range the higher molecular weight material may be considered as thermoplastic liquid crystalline elastomers (TPLCE). Cyclic stress-strain measurements shown in Fig. 2 show the typical hysteretic behaviour of TPE's. The permannt set is much more pronounced in the triblock copolymer of lower molecular weight. This is explained by the deformation of the PS cylindrical domains in addition to slow reorientation of the cylinders into the direction of strain. Permant set is diminished when the samples are annealed for some time at the measuring temperature. The initial state is completely restored after annealing at 160°C.

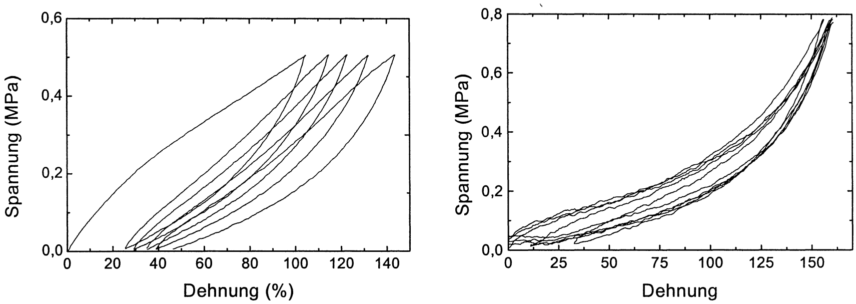

Figure 2: cyclic stress-strain of triblock with Mn = 84 000 g/mol (left) and with Mn = 411 000 g/mol (right)

Fig. 3 shows DMA curves measured with the higher molecular weight triblock copolymer. The pronounced drop of the shear modulus G' at the nematic-isotropic transition has also been observed for the homopolymer proving that the effect is not due to the morphological transition from cylindrical to spherical morphology that is induced by the phase transition. The effect is remarkable because in other nematic polymers only weak softening or even hardening was observed at T_{ni}[5,6]. The effect is reversible on heating and cooling.

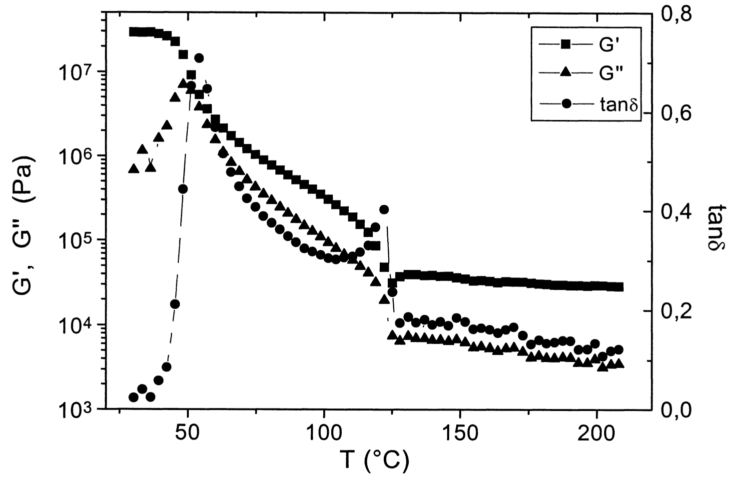

Figure 3: Dynamic mechanical behaviour of triblock with Mn = 411 000 g/mol

Orientation under strain

In previous work it was shown that by large oscillatory shear that optically uniaxial transparent films were obtained having the properties of single liquid crystals[3]. It was shown that the nematic director and PS cylinders were oriented perpendicular to the shear plane having order parameters of 0.66 and 0.50, respectively. In order to determine the orientation behaviour under uniaxial strain the 2D WAXS pattern during stretching of a rectangular film at a temperature of 55°C was measured. Before data collection the sample was annealed for 30 min at the measurement temperature. Fig. 4 shows the intensity distribution of a sample strained to maximum strain.

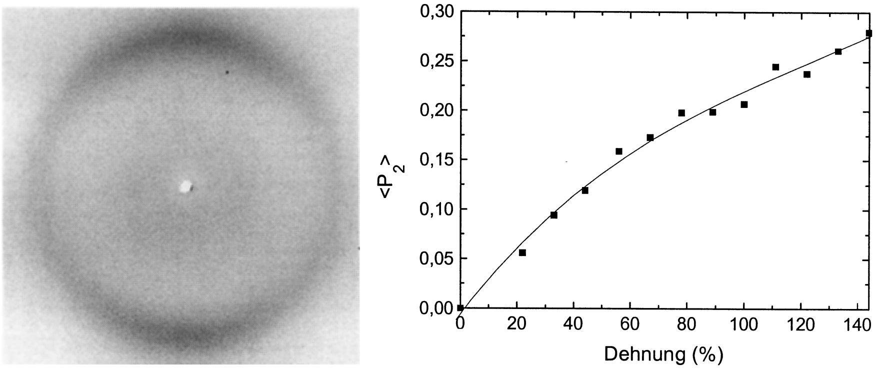

Figure 4: WAXS pattern at maximum extension(strain axis vertical) and order parameter as function of strain

The pattern shows that the mesogens are preferentially oriented perpendicular to the axis of strain and parallel to the film surface. A similar behaviour was found for chemically crosslinked nematic elastomers[7]. The orientation parameter $< P_2 >$ calculated from the azimuthal intensity distribution as a function of strain is also displayed. Order is reduced as compared to the order achieved under shear deformation. Also the sample remained turbid under uniaxial deformation, i. e. optical uniaxiality could not be achieved under these conditions as in the case of shear. At the present state we have no information about the orientation of the PS cylinders.

Discussion

The preferred perpendicular orientation of the mesogens to the direction of strain indicates that the SLCP belongs to the class of LC polymers in which the main chain adopts an oblate chain configuaration with respect to the nematic director[8]. The additional orientation parallel to the film surface is explained by preferred homogeneous orientation of the nematogens at the film surfaces under condition of uniaxial strain(to be distinguished from planar shear where homeotropic anchoring in conjunction with the formation of smectic clusters is observed). As in the triblock copolymers a single-crystal-like state could not be achieved by uniaxial strain. Apparently the stretching of main chains along the strain axis on the one side and the perpendicular orienation of the director on the other side generates an unfavourabele entropic situation rich of defects.

Another reason of low LC order in the TPLCE's is the interaction of the LC phase with the PS cylinders. From the experiments with sheared block copolymers it is known that the long axes of the cylinders tend to be aligned along the nematic director, in other words homogeneous anchoring of the mesogens at the internal interfaces of the microdomains is preferred. When we assume that under uniaxil strain the cylinders are rotated into the direction of strain as it is the case for isotropic block copolymers with cylindrical morphology we see that there is a conflict between a tendency for parallelization of cylinders along the strain axis and the ordering tendency of the mesogens perpendicular to that direction. The results are not in contradiction to the behaviour under shear where both mesogens and cylinders were oriented perpendicular to shear direction and shear planes. The different behaviour is caused by a different orientation mechanism and different symmetry. Under shear the oblate chain conformations present in the LC polydomains are not only stretched but also rotated. If we suppose the rotation is the primary process and leads to preferential parallelization of the oblate chain configuation to the shear planes the interaction of the mesogens with the main chain will lead to perpendicular orientation of the director to the shear plane and also of the cylinders by minimization of the elastic energy.

In comparison to isotropic TPE's maximum elongation, E-modulus and tear strength are lower for the LC triblock copolymers. There are mainly two reasons that limit the extensibility of the materials. First one has to consider the anisotropy of the chain statistics which reduces chain extension. Second, and more important, the relation between the chain length to the molecular weight of the elastomeric block and to the critical chain length between entanglements is much smaller for SLCP's. Molar masses of mesogenic repeat units are about 6 – 9 times larger than molar masses of non-mesogenic units. Chain lengths are correspondingly shorter at a given molecular weight. Entanglement spacings of conventional elastomers correspond to degrees of polymerisation of the order of 100⁹⁾. For typical SLCP's entanglement molecular weights of about $3x10^5$ g/mol were measured in the isotropic state corresponding to a degree of polymerization of about 730⁶⁾. In the nematic state values between $8x10^5$ g/mol and $2.1x10^6$ g/mol were measured by different methods yielding DP's between 1940 and 5090. The DP values of the triblock copolymers of this work are only 200 and 1050, respectively. Since the molecular weight determining elastic properties of TPE's are mainly influenced by the entanglement molecular weight⁴⁾, the corresponding properties must be inferior in the LC triblock copolymers.

The comparatively low tear strength and E-modulus of the TPLCE's is connected to the properties of the PS-domains. The styrene content of the LC triblock copolymers is lower than in conventional TPE's which explains the reduced E-modulus. In conventional SIS triblock TPE's the tear strength is independent of the styrene content if the PS molecular weight is greater than 10 000 g/mol[4)]. Although the molecular weight of the PS blocks of sample B is significantly lower than the threshhold value below which the tear strength starts to decrease for conventional TPE's, its tear strength is not lower than that of sample A the PS blocks of which surpasses that threshhold value two times. Therefore one concludes that the threshhold value is lower for the LC triblock copolymers due to a stronger tendency for microphase separation. The origin for lower tear strength of these materials must rather be seen in the closer distance to the glass transition of the PS-domains. Due to the molecular weight dependence of Tg flow sets in at lower temperature for the LC triblock copolymer having PS blocks of lower molecular weight.

The softening of the material at the nematic-isotropic transition is unusual with regard to results reported in literature. For nematic networks[5)] a very small decrease or even an increase of the modulus was found[6)]. The latter occurred for polymers with molecular weights above the entanglement molecular weight.M_e. No modulus change was found for molecular weight below M_e. The different behaviour observed for block copolymers and homopolymers in our case is thought to be due to the different response of the nematic director to shear. In the work of Rubin et al.[6)] the mesogens were aligned parallel to the shear plane whereas in our case the director has a perpendicular orientation at large shear amplitudes. Even though only small shear amplitudes were applied in the DMA experiment and complete alignment is not expected we think that the greater modulus and viscosity in shear deformation is to be attributed to the tendency of the alignment of the mesogens paralallel to the gradient direction as in the previous experiments.

Conclusion

It has been shown that under uniaxial strain the LC triblock copolymers have elastic properties in the nematic phase in a temperature range between the Tg of the amorphous PS blocks and the liquid crystalline center block. With the limitation of the temperature range of rubber-like behaviour they have properties of thermoplastic liquid crystalline elastomers(TPLCE). Ultimate properties and E-modulus are smaller than for conventional TPE's mainly due to the lower entanglement molecular weight of the SLCP. The orientation induced by strain is smaller than in chemically crosslinked elastomers because of an antagonistic orientation behaviour of the orientation of the mesogens transversal to the strain axis and of the orientation of the polystyrene cylindrical microdomains that orient parallel to the strain axis. The latter behaviour is an intrinsic property of the SLCP of the present system and may be different for a system having a prolate conformation. of the main chain.

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