

Grafting of liquid crystalline polymers on a styrene–butadiene–styrene triblock copolymer and orientation induction

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We show an easy way to graft side-chain liquid crystalline polymers (SCLCPs) on the styrene–butadiene–styrene (SBS) triblock thermoplastic elastomer. The method is based on performing a radical polymerization of the monomers of SCLCPs in a solution with dissolved SBS, graft copolymers can be formed through radical transfer to the polybutadiene block which initiates subsequent polymerization. Polymerization of two different monomers containing, respectively, a phenyl benzoate and a biphenyl mesogenic group was carried out. We show that the resulting samples exhibit very different properties as compared with solution-cast SBS/SCLCP blends. The improvement is mainly characterized by (1) a much stronger mechanical strength, (2) an essentially homogeneous morphology with the liquid crystalline component uniformly dispersed, and (3) an enlarged liquid crystalline phase in some cases. One particular feature of this system is the maintenance of the thermoplastic elasticity in samples having a SCLCP content up to 52 wt%. Orientation induction of thin films upon mechanical stretching was investigated through *i.r.* dichroism. We show that a uniform macroscopic orientation of the mesogenic groups in SCLCPs can easily be achieved upon elongation of the films. More interestingly, a suitable thermal treatment of the deformed films can result in relaxed, free standing films which have almost the initial length before stretching, and in which the stretching-induced macroscopic orientation of the mesogenic groups is retained. We discuss this easy orientation induction and preservation in this system having a complex structure and morphology. Copyright © 1996 Elsevier Science Ltd.

(Keywords: side-chain liquid crystalline polymers; graft copolymers; polymer blends; orientation induction)

INTRODUCTION

In a previous study¹, we found that mechanical stretching an immiscible blend with a side-chain liquid crystalline polymer (SCLCP) dispersed in a non-liquid crystalline polymer matrix could lead to a uniform macroscopic orientation of the mesogenic groups. A matrix polymer of particular interest is the styrene–butadiene–styrene (SBS) triblock copolymer which is a thermoplastic elastomer. Films of the solution-cast SBS/SCLCP blend still display elasticity, and can be stretched from room temperature to about 60°C to induce the orientation in SCLCPs. Moreover, a thermal annealing of the deformed films under strain at temperatures below 60°C can cause loss of elasticity of the films, which is a consequence of a rearrangement of the polystyrene microdomains in SBS²; and the macroscopic orientation of the mesogenic groups can be retained in the relaxed blend films after removal of the mechanical force. The above experiments demonstrate an interesting approach for a possible control and manipulation of the macroscopic orientation in SCLCPs. This blend, at the same time, represents an interesting multi-phase-system which has a complex morphology and anisotropic features arising from both

block copolymers and liquid crystals. However, there is a major drawback for SBS/SCLCP blends: because of the immiscibility the blend films, prepared through solution-casting, are opaque and have a rough surface. Visibly they show a poor mechanical strength; repeated stretching rapidly leads to cracks in the films, and the films eventually break. The SCLCP's content in the blend should be limited to 30 wt% or lower, and at higher concentrations the films are not strong enough for mechanical stretching.

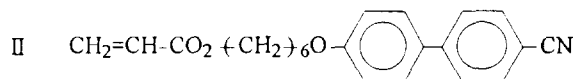
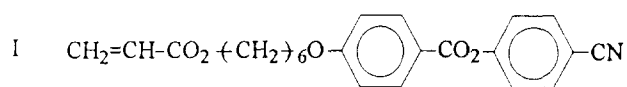
The purpose of this work is to explore further this interesting SBS/SCLCP system, and to prepare SBS/SCLCP blends of improved compatibility and, hence, improved properties. It is known that polymerization of the styrene monomer in a solution with dissolved polybutadiene (PB) results in polystyrene (PS) grafts on PB chains³. We employed this approach by polymerizing the monomers of SCLCPs in a solution with dissolved SBS. The results indicate the grafting of SCLCPs on the SBS copolymer, and the resulting SBS/SCLCP samples exhibit much improved properties compared to the solution-cast blends.

EXPERIMENTAL

Two acrylate monomers of SCLCPs (I and II) were

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prepared following the methods described in the literature⁴.



Homopolymers were prepared from monomer I and monomer II, and they will be referred to as PA and BiPA, respectively. The SBS sample was purchased from Aldrich, and it contains 30 wt% of polystyrene and has a molecular weight of about 140 000.

The typical procedure for the polymerization of monomer I or II in a solution with dissolved SBS is as follows: the SBS copolymer was first dissolved in toluene, then the monomer and the initiator, benzoyl peroxide, were added to the solution and solubilized. The mixture was heated to 65°C for polymerization under rigorous stirring and a nitrogen atmosphere; the reaction lasted for 40 h. The sample was collected after repeated precipitation in methanol at room temperature, and dried under vacuum at 50°C. Benzoyl peroxide was utilized as the initiator because it was shown to favour the grafting of PS on PB³, and its concentration was 1 mol% with respect to the amount of the monomer. On the other hand, the weight concentration of the monomer in the toluene solution was kept at 5%, regardless of the amount of the SBS copolymer. It should be mentioned that precipitation in methanol from a toluene solution is known to be efficient for purification of the SBS copolymer, while the homopolymers of the acrylate-based SCLCPs, such as PA and BiPA, are usually precipitated in cold ether. The final samples are denoted as SBS/SCLCP *in situ* hereafter to distinguish them from SBS/SCLCP blend cast from a toluene solution. The content of the SCLCP component in the *in situ* samples was determined through i.r. spectroscopy using a calibration straight line obtained by plotting the concentration of the SCLCP in a series of SBS/SCLCP blends of known compositions vs the ratio of the i.r. absorbances at 2230 and 967 cm⁻¹; the two bands arise from SCLCP and SBS, respectively.

The orientation measurements on deformed films were performed by means of i.r. dichroism. Details of this technique are reported elsewhere¹. I.r. spectra were recorded on a Bomen MB-102 FTIR spectrometer. For other characterizations, differential scanning calorimetry (d.s.c.) measurements were carried out on a Perkin-Elmer DSC-7 instrument, and all reported curves were obtained from a second scan after retaining the sample at 140°C for 5 min. The photomicrographs of the samples were taken using a Leitz DMR-P polarizing microscope equipped with an Instec hot stage.

RESULTS AND DISCUSSION

Characterization

The concentration of the SCLCP component in the SBS/SCLCP *in situ* samples can be increased by adding more monomer relative to the amount of SBS for the polymerization. For four SBS/SCLCP *in situ* samples,

Table 1 Prepared *in situ* samples

Sample	Monomer used	Weight ratio of SBS to monomer	SCLCP content (wt%)
SBS/PA (82/18)	I	1/1	18
SBS/PA (70/30)	I	1/2	30
SBS/PA (48/52)	I	1/3	52
SBS/BiPA (76/24)	II	1/1	24

Table 1 shows the monomer used, the initial weight ratio of monomer to SBS before reaction, and the obtained SCLCP content in the *in situ* samples. The acronyms of the samples reflect the information. Obviously, if no SCLCP chains were grafted on the SBS polymer during the polymerization, the final samples should simply be a mixture of SBS and SCLCPs. In order to perform comparative studies, for the *in situ* samples listed in Table 1 we prepared toluene solution-cast blends of the same compositions.

The first indication of significant differences between SBS/SCLCP *in situ* and blend samples comes from the films of the *in situ* samples. In contrast with the blend films, they look translucent, quite similar to a SBS film, and have a smooth surface. Also, they are mechanically much stronger, and repeated stretching leads to no cracks. This is true even for SBS/PA 48/52, the sample containing 52% of SCLCP. All this indicates an improved compatibility between SBS and the SCLCP component.

Figure 1 shows examples of the photomicrographs under crossed polarizers. All samples were first heated to 140°C, in the isotropic state, for 5 min, and then, for the taking of the photomicrographs of the same magnification, cooled to 80°C for PA and SBS/PA (70/30) *in situ* and blend samples, and to 100°C for BiPA and SBS/BiPA (76/24) *in situ* and blend samples. Drastic differences are evident. As PA has only a nematic phase, with a nematic-isotropic transition at around 124°C, it displays a threaded nematic texture (Figure 1a). BiPA has a more complex sequence of mesophases, exhibiting, when cooled from the isotropic state, a transition into a nematic phase at 129°C, then a transition into a smectic-A phase at 119°C, and finally a transition into a re-entrant nematic phase at 80°C. Therefore, at 100°C it displays a smectic texture (Figure 1d). For their blend samples (Figures 1b and e) two distinct phases are evident. The SBS phase, which is amorphous, appears dark under crossed polarizers, while the birefringent regions arise from the phase of the SCLCP component. Within the SCLCP phase, the same liquid crystalline textures as those of PA and BiPA can be seen. Now, for the *in situ* samples (Figures 1c and f), interestingly, they all display a much more homogeneous morphology with no clearly distinguishable phases of SBS and SCLCP like those for the blend samples. Apparently, a nematic-like, threaded texture can still be noticed, but it is more likely the result of a uniform distribution of the SCLCP component throughout the sample. This is particularly clear for SBS/BiPA (76/24) *in situ* for which no smectic texture can be identified. Similar photomicrographs were obtained for other *in situ* samples.

The above polarizing microscopic observations are very significant. The results imply that in these *in situ*

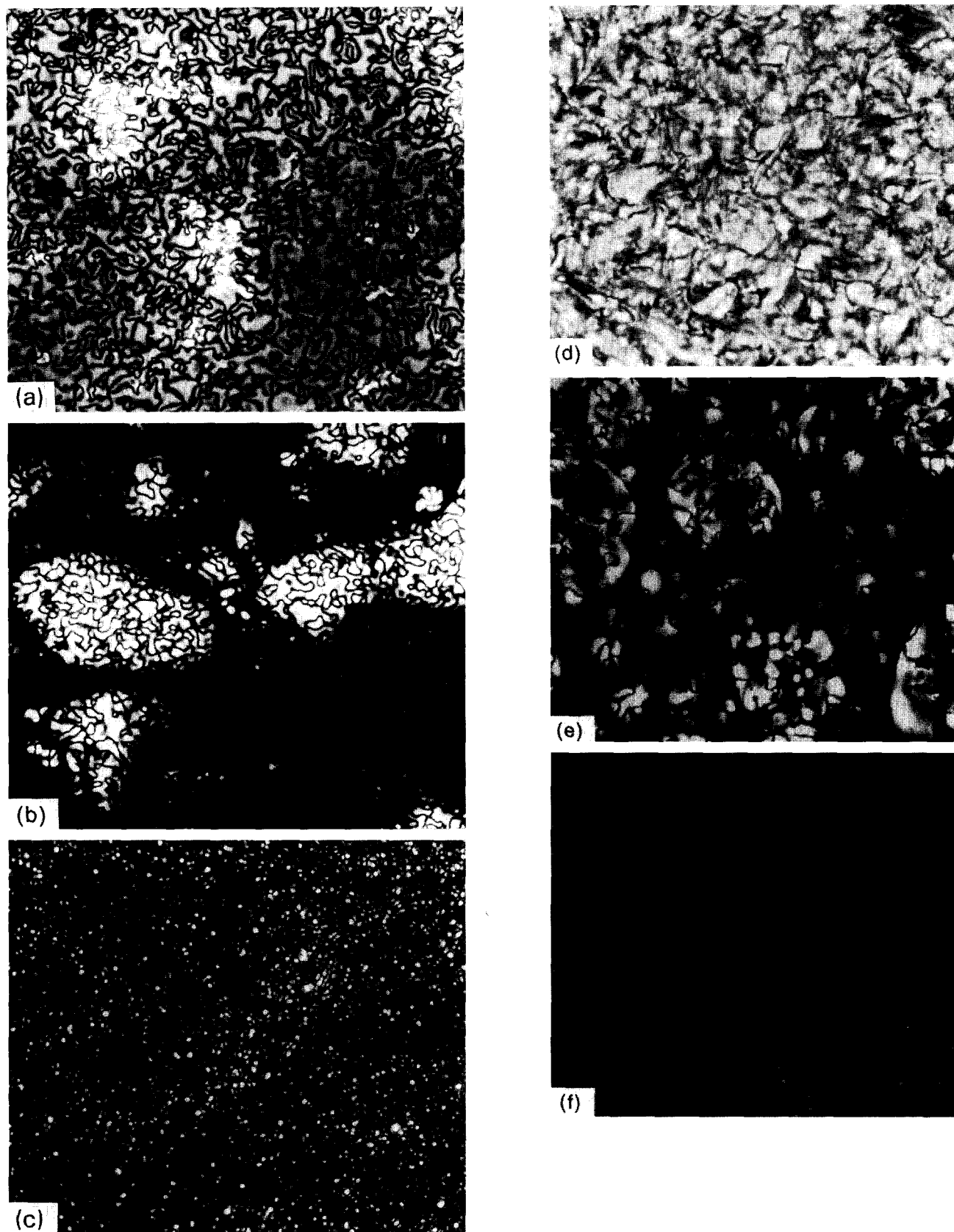


Figure 1 Polarizing photomicrographs for (a) PA, (b) SBS/PA (70/30) blend, (c) SBS/PA (70/30) *in situ*, (d) BiPA, (e) SBS/BiPA (76/24) blend, and (f) SBS/BiPA (76/24) *in situ*. Magnification: 410 \times . See *Table 1* for sample assignments and text for other details about taking of the photomicrograph

samples the SCLCP component is essentially randomly dispersed, and located in a sort of 'microphase', even though we have no evidence to suggest the true, immiscibility-induced microphase conferred on block and graft copolymers. In our experiments, the possible mechanisms which lead to a grafting of the SCLCP on the SBS polymer should be similar to those for the grafting of PS on PB³. They include (1) a radical transfer, either from a primary radical formed after the thermal decomposition of the initiator or from a propagating radical, to the methylene group of the PB block, which then initiates the polymerization of the monomer and results in SCLCP grafts on the PB block, and (2) a direct reaction between the double bonds of the PB block and the propagating radicals. The second process is known to be more important for PB containing high vinyl groups. As the SBS sample used in this study contains more 1–4 units the radical transfer could be the main reaction for the grafting. According to the above grafting mechanisms, the *in situ* samples could be a mixture of graft copolymer with homopolymer of SCLCP and possibly some ungrafted SBS as well. At this point we cannot say what could be the proportions of copolymer and homopolymer, but one thing, which seems to be certain, is that the *in situ* samples contain, at least, a significant amount of SBS–SCLCP graft copolymer. This copolymer in the mixture could play the role of a

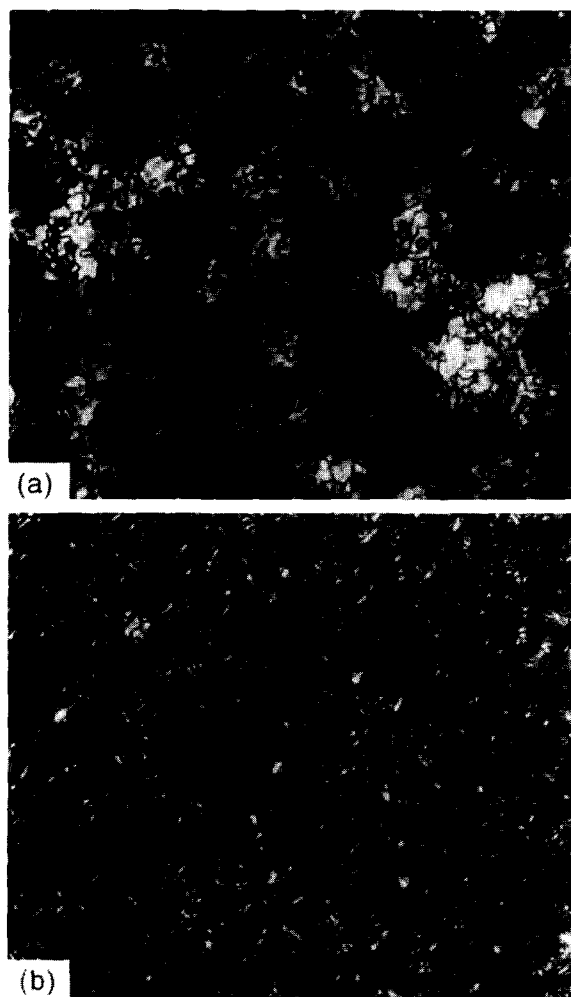


Figure 2 Polarizing photomicrographs for SBS/PA (48/52) *in situ* sample: (a) before, and (b) after the first precipitation in methanol

compatibilizing agent which tends to bring together the liquid crystalline homopolymer and the ungrafted SBS. Otherwise, such a drastic change as shown in Figure 1 could not be possible.

It is worthwhile mentioning that the precipitation in methanol that we used for sample purification should help in removing not only the unreacted monomer but also some homopolymer of SCLCPs. This is revealed in Figure 2 which shows the photomicrographs at 80°C of the SBS/PA (48/52) *in situ* sample before and after the first precipitation in methanol. It is seen that before the precipitation (Figure 2a) the sample contains regions displaying the typical nematic texture of the homopolymer PA (Figure 1a), indicating the existence of SCLCP which is not grafted on SBS. (The monomer is not liquid crystalline). While the sample after the first precipitation (Figure 2b) already shows no such homopolymer regions, and displays a mostly homogeneous morphology. Clearly, at least some of the homopolymer can be eliminated through this precipitation process.

Differences in thermal transition behaviour between the *in situ* and the blend samples are also observed. The d.s.c. heating curves of some samples are presented in Figure 3. An interesting case can be found by comparing the SBS/PA (82/18) blend with the *in situ* sample (curves a and b). The 18% PA in the blend behaves essentially like pure PA, exhibiting a T_g at about 32°C and a nematic isotropic transition temperature T_{ni} centred at 124°C. While the *in situ* sample has a T_g of PA lowered to 22°C, and a slightly higher T_{ni} at 127°C. The decrease in T_g must be induced by a plasticizing effect, suggesting that in the *in situ* sample there is a greater interaction between the chains of SCLCP and the PB block in the SBS copolymer which has a low T_g at about -80°C (not shown for the sake of clarity). This should be the situation with SCLCP grafted on the PB block. Surprisingly, a plasticizing effect generally lowers both T_g and T_{ni} by a similar magnitude, here the *in situ* sample's T_{ni} is not lowered, but instead it is higher than that of the blend. Now, comparing the SBS/PA (70/30) blend and *in situ* samples (curves c and d), similar observations can be

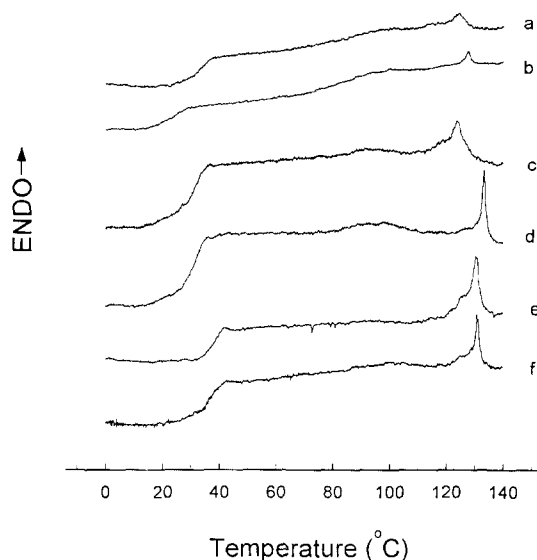


Figure 3 D.s.c. heating curves for (a) SBS/PA (82/18) blend, (b) SBS/PA (82/18) *in situ*, (c) SBS/PA (70/30) blend, (d) SBS/PA (70/30) *in situ*, (e) SBS/BiPA (76/24) blend, and (f) SBS/BiPA (76/24) *in situ*

made. Although T_g is only lowered from 32°C in the blend to 29°C in the *in situ* sample, the increase in T_{ni} is greater, shifting from 124°C for the former to 133°C for the latter. Also, it is interesting to notice that the nematic–isotropic transition region has a more definite shape for the *in situ* sample. For both SBS/PA *in situ* samples, the nematic phase between T_g and T_{ni} is significantly enlarged (by about 12°C) as compared with their corresponding blends. In the case of SBS/BiPA (76/24) (curves e and f), smaller differences can be noticed between the *in situ* and the blend samples. In all cases, the glass transition at about 85°C is due to the PS microdomains in SBS.

Orientation behaviour

The development of a macroscopic orientation of the mesogenic side groups in three *in situ* samples is illustrated in Figure 4 by plotting the order parameter P_2 as a function of the draw ratio λ which is defined as the film length after stretching over the film length before stretching. The stretching experiments were carried out at room temperature for SBS/PA (82/18), and at room temperature and 50°C for both SBS/PA (70/30) and SBS/BiPA (76/24). The order parameter is a measure of the orientation averaged over all mesogenic groups; $P_2 = 0$ corresponds to no macroscopic orientation, $P_2 = 1$ indicates a perfect orientation of all mesogenic groups (their long axes) along the stretching direction, and negative values of P_2 mean a macroscopic orientation perpendicular to the stretching direction. Keeping the above in mind, it is clear that a macroscopic orientation is easily achieved upon stretching of the *in situ* samples. For SBS/PA (82/18) (Figure 4a), a plateau P_2 value close to 0.5 is obtained after about 200% of film stretching at room temperature. This reflects the low T_g (22°C) of this sample; at room temperature the SCLCP component is in its nematic phase, and the stretching results in an effective alignment of the nematic domains. In the cases of SBS/PA (70/30) (Figure 4b) and SBS/BiPA (76/24) (Figure 4c), they have a higher T_g which is above the room temperature. Consequently, stretching at room temperature only induces a low macroscopic orientation, while when stretched at 50°C, i.e. in their liquid crystalline state, the films show as strong a macroscopic orientation as that of SBS/PA (82/18). It should be emphasized that the almost constant P_2 value near 0.5 observed for all samples corresponds to a quite perfect alignment of the directors of the liquid crystalline domains, since the orientation of the mesogenic groups within the liquid crystalline domains along the directors (microscopic orientation) is known to be characterized by an order parameter of this magnitude⁴.

The orientation induction of the *in situ* samples is similar to that observed for side-chain liquid crystalline elastomers (SCLCEs), i.e. low T_g -SCLCPs with chemical cross-links^{5,6}. A known drawback for SCLCEs is that the macroscopic orientation of the mesogenic groups is lost when the film sample recovers its initial length after the removal of the mechanical force. In the previous study on SBS/SCLCP blends¹, we have already exploited the fact that the elastic deformation of the SBS copolymer could be eliminated by thermally annealing a deformed film under strain to preserve the macroscopic orientation. In the present work, we further investigated the possibility of retaining the macroscopic orientation in the *in situ* samples by using the following

thermal annealing process which is composed of two treatments.

First, a film was stretched to a deformation of 400% at 50°C, i.e. the initial draw ratio $\lambda_i = 5$, to reach the maximum orientation; then the deformed film was annealed under strain at 40°C for different times, and

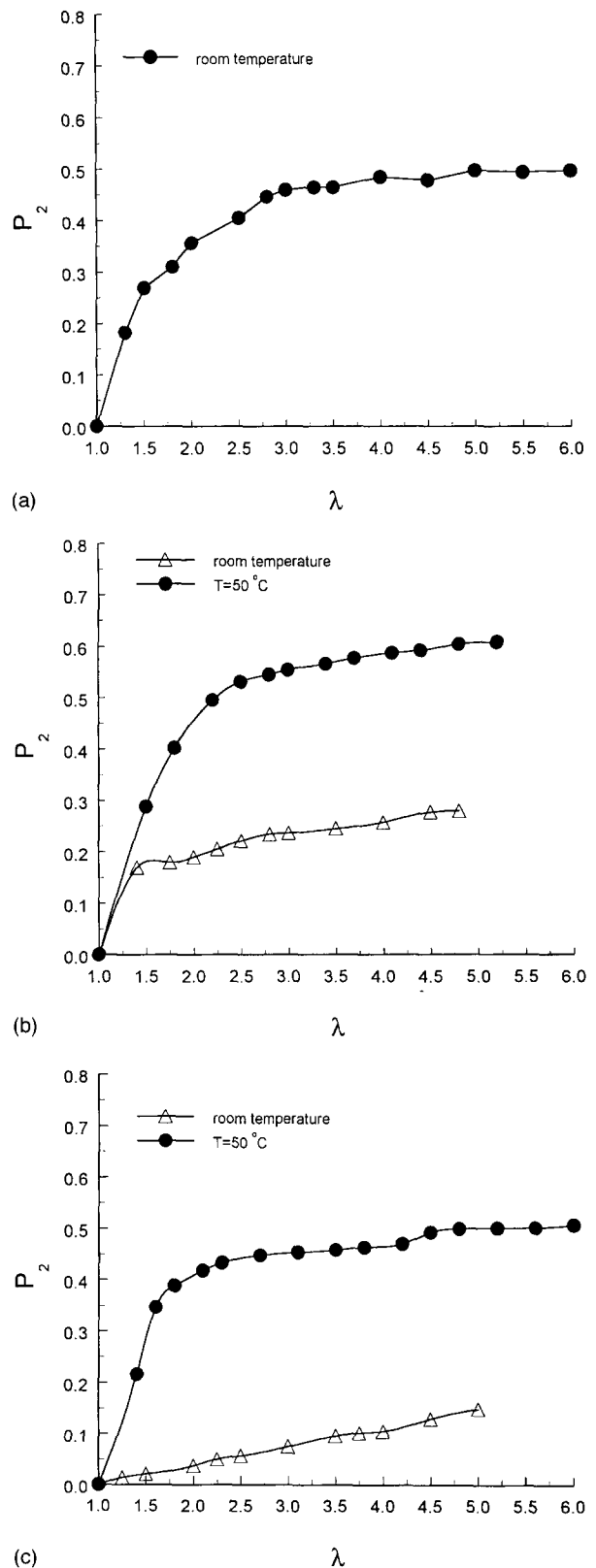


Figure 4 Order parameter S vs draw ratio for (a) SBS/PA (82/18) *in situ*, (b) SBS/PA (70/30) *in situ*, and (c) SBS/BiPA (76/24) *in situ*. Stretching temperatures are indicated in the figure

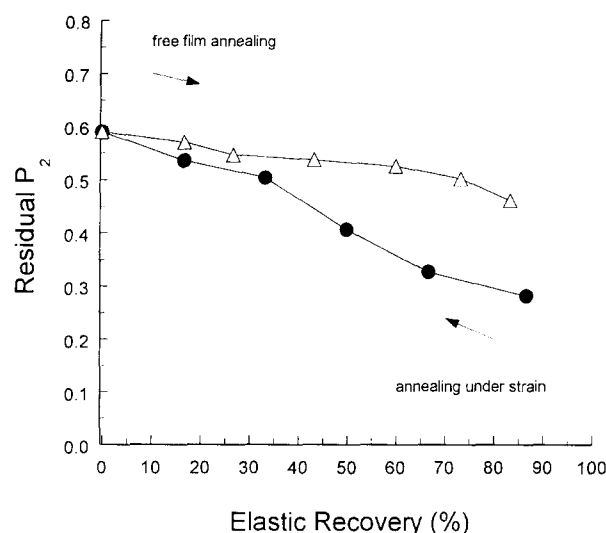


Figure 5 Residual order parameter P_2 in relaxed film vs film elastic recovery for SBS/PA (70/30) *in situ* after (●) thermal annealing on deformed film under strain, and (△) free film annealing on a relaxed film showing zero elastic recovery. See text for details

after each annealing time, the film was allowed to relax by removing the mechanical force. Because of the orientation relaxation of the elastic PB chains^{2,7}, which occurred during each annealing under strain as a consequence of a rearrangement of the PS microdomains (cylindrical domains in SBS containing 30 wt% of PS), the relaxed film could not recover its initial length. This means that the residual draw ratio λ_r was higher than 1, and that the elastic recovery of the film, which is defined as $(\lambda_i - \lambda_r)/(\lambda_i - 1)$ was less than 100%. Obviously, the elastic recovery decreases as the annealing time increases. After each annealing under strain, we measured the residual macroscopic orientation in the relaxed film.

Then, a second treatment was conducted on a relaxed film which showed a zero elastic recovery, i.e. $\lambda_r = 5$, after having been subjected to the first thermal treatment under strain. In such a relaxed film, it is known that the arrangement of the PS microdomains is anisotropic^{2,7}; when it is heated to a temperature above the room temperature, a so-called healing effect occurs since the PS microdomains tend to recover their initial arrangement before the stretching. The film length decreases, and the apparent elastic recovery increases. We used a film with $\lambda_r = 5$, and heated it to 40°C for different times. After each instance of this free film annealing treatment we also determined the residual macroscopic orientation.

The results for SBS/PA (70/30) and SBS/BiPA (74/26) are shown in Figures 5 and 6, respectively, where the residual P_2 is plotted vs the elastic recovery. It can be seen that with the first treatment of annealing under strain a macroscopic orientation of the mesogenic groups is conserved in the relaxed film. This preserved orientation increases as the elastic recovery of the film decreases. In the relaxed film exhibiting a zero elastic recovery, the same macroscopic orientation as the film just after the 400% stretching is retained. Now, when this relaxed film is subjected to the second treatment of free film annealing at 40°C, the film length decreases and the apparent elastic recovery is no longer zero. The elastic recovery increases with the annealing time, and finally reaches 85% which corresponds to $\lambda_r = 1.6$. However, the preserved macroscopic orientation remains high,

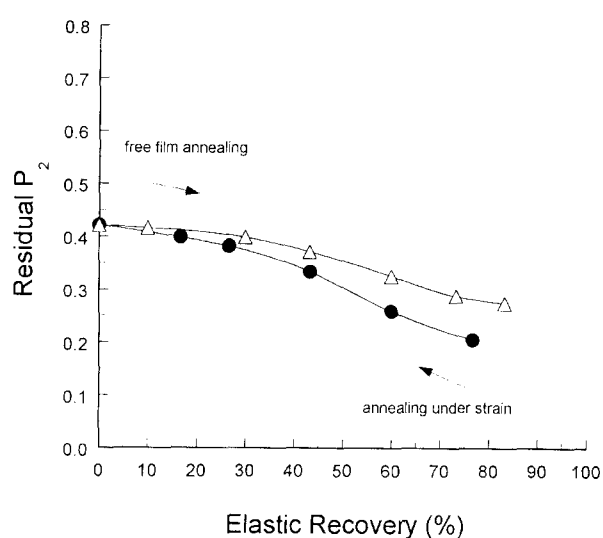


Figure 6 Residual order parameter P_2 in relaxed film vs film elastic recovery for SBS/BiPA (76/24) *in situ* after (●) thermal annealing on deformed film under strain, and (△) free film annealing on a relaxed film showing zero elastic recovery. See text for details

decreasing only slightly, in particular for SBS/PA (70/30) (Figure 5). These results indicate that with the above thermal annealing process the stretching-induced macroscopic orientation of the mesogenic groups can be preserved in a relaxed, free-standing film which is thermally stable, and has a length close to the initial film length before the stretching experiment. This capacity of orientation induction and preservation is particularly interesting.

The morphology of the *in situ* samples should be complex, which includes PS microdomains dispersed in a PB matrix and a very small size-phase, if not a microphase, of the SCLCP component. At low SCLCP content, like SBS/PA (82/18), the SCLCP phase could also be dispersed in the PB matrix; while at high SCLCP content, like SBS/PA (48/52), two continuous phases of PB and SCLCP could be present. But in any case, an important interaction between the phases of PB and SCLCP must exist. Despite this complexity, the above results suggest that the orientation behaviour of the SCLCP component is mainly determined by its own response to the stretching. The macroscopic orientation of the mesogenic groups is completed at an early stage of the sample's deformation, and further stretching only involves a high orientation of the rubbery PB chains and the alignment of the PS cylindrical microdomains acting as cross-links. During the annealing under strain, which induces relaxation of stretched PB chains and rearrangement of aligned PS microdomains, apparently no orientation relaxation of the mesogenic groups takes place. The treatment of free film annealing, which produces further rearrangement of the PS domains and leads to film shrinkage, has little effect on the macroscopic orientation in the SCLCP phase.

CONCLUSION

Polymerizing the monomers of SCLCPs in a solution which dissolved SBS can result in grafts of SCLCPs on the PB block of SBS. The resulting samples differ very much from the solution-cast SBS/SCLCP blends. In contrast with the blends, they have a much more

homogeneous morphology when viewed under crossed polarizers. Translucent, and mechanically much stronger films can be obtained through solution-casting of the *in situ* samples with a SCLCP content up to 52 wt%. Assuming the presence of the liquid crystalline homopolymer in the *in situ* samples, it is however clear that at least a significant amount of SBS-SCLCP graft copolymer is formed during the polymerization, which accounts for the drastic changes in the properties as compared with the blends. A uniform macroscopic orientation of the mesogenic groups of the SCLCP component in the *in situ* samples can easily be induced by stretching of the elastic films. More interestingly, this macroscopic orientation can almost be totally preserved in a relaxed, free standing film after a thermal treatment process. The treatment is based on, firstly, annealing a deformed film under strain to eliminate the elastic recovery after the removal of the mechanical force and, then, annealing the relaxed film to induce film shrinkage.

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