

Rheo-Optical Fourier Transform Near-Infrared Spectroscopy of Polydimethylsiloxane/Polycarbonate Block Copolymers

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ABSTRACT: A series of polydimethylsiloxane (PDMS)/polycarbonate (PC) block copolymers with varying compositions were investigated by simultaneous mechanical and Fourier transform near-infrared (FTNIR) spectroscopic (rheo-optical) measurements to study segmental orientation during elongation-to-break and cyclic elongation–recovery procedures. Depending on the composition and the block lengths of the copolymers, different orientational and recovery phenomena were observed for the hard (PC) and soft (PDMS) segments. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 70: 1349–1357, 1998

Key words: polydimethylsiloxane/polycarbonate block copolymers; rheo-optics; deformation; segmental chain orientation; Fourier transform near-infrared spectroscopy

INTRODUCTION

The unique properties of polysiloxanes such as chemical inertness, insensitivity to temperature extremes, surface properties, and physiological indifference are traceable to their molecular structure and have made these polymers and their copolymers extremely important materials for a broad variety of applications. Polydimethylsiloxane (PDMS) is the most important of the silicone elastomers and has several applications (e.g., in gaskets and seals, wire and cable insulation, and surgical and prosthetic devices) where high environmental stress may occur.^{1–3} In an attempt to modify the elastomeric properties of PDMS for specific technical applications, copolymers with polycarbonate (PC) were prepared in varying compositions and block lengths (Fig. 1). Such copolymers can be processed thermoplastically and have interesting automotive applications due to their low-temperature resistance. Al-

ternatively, at suitable compositions, highly transparent materials may be obtained for the production of contact lenses by thermoforming.⁴

Generally, rheo-optical Fourier transform infrared (FTIR) spectroscopy of polymer films with a thickness in the range of 10–50 μm has proved an extremely powerful tool to study orientation phenomena in segmented polymers.^{5–8} However, due to the very intense absorption bands of the fundamental vibrations of PDMS and PC,⁹ mid-infrared spectroscopy cannot be applied to their copolymers, because they had to be prepared in such small film thicknesses which are far beyond a routine handling procedure for rheo-optical measurements. With the recent, more efficient exploitation of the near-infrared region alongside the application of light-fiber optics, rheo-optical Fourier transform near-infrared (FTNIR) spectroscopy has become less restrictive with respect to the sample geometry and sample positioning. Thus, polymer tensile test samples with a thickness up to 1 mm may be investigated in conventional tensile testers which are separated from the spectrometer over distances of several meters.^{7,8}

Although NIR spectra are frequently considered less informative than their midinfrared an-

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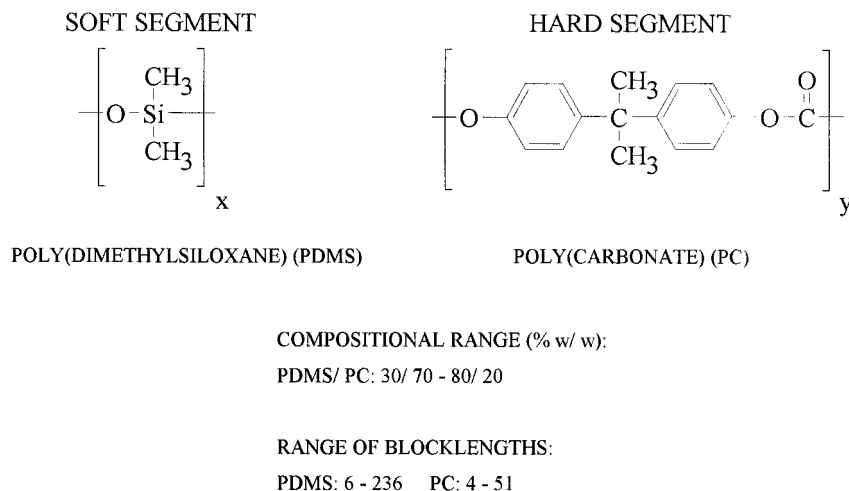


Figure 1 Chemical structure, compositional range, and block lengths of the investigated copolymers.

alogs due to the overlap of overtones and combination bands in this wavenumber region ($4000\text{--}12,500\text{ cm}^{-1}$), Figure 2 clearly demonstrates that the NIR spectrum of a PDMS/PC 50/50 (% w/w) copolymer film (thickness $250\text{ }\mu\text{m}$) contains absorption bands which can be exclusively assigned to the first overtone of the $\nu(\text{CH}_3)$ mode of PDMS (5872 cm^{-1}) and the second overtone of the $\delta(\text{CH}_3)$ vibration of PC (4075 cm^{-1}). Thus, two specific absorption bands with transition moments perpendicular to the chain axis are available for the characterization of the hard (PC) and soft (PDMS) segment orientation in the copolymers under examination.

EXPERIMENTAL

Materials

The investigated PDMS/PC block copolymers were synthesized by phase-boundary polymerization in methylene chloride/NaOH at room temperature.⁴ For the rheo-optical measurements, film samples with a thickness of approximately $250\text{ }\mu\text{m}$ were prepared by casting from methylene chloride solutions on surface-roughened glass plates and drying at 323 K in a vacuum overnight. The films were carefully peeled off the glass plates in warm water and finally dried again in a vacuum for 24 h . For the rheo-optical experi-

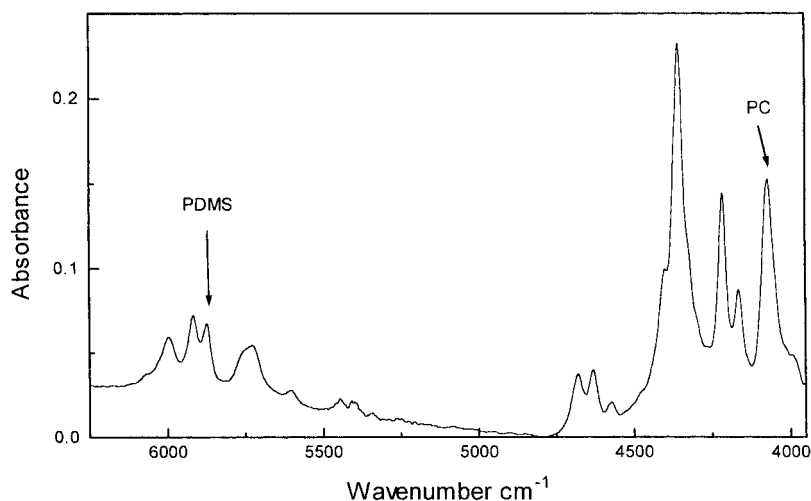


Figure 2 NIR spectrum of a PDMS/PC 50/50 (% w/w) copolymer film (thickness $250\text{ }\mu\text{m}$).

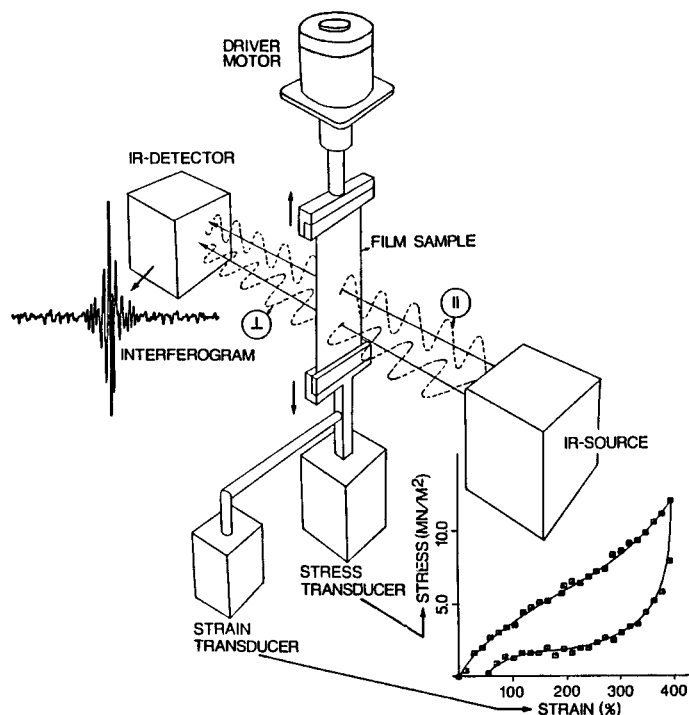


Figure 3 The principle of rheo-optical FTIR/FTNIR spectroscopy of polymer films.

ments, specimens with gauge dimensions 15×5 mm² were cut from these films.

Instrumentation

The experimental principle of rheo-optical vibrational spectroscopy is based on the simultaneous acquisition of spectra and stress-strain diagrams during deformation, recovery, or stress relaxation of the polymer sample under investigation (Fig.

3).⁶⁻⁸ The film specimen to be tested can be uniaxially drawn and recovered in a miniaturized stretching machine which fits into the sample compartment of the spectrometer or in a separate tensile tester which is connected by optical light fibers. During the mechanical treatment, interferograms are acquired in small time/strain intervals with radiation polarized alternately parallel and perpendicular to the stretching direction, and

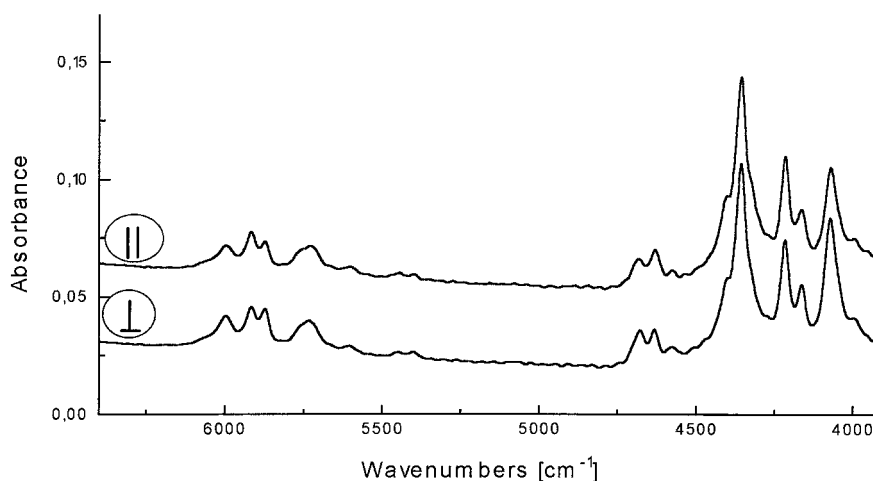


Figure 4 NIR polarization spectra of a PDMS/PC 50/50 (% w/w) copolymer film (PDMS/PC block length 20/6) drawn to 300% strain. (||/⊥) Polarization of the incident radiation relative to the drawing direction.

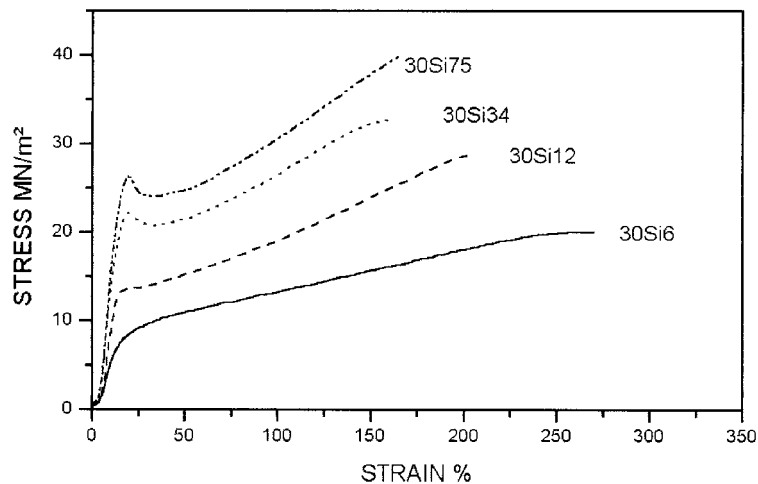


Figure 5 Stress-strain diagrams taken during elongation to break of PDMS/PC 30/70 (% w/w) copolymer films with PDMS/PC block lengths of 6/4, 12/8, 34/23, and 75/51.

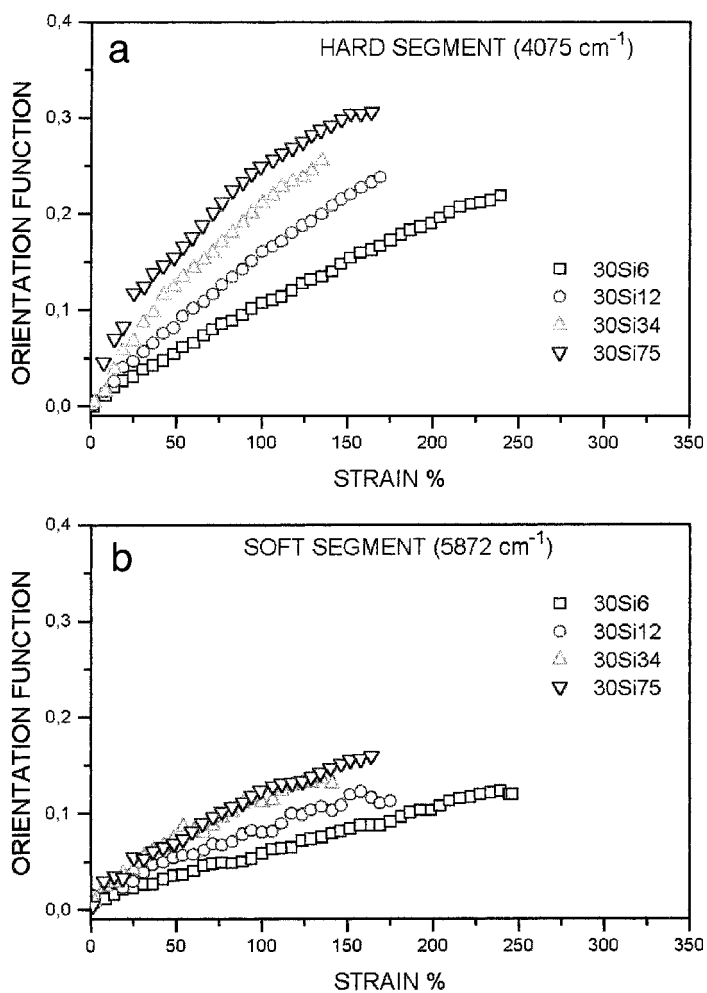


Figure 6 Orientation function/strain diagrams for the (a) hard and (b) soft segments corresponding to the mechanical data shown in Figure 5.

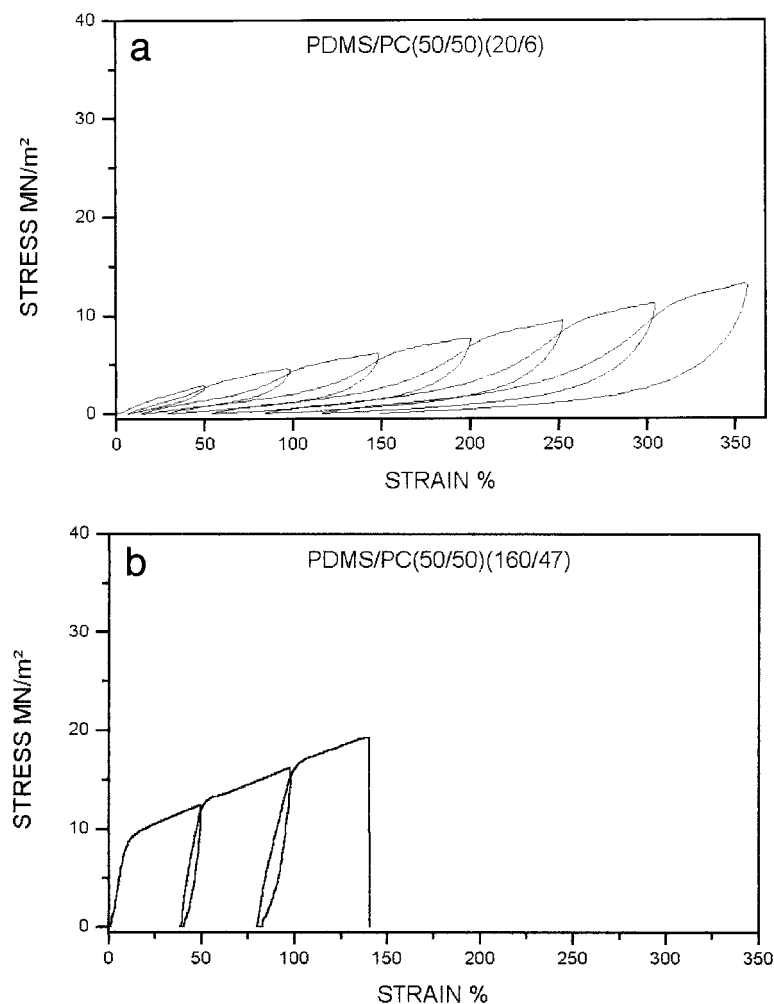


Figure 7 Stress-strain diagrams taken during loading-unloading cycles of PDMS/PC 50/50 (% w/w) copolymer films with PDMS/PC block lengths of (a) 20/6 and (b) 160/47.

upon completion of the experiment, the interferograms are transformed to the corresponding spectra for further processing of the conventional data. In the final analysis, the spectroscopic and mechanical data then allow a correlation of the microscopic and macroscopic changes of the sample during the mechanical treatment. The electro-mechanical apparatus used for the rheo-optical FTNIR measurements was described in detail.^{7,8}

The film samples under investigation were either elongated up to fracture or subjected to subsequent elongation-recovery cycles at 300 K. The data collected during the mechanical measurements were transformed into stress-strain diagrams by taking into account the original cross section of the sample.

The spectroscopic part of the work was performed on a Bruker IFS 88 spectrometer

adapted for the NIR region with a tungsten-halogen source, a quartz beam splitter, and a liquid nitrogen-cooled InSb detector. During the mechanical treatment 20-scan interferograms were taken in 3-s intervals with a spectral resolution of 5 cm^{-1} .

The spectra series were automatically evaluated by a special software¹⁰ in terms of the orientation function f (refs. 11,12) of the absorption bands whose transition moment directions are perpendicular to the polymer chain axis:

$$f = -2 \frac{(R - 1)}{(R + 2)}$$

where $R = A_{\parallel}/A_{\perp}$ is the dichroic ratio of this absorption band. The values of this parameter for

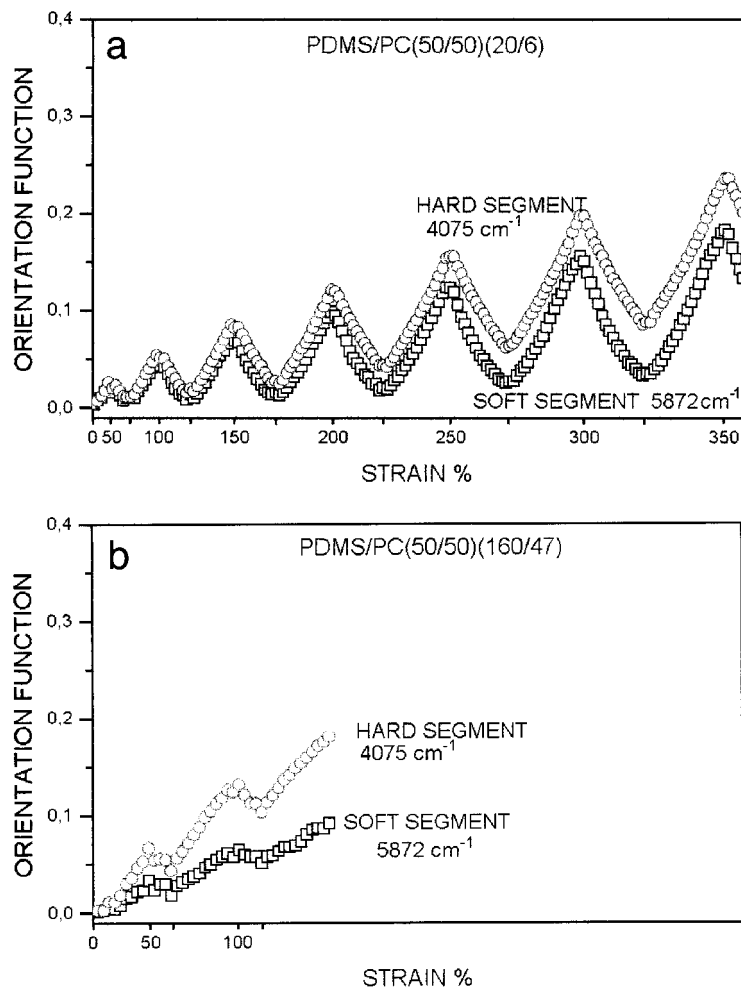


Figure 8 Orientation function/strain diagrams for the hard and soft segments of PDMS/PC 50/50 (% w/w) copolymer films with PDMS/PC block lengths of (a) 20/6 and (b) 160/47.

the specified absorption bands of the individual spectra were determined by appropriately correlating the successively measured absorbance values A_{\parallel} and A_{\perp} . Upon data processing, the orientation functions were plotted versus strain in an operator-selected format.

RESULTS AND DISCUSSION

To illustrate the dichroic effects, the polarization spectra of a PDMS/PC 50/50 (% w/w) film drawn up to 300% strain are shown in Figure 4. To eliminate the interference of slightly overlapping absorption bands, the high wavenumber wing of the PC-specific 4075-cm^{-1} absorption and a central portion around the peak maximum (15 cm^{-1} in width) of the 5872-cm^{-1} PDMS band were in-

tegrated for the calculation of the orientation functions.

The effect of the block length on the mechanical and orientational properties of the copolymers is demonstrated by the results obtained with PDMS/PC 30/70 (% w/w) copolymers with the block length of PDMS and PC varying between 6–75 and 4–51 (see Fig. 5), respectively. With increasing block lengths of the soft and hard segments, the stress–strain diagrams (Fig. 5) reflect the transition to a typical thermoplastic polymer. The increase in stress level is accompanied by a decrease of the elongation to break and the development of a yield point below 25% strain. The mechanical behavior of the copolymer at this composition is dominated by a structure of hard segments, which increasingly aggregate as a function of block length. This picture is also supported by

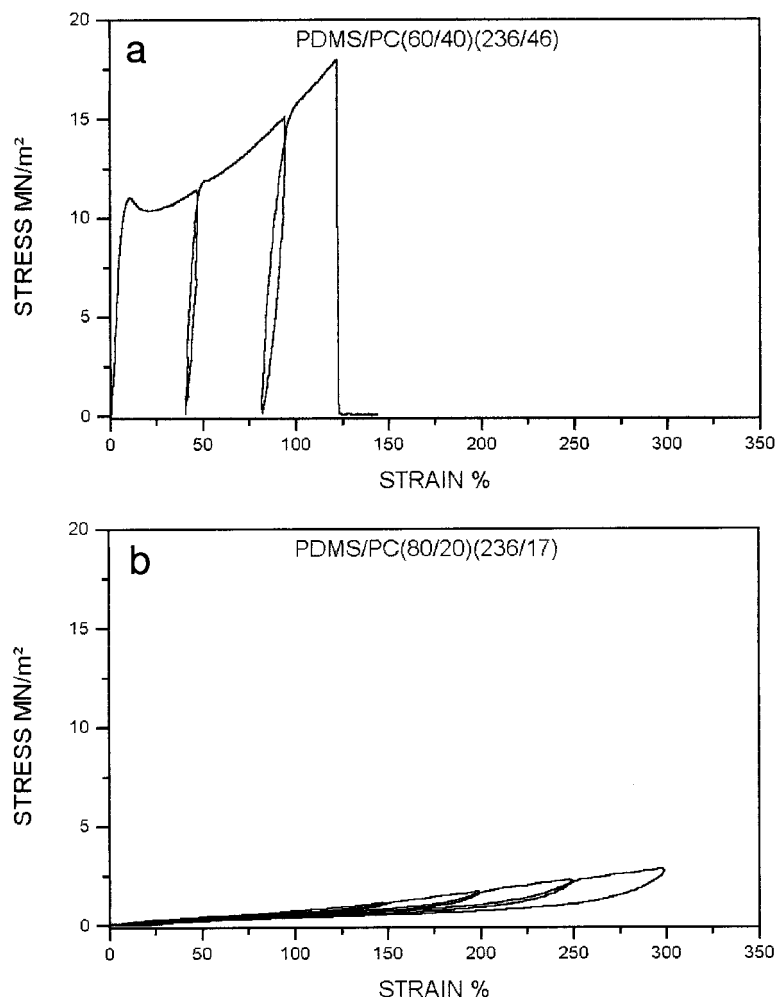


Figure 9 Stress-strain diagrams taken during loading-unloading cycles of (a) a PDMS/PC 60/40 (% w/w) copolymer film and (b) a PDMS/PC 80/20 (% w/w) copolymer film with PDMS/PC block lengths of 236/46 and 236/17, respectively.

the fact that for these copolymers the hard segments have a much larger geometrical extension than that of the soft segments and that a melting endotherm for the PC domains can be observed in the DSC diagrams of copolymers with very high PC content.¹³

The orientation effects for the PDMS and PC segments as a function of strain are illustrated in Figure 6(a,b). In agreement with the above picture, the hard segments always orient better than do the soft segments and also reflect a more significant chain alignment with increasing block length.

Furthermore, the block length has significant implications for the reversibility of the strain-induced orientation. Figure 7(a,b) shows the stress-strain diagrams for successive loading-unloading cycles of two copolymers with the same

composition [PDMS/PC 50/50 (% w/w)], but with different PDMS/PC block lengths (20/6 and 160/47). Apart from the increase in stress level with increasing block length, a drastic decrease of the reversibility of the mechanical deformation can be derived from the stress-strain diagrams. The orientation function/strain plots corresponding to these mechanical treatments are shown in Figure 8(a,b). The observed data reflect the reversible orientation of the hard and soft segments at low block lengths [Fig. 8(a)], whereas they are clearly indicative of the strain-induced destruction of the hard-segment structure at high block lengths with the accompanying effect that the soft segments also cannot recover during unloading [Fig. 8(b)].

The orientational effects described above are only valid at PDMS contents $\leq 60\%$. When the

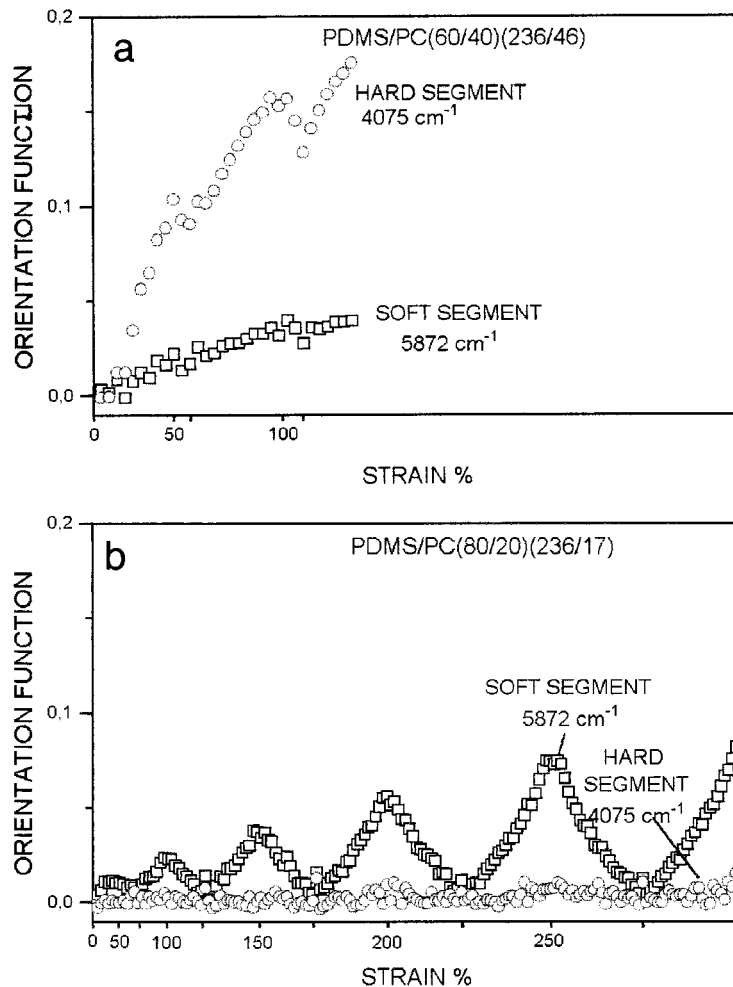


Figure 10 Orientation function/strain diagrams for the hard and soft segments of (a) a PDMS/PC 60/40 (% w/w) copolymer film and (b) a PDMS/PC 80/20 (% w/w) copolymer film.

PDMS composition exceeds 60%, an inversion of the previously observed trends are observed. In Figure 9(a,b), the stress–strain diagrams of cyclic elongation–recovery procedures of a PDMS/PC 60/40 and 80/20 (% w/w) with PDMS/PC block lengths of 236/46 and 236/17, respectively, are shown. By increasing the PDMS percentage from 60 to 80%, a dramatic decrease of the elongational force and the hysteresis in the stress–strain data can be observed. These differences are also manifested in the orientation function/strain plots [Fig. 10(a,b)]. However, at the PDMS/PC composition of 80/20 (% w/w), only the soft segments exhibit a detectable, highly reversible chain alignment, whereas the hard segments do not orient any more. At 70% PDMS content, the geometrical length of the PC blocks becomes significantly smaller than the PDMS block length, with the consequence that the predominating hard-seg-

ment aggregation obviously disappears and individual PC blocks become dispersed in a soft PDMS matrix. Hence, the soft segment is now dominating the mechanical properties, and with further increasing PDMS content, the decreasing extensional forces eventually cannot induce any more hard-segment alignment.

CONCLUSIONS

Rheo-optical FTNIR spectroscopy provides a potential tool for the detailed characterization of the orientational response of the investigated PDMS/PC block copolymers to the applied mechanical treatment. For variable compositions and block lengths, the following conclusions could be drawn:

- For the investigated copolymers, the deformational stress decreases with increasing PDMS content. Concomitantly, the degree of hard- and soft-segment orientation at equivalent elongation decreases. The reversibility, however, of the induced mechanical and orientational effects upon unloading increases.
- At PDMS contents $\leq 60\%$, the hard segments of the copolymers always orient better than do the soft segments upon elongation. In the same compositional range, a reduction of block length decreases the elongational force and enhances the reversible character of the loading–unloading procedures. The hard segments aggregate to larger domains and dominate the mechanical properties.
- At PDMS contents $>60\%$, an inversion of these last-mentioned effects can be observed. In fact, at high PDMS content and high block lengths, no chain alignment of the hard segments can be detected upon elongation. Now, the copolymer structure is characterized by isolated PC segments dispersed in the PDMS matrix. The copolymer exhibits typical elastomeric behavior.

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