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Shear-Induced Order in Nematic Polymers

Patrick Becker,[1] *Hartmut Siebert,*[1] *Laurence Noirez,*[2] *Claudia Schmidt**[3]

[1]Institut für Makromolekulare Chemie, Albert-Ludwigs-Universität Freiburg, Stefan-Meier-Straße 31, D-79104 Freiburg, Germany
[2]Laboratoire Léon Brillouin, CE-Saclay, F-91191 Gif-sur-Yvette, France
[3]Fakultät für Naturwissenschaften, Department Chemie, Universität Paderborn, Warburger Straße 100, D-39089 Paderborn, Germany
E-mail: schmidtc@chemie.uni-paderborn.de

Summary: Several nematic side-chain polysiloxanes with the same backbone and the same mesogens but containing various ratios of two spacers having different lengths were prepared. Within this series of homo- and copolymers, the phase behavior changes continuously from purely nematic for the homopolymer containing only the shorter of the two spacers to nematic plus smectic for the homopolymer containing only the longer spacer. The flow behavior determined by in situ deuterium NMR spectroscopy under shear and the anisotropy of the coil conformation measured by small angle neutron scattering exhibit a continuous change as well.

Keywords: liquid-crystalline polymer (LCP); neutron scattering; NMR; shear; X-ray

Introduction

Nematic liquid crystals exhibit peculiar phenomena in shear flow which are caused by the coupling between director orientation and flow.[1-3] According to the theory of Leslie and Ericksen[4-5] there are two different types of nematics: flow-aligning materials, which adopt a stable director orientation in shear flow, and tumbling materials, which are characterized by the absence of a stable director orientation when sheared. The type of flow behavior is determined by the reactive parameter, λ, which is a function of the two Leslie coefficients α_2 and α_3; $\lambda = -(\alpha_3+\alpha_2)/(\alpha_3-\alpha_2)$. Tumbling occurs if $|\lambda| < 1$, otherwise a nematic material is flow aligning. The application of shear to a flow-aligning nematic leads to a high degree of order, whereas tumbling materials are expected to get only partially aligned. Since shear forces occur during the processing of bulk liquid-crystalline polymers (LCPs) or during the coating of surfaces by thin layers of LCPs, knowledge of the flow properties of LCP materials is useful when a certain degree of order is desired for an application.[6]

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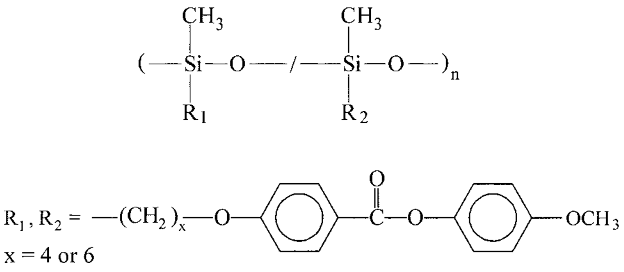

Figure 1. Structure of the liquid-crystalline polysiloxanes. Statistical copolymers with different mole ratios of R_1 and R_2 and the two homopolymers with either R_1 or R_2 were investigated.

When our rheo-NMR investigations of the orientation of nematic side-chain LCPs under shear were started[7] little was known about the flow behavior of these materials. Measurement of the director orientation by NMR spectroscopy as a function of the shear rate allows us to determine the flow-aligning parameter, λ. To date several types of side-chain LCPs have been studied either in the bulk or in solution by using rheo-NMR, microscopy, or rheological experiments, and the flow-aligning parameter has been found to vary over a wide range from $\lambda > 1$ to $\lambda < 1$.[8-17] Our studies of two particular polysiloxanes with the same mesogens, but having spacers of different lengths (cf. Figure 1), showed that the polymer with the shorter spacer of four methylene units is flow-aligning, while the one with the longer spacer of six methylene units exhibits the tumbling instability.[15] Based on previous reports about low molar mass nematics, which show tumbling in the vicinity to a smectic phase,[18-21] we attributed this difference in flow behavior to the different phase structures of the polymers. Indeed, it is the polymer of the tumbling type, which has a low-temperature smectic phase. By preparing statistical copolymers with mixed spacers, as shown in Figure 1, or with mixed mesogens we modified the phase structure of the LCPs systematically. The analysis of the shear flow properties of these polymers by rheo-NMR experiments[16] established the expected correlation of the flow behavior and the phase structure, which is investigated by X-ray diffraction.[22]

Besides the orientational order of the local directors of the domains in a macroscopic sample, which is influenced by shear and can vary from completely random to perfectly aligned, another aspect of partial order is the deformation of the polymer backbone induced by the nematic phase. In an isotropic melt a polymer coil is on average spherical, but in nematic phases a deformed coil conformation is expected.[23,24] Prolate coils, which are extended along the director axis, as well as oblate coils, compressed along the director, have been observed by small angle neutron scattering.[25] Oblate coils are generally found in nematic polymers close enough to a smectic phase, that is, materials which actually form a smectic phase at lower temperature.[25] In a series of liquid-crystalline polymers with systematically varying phase structure also a systematic change of the molecular shape is expected.

In this contribution we report on rheo-NMR, X-ray, and neutron scattering performed on a series of homopolymers and copolymers having mixed spacers; their chemical structures are shown in Figure 1. The results reveal a systematic change of the flow behavior, the phase structure, and the polymer conformation as a function of the chemical composition of the polymers.[26,27]

Materials and Methods

The chemical structure of the polysiloxane LCPs, which were synthesized via a polymer analogous hydrosilylation reaction,[28,29] is shown in Figure 1. The homopolymers with only one type of side chain and two statistical copolymers with mixed spacers were prepared. Using the homopolymer with the short spacer of four methylene units (PSi4) as a reference, the polymers used are labelled PSi4-0, PSi4-25, PSi-75, and PSi-100, where the number specifies the mole fraction (in per cent) of the side chains with the short spacer. For deuteron NMR measurements the phenylene ring carrying the methoxy group is deuterated, while neutron scattering was performed on 1:1 mixtures of protonated and deuterated polymers. The degree of polymerization, P_n, is about 90 unless stated otherwise. The phase behavior was determined by differential scanning calorimetry. Glass transition temperatures between 272 and 280 K were found for all polymers. Typical temperatures of the nematic-to-isotropic transition are 375, 363, 355, and 368 K for PSi-0, PSi-25, PSi-75, and PSi-100, respectively. These are the values for the samples used in the neutron experiments; in general, the phase transition temperatures for the same type of polymer varies somewhat from batch to batch. PSi-0 has an additional smectic C phase with a transition to the nematic phase at 311 K.

^{2}H NMR experiments under shear were performed on a Bruker MSL 300 spectrometer using a home-built probe with an integrated cone-and-plate shear cell.[7] The axis of the cone-and-plate device is parallel to the magnetic field, that is, the velocity gradient is parallel and the flow direction perpendicular to the magnetic field.

Small angle neutron scattering experiments were carried out at the Laboratoire Léon Brillouin using the two-dimensional detector PAXY.[25] Both the wavelength of the neutrons and the distance between sample and detector were adjusted to obtain a range of the scattering vector, *q*, suitable for either determination of the radius of gyration or detection of layer reflections due to diffraction by smectic clusters.

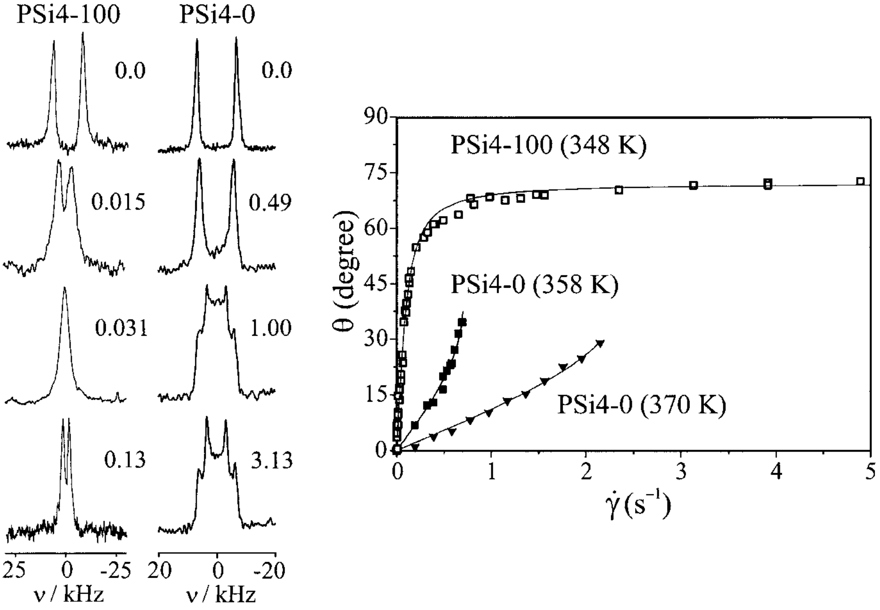

Figure 2. Left: ^{2}H NMR spectra of a flow-aligning (left column, PSi4-100 at 348 K) and a tumbling polysiloxane (right column, PSi4-0 at 358 K) under shear. The shear rate, $\dot{\gamma}$, (in s^{-1}) is given to the right of each spectrum. Right: Director orientation θ with respect to the magnetic field or velocity gradient axis as a function of shear rate. The curves are obtained by fitting Eq. (1) to the experimental data.

Flow Behavior

The type of flow behavior and the flow-aligning parameter λ are determined by rheo-deuterium-NMR spectroscopy.[7,11] Sample spectra of the nematic polymers in shear flow are depicted in Figure 2. At rest (spectra on top) the director aligns along the magnetic field, that is the angle θ between director and magnetic field is zero. Using the relationship between quadrupole splitting, $\Delta\nu$,[30] and director orientation, $\Delta\nu = \delta(3\cos^2\theta - 1)$, the motionally averaged coupling constant δ is obtained from the spectrum at $\theta = 0$. This value is then used to calculate the orientations from the spectral splittings at various shear rates, $\dot{\gamma}$. Upon increasing shear rate the director is tilted more and more away from the magnetic field. For the flow-aligning polymer PSi4-100 (left column in Figure 2) the director orientation stays uniform throughout the sample, which is evident from the simple doublet spectra, as the director approaches a limiting angle between director and flow axis. The tumbling polymer PSi4-0, on the other hand, exhibits uniform director orientations with simple doublet line shapes (spectra at shear rates of 0 and 0.49 s^{-1}) only below a critical value of the shear rate, as long as tumbling is suppressed by the magnetic field.[11] When the critical shear rate is exceeded (spectra at 1.0 and 3.12 s^{-1}) tumbling results in a polydomain structure whose orientational distribution of the director is reflected in the NMR line shape.[16] Thus, flow-aligning and tumbling behavior can be easily distinguished by a qualitative inspection of the spectra.

The quantitative analysis of the director orientation as a function of the applied shear rate, shown on the right side of Figure 2, according to[11]

$$\tan\theta = \mp\frac{\chi_a B_0^2}{2\mu_0|\alpha_3|\dot{\gamma}} \pm \sqrt{\left(\frac{\chi_a B_0^2}{2\mu_0|\alpha_3|\dot{\gamma}}\right)^2 \pm \frac{|\alpha_2|}{|\alpha_3|}} \qquad (1)$$

yields α_2/χ_a and α_3/χ_a as fit parameters, from which the flow-alignment parameter λ can be calculated. In the equation above B_0 represents the magnetic field, μ_0 is the permeability of free space and χ_a is the anisotropy of the magnetic susceptibility per unit volume of the liquid crystalline polymer. For tumbling polymers only the splittings of spectra below the critical shear rate are evaluated. This procedure yields λ values of 1.23, –0.16 and –0.12 for PSi4-100 at 348 K and PSi4-0 at 358 and 370 K, respectively. As expected, $|\lambda| > 1$ for the flow-aligning polymer PSi4-100 and $|\lambda| < 1$ for the tumbling system PSi4-0. Similar rheo-NMR experiments on the copolymers show that PSi4-75 is also flow-aligning, whereas PSi4-50 and PSi4-25 show a temperature-induced transition between tumbling at low temperature and flow-aligning at high temperature.[16]

The rheo-NMR experiments reveal a continuous change of the flow behavior as the polymer composition is changed from PSi4-0 to PSi4-100. Assuming that the phase structure also changes continuously, this indicates that there is a relationship between phase structure and flow behavior, in keeping with experiments on low molecular weight nematics. The temperature dependence of the flow-aligning parameters, λ, confirms this relationship, since we always find a decrease of λ or even a transition from $\lambda > 1$ to $\lambda < 1$ when the temperature is lowered, that is, when the smectogenic character of the sample is increased.[16]

A higher degree of polymerisation, P_n, appears to shift the flow behavior towards the tumbling regime.[27] PSi4-25 with P_n = 90 shows a transition from tumbling at low temperature to flow-aligning at high temperature, whereas only tumbling is found when P_n =150. For PSi4-75 the same change of P_n does not change the type of flow behavior (the polymer is always flow-aligning) but the flow-aligning parameter becomes smaller, approaching the critical value of $\lambda = 1$.

Phase Structure

X-ray scattering on the polymers was performed to test our hypothesis that the phase structure changes gradually when the polymer composition is modified. The polymers were aligned in a magnetic field prior to the X-ray experiments. Figure 3 shows the diffraction patterns of the homopolymer PSi4-0 and the copolymers. The reflections close to the equator are due to the lateral order of the rodlike mesogens, which are aligned by the magnetic field. Perpendicular to these wide-angle reflections there are small-angle reflections indicating the presence of clusters with smectic order. This phenomenon of smectic clusters in nematic samples is well known; liquid crystals showing this feature are called cybotactic nematic. The patterns in Figure 3 make evident that the intensity of the layer reflections gets weaker, indicating that the relative amount of smectic clusters in the nematic samples decreases, as the mole fraction of the short spacer is increased. For PSi4-100 (not shown) the intensity of the layer reflections is below the detection threshold of the X-ray experiments, but they can be observed by neutron diffraction (see below).

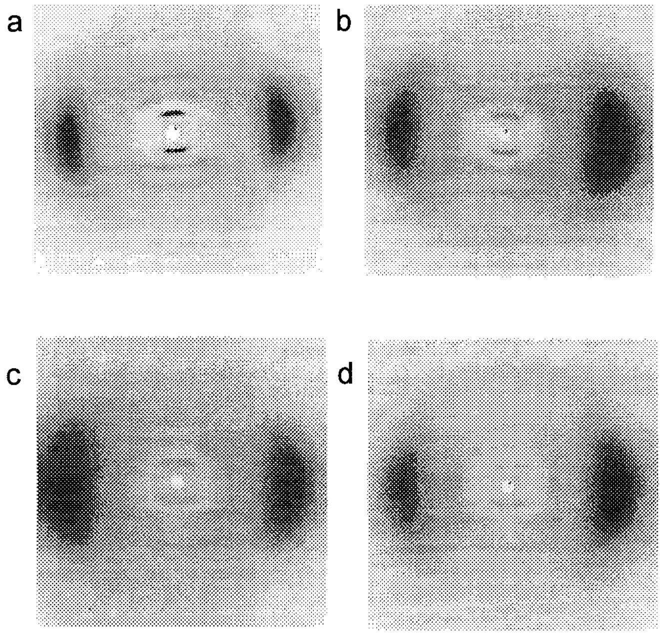

Figure 3. X-ray diffraction patterns of magnetically oriented PSi4-0 (a), PSi4-25 (b), PSi4-50 (c), and PSi4-75 (d) at a reduced temperature $T/T_{ni} = 0.84$.

To obtain a more quantitative measure of the relative amount of smectic clusters the intensity of the small-angle reflections, I_{sa}, is normalized by dividing it by the intensity of the wide-angle reflections, I_{wa}. The results are shown in Figure 4. There is a clear tendency of the intensity ratio I_{sa}/I_{wa}, and hence of the amount of smectic clusters, to decrease with increasing temperature and with increasing mole fraction of short spacer. Thus the changes in phase structure clearly go hand in hand with the change of the flow behavior, although a quantitative relationship or a threshold value for the amount of smectic clusters above which tumbling occurs can not be given.

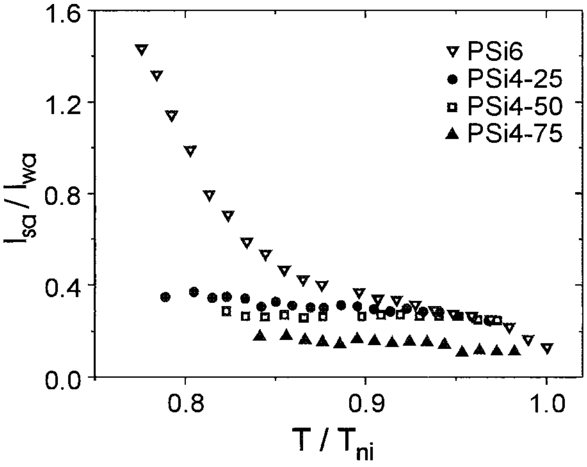

Figure 4. Ratio of the intensities of small and wide angle X-ray reflections versus reduced temperature.

The small-angle reflections in Figure 3, in particular the higher order peaks, are split in two, indicating that the layer structure of the clusters is of the smectic C type with a tilt between layer normal and nematic director. The tilt angle was determined by neutron diffraction experiments performed on samples in a magnetic field. PSi4-0, the only polymer with a true smectic phase, has a tilt angle of 7° in the smectic phase. At the smectic-to-nematic phase transition the tilt angle begins to increase strongly and reaches 28°. The tilt angles of the other polymers, obtained by avering over a range of temperatures with fairly constant tilt angle, are 31°, 37°, and 43° for PSi4-25, PSi4-75, and PSi4-100, respectively. This result shows a clear correlation of tilt angle and polymer composition: the higher the fraction of short spacer, the smaller the tilt angle.

One can speculate that the tilt angle is imposed by conformational restrictions of the spacer. With the longer spacer a better decoupling of the orientations of main chain and mesogens is achieved. Assuming that the main chain in a smectic phase is mainly accommodated between layers of mesogens, main chain and mesogens should be almost perpendicular to each other if there is a layered structure. The ideal case is a smectic A phase without tilt (tilt angle 0°). It appears that if the spacer is too short the tilt angle cannot become small enough to support the formation of a smectic phase.

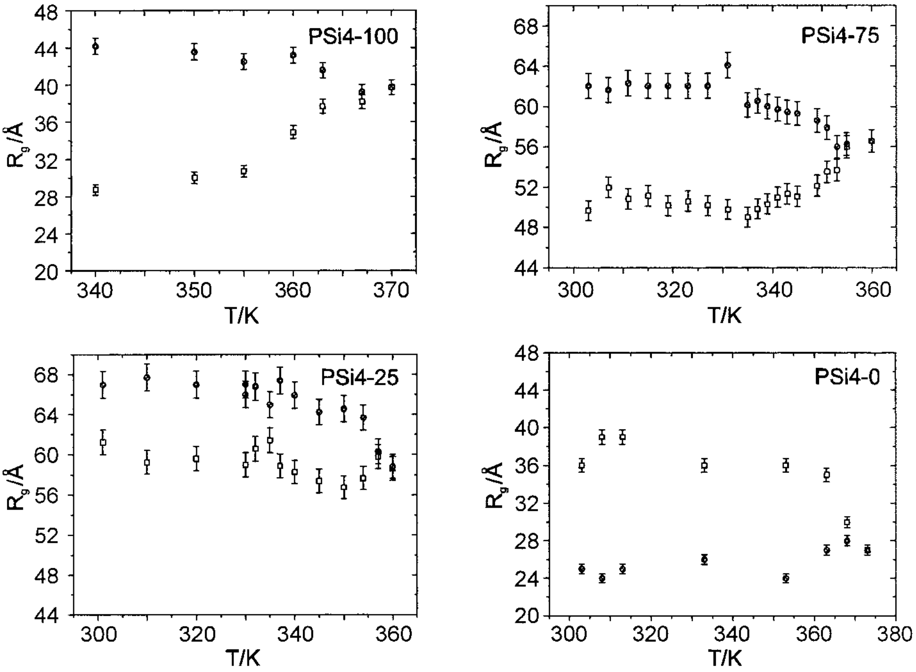

Figure 5. Radius of gyration (R_g) parallel (filled circles) and perpendicular (open squares) to the nematic director for the different LCPs. The degree of polymerisation of PSi4-100 and PSi4-0 is about 90, whereas that of PSi4-75 and PSi4-25 is about 150.

Polymer Shape

The series of polysiloxanes with its continuous change of phase structure provides an ideal model system to investigate whether the relationship between phase structure and polymer conformation of side-chain LCPs found by small angle neutron scattering[25]—that purely nematic polymers are prolate and polymers with smectic phases are oblate—applies. The anisotropies of the radii of gyration, R_g, determined by neutron scattering on samples of our polysiloxanes aligned in a magnetic field are shown in Figure 5. All polymers show a clear difference of the radii of gyration parallel ($R_{g,para}$) and perpendicular ($R_{g,perp}$) to the nematic director. The difference vanishes as the nematic-to-isotropic transition is approached. It should be noticed that the measured values of R_g reflect the global shape of the polymer molecules including the side chains since the deuteriated sites are in the mesogens. Furthermore, the radii represent averages over the orientational distribution of molecules due to differently aligned smectic clusters. In the magnetic field only the nematic director is aligned while the layer normal vectors are distributed on a cone. The data in Figure 5 show that the homopolymer with the short spacer and both copolymers have prolate shapes with $R_{g,para} > R_{g,perp}$, whereas the homopolymer with the long spacer, the only polymer which also has a smectic phase, is oblate ($R_{g,para} < R_{g,perp}$). The ratio $R_{g,para}/R_{g,perp}$ averaged over the plateau region at lower temperatures in the nematic phase changes from 1.46 for PSi4-100 over 1.23 (PSi4-75) and 1.12 (PSi4-75) to 0.67 for PSi4-0.

The model of a nematic PSi4-100 with a backbone elongated along the director axis due to preferentially parallel alignment of mesogens and main-chain segments, on the one hand, and a cybotactic nematic PSi4-0 with a backbone compressed along the director axis due to smectic clusters, on the other hand, is supported by ^{29}Si solid state NMR studies[31,32]. From the orientation of the ^{29}Si chemical shift tensors in magnetically aligned samples frozen into the glassy state, the order parameter of the main-chain segments, that is, the axis connecting the oxygen atoms next to a silicon atom, was determined as 0.18 and –0.23 for PSi4-100 and PSi4-0 under the assumption of transverse isotropy.[32] Thus, the main-chain segments are mostly parallel to the director axis for the prolate PSi4-100 and mostly perpendicular to it for the oblate PSi4-0. The local order determined by ^{29}Si NMR and the global shape of the polymers derived from the neutron scattering experiments, as shown schematically in Figure 6, are in good agreement.

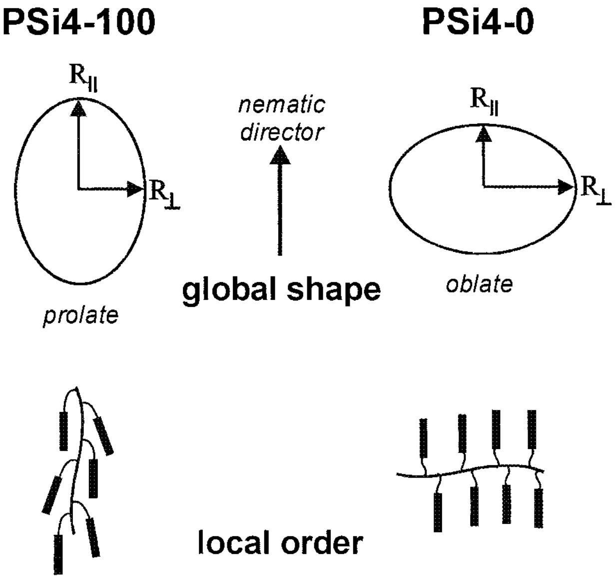

Figure 6. Schematic model of the global shape of the polymer coils and the corresponding local relative orientations of mesogens and main-chain segments in prolate and oblate polymers, such as PSi4-100 and PSi4-0.

Conclusions

The correlation of flow behavior and phase structure of the LCPs with similar chemical structure studied here shows that the tumbling instability of polymers with a moderate degree of polymerisation is caused by smectic clusters in the nematic phase, in keeping with previous reports on low molar mass nematics. Our experiments on polymers with different degree of polymerisation indicate that tumbling is more likely when the polymer backbone gets longer. If the degree of polymerisation gets much larger, the flow orientation may be completely controlled by the polymer backbone.[17] In addition, the comparison of phase structure and polymer shape for the polysiloxanes investigated here provides a further example supporting the rule that purely nematic polymers have prolate backbones, whereas smectogenic polymers have oblate ones. The spacer connecting mesogens and backbone obviously plays a crucial role in forming the liquid crystalline structures. In summary, our results show that tailoring of the chemical structure, in this case the copolymer composition, provides a means to control the phase structure of side-chain LCPs and therefore to tune the flow behavior of these materials.

Acknowledgements

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