Isotropic−Nematic Phase Transitions of Lyotropic, Two-Dimensional Liquid Crystalline Polymer Solutions

Kang Sub Yim and Gerald G. Fuller*

Department of Chemical Engineering, Keck Science Building, Stanford University, Stanford, CA 94305-5025

Achim Datko and Claus D. Eisenbach

Institut für Kunststofftechnologie, Universität Stuttgart, Böblinger Strasse 70, D-70199 Stuttgart, Germany

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ABSTRACT: Few studies of the isotropic−nematic phase transition temperature, T_{IN}, in two dimensions have been reported experimentally in contrast to that of liquid crystalline polymers in three dimensions. The purpose of this paper is to examine molecular orientational hydrodynamics through studies of monolayer films at the air−water interface and to understand the phenomenon of the phase transition in two dimensions. UV absorption spectroscopy was used to determine molecular orientation in hairy-rod polymeric monolayers of poly(*p*-phenylene) sulfonic acid (PPPSH). A well-defined extensional flow is imposed in the monolayer to study the dynamics of flow-induced anisotropy. A solvent of stearic acid (SA) at moderate concentrations is added to the polymer solution to fluidize the film, and the effect of solvent on the isotropic−nematic transition is observed. Above T_{IN}, complete relaxation of molecules is observed after flow cessation, while a nematic, ordered phase is obtained below T_{IN}. Measurements of the surface rheological properties were also performed to further interrogate the phase transition.

Introduction

Langmuir−Blodgett (LB) films of liquid crystalline polymers have the advantage of high thermal and mechanical stability and homogeneity.[1] This stability is derived from the polymeric nature of the molecules, and the improved homogeneity of these films is linked to the two-dimensional, nematic structure of the monolayers from which they are deposited.[2,3] The latter characteristic helps to create long-range orientational order with fewer defects. Indeed, the ability to create highly oriented films is often an advantage for applications such as optoelectronic devices, sensors, and displays.[4] For this reason, the conditions that are necessary to create nematic Langmuir films are of practical as well as scientific interest.

The investigation of isotropic-to-nematic phase transitions of bulk, three-dimensional binary systems has a long history. The "guest−host" effect in nematic liquid crystals has received attention because of its relevance to electrooptical liquid crystal display devices.[5] In this application, dichroic dyes residing as guests within a liquid crystalline host become aligned with their long axis parallel to the director of the host. These systems are capable of producing displays with higher image brightness at lower cost.[6]

The addition of nonmesogenic solvent compounds to liquid crystals has also been studied. The early work by Dave and Dewar[7] showed that such additives cause a depression of the isotropic−nematic transition temperature, T_{IN}, and that the perturbing effect of the solvent increases with its molecular size.

Very little experimental work has considered two-dimensional nematics. Certainly, the reduction in dimension is known to have a profound effect on the isotropic−nematic transition.[8] In three dimensions, this transition is first-order, and the order parameter is discontinuous. On the other hand, mean field theory predicts that the transition should be second-order in two dimensions, with a continuous order parameter.[9−12]

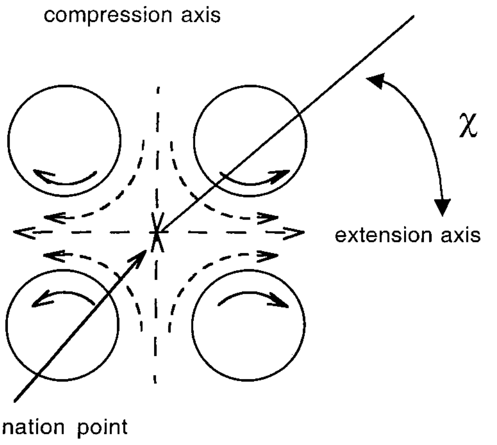

Figure 1. Top view of the four-roll mill to produce extensional flow.

In a previous study from our laboratory,[13,14] a surface-pressure-induced isotropic−nematic transition for polymer monolayers was investigated using both UV dichroism to measure the order parameter during flow and interfacial rheometry. In the present paper, thermally induced transitions are studied, along with the influence of distributing a nonmesogenic amphiphile within matrixes of monolayers composed of rodlike polymers. The results found for these monolayers systems are compared to analogous results for three-dimensional materials.

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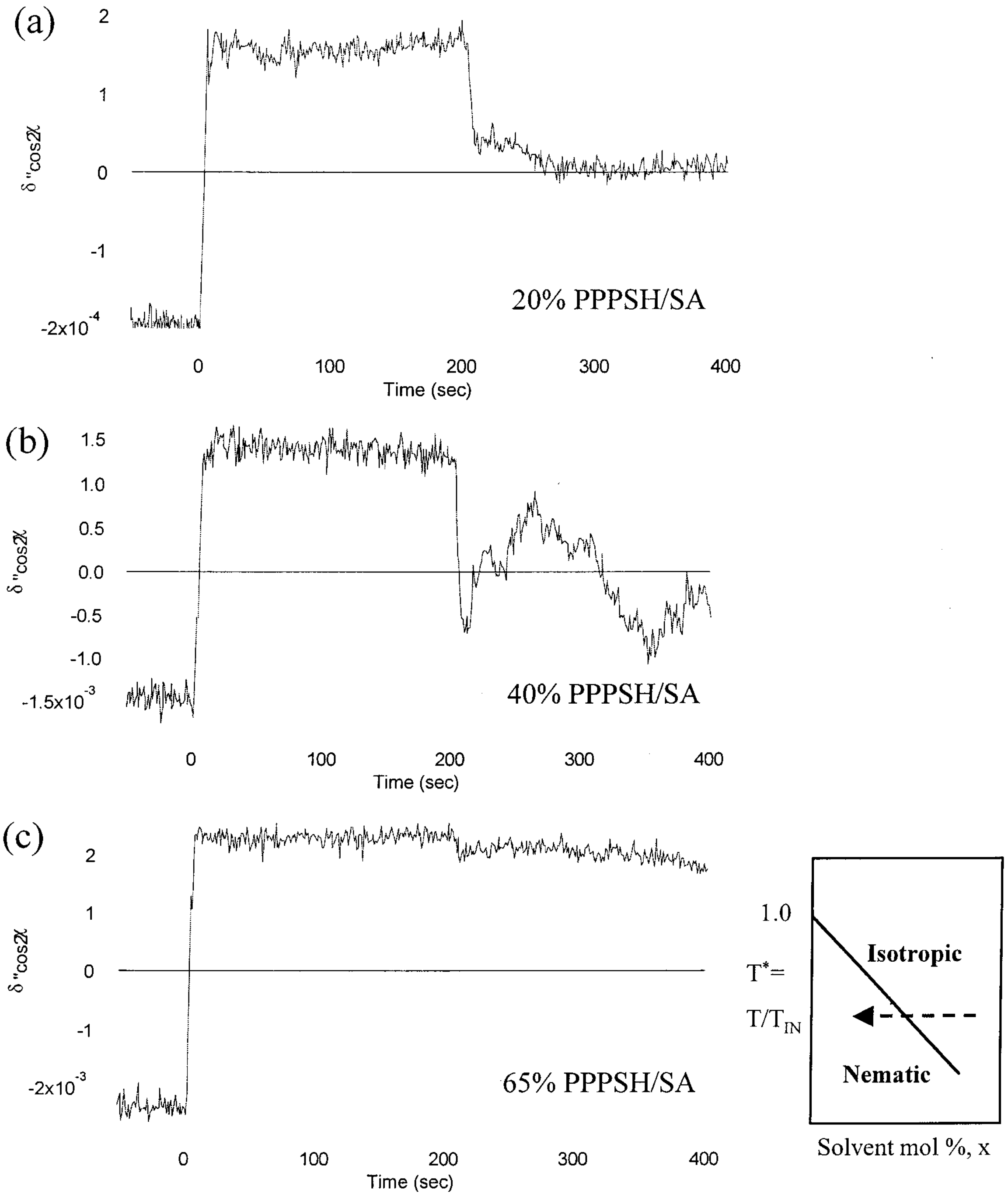
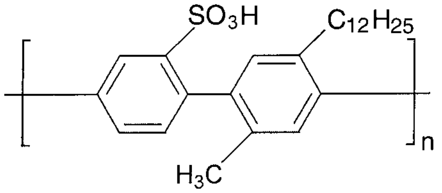


Figure 2. Lyotropic phase behavior: isotropic−nematic transition induced by change of solvent concentration at 31 °C. (a) 20, (b) 40, and (c) 65 mol % PPPSH/SA. The inset represents schematically the transition in the phase diagram.

Materials and Methods

The rigid-rod polymer poly(*p*-phenylene) sulfonic acid (PPPSH) of $M_n = 5080$ was synthesized[15] and is shown schematically below.



PPPSH

Stearic acid (SA, $C_{18}H_{36}O_2$) was used as a nonmesogenic solvent and was purchased from Sigma. Mixtures of PPPSH with stearic acid with varying concentrations were made in chloroform.

Monolayers were formed on a 35.0 × 7.5 cm Langmuir trough made of Teflon and equipped with a Wilhelmy balance for surface pressure measurements. Flow-induced orientation of the monolayers was accomplished using an extensional flow generated by a four-roll mill (Figure 1). A detailed description of a four-roll mill and the resulting flow field has been provided previously.[16] Isotherms of mixtures of PPPSH and SA of concentration can also be found in a previous paper.[14]

The degree of molecular order induced by flow on the monolayers was determined using UV linear dichroism. A description and analysis of the optical train for the dichroism measurements have been supplied previously.[13] The dichroism, $\Delta n''$, is recovered from the anisotropy parameter, $\delta'' = (2\pi\Delta n'' d)/\lambda$, where d is the thickness of the monolayer and λ is the wavelength of the incident light. The order parameter,

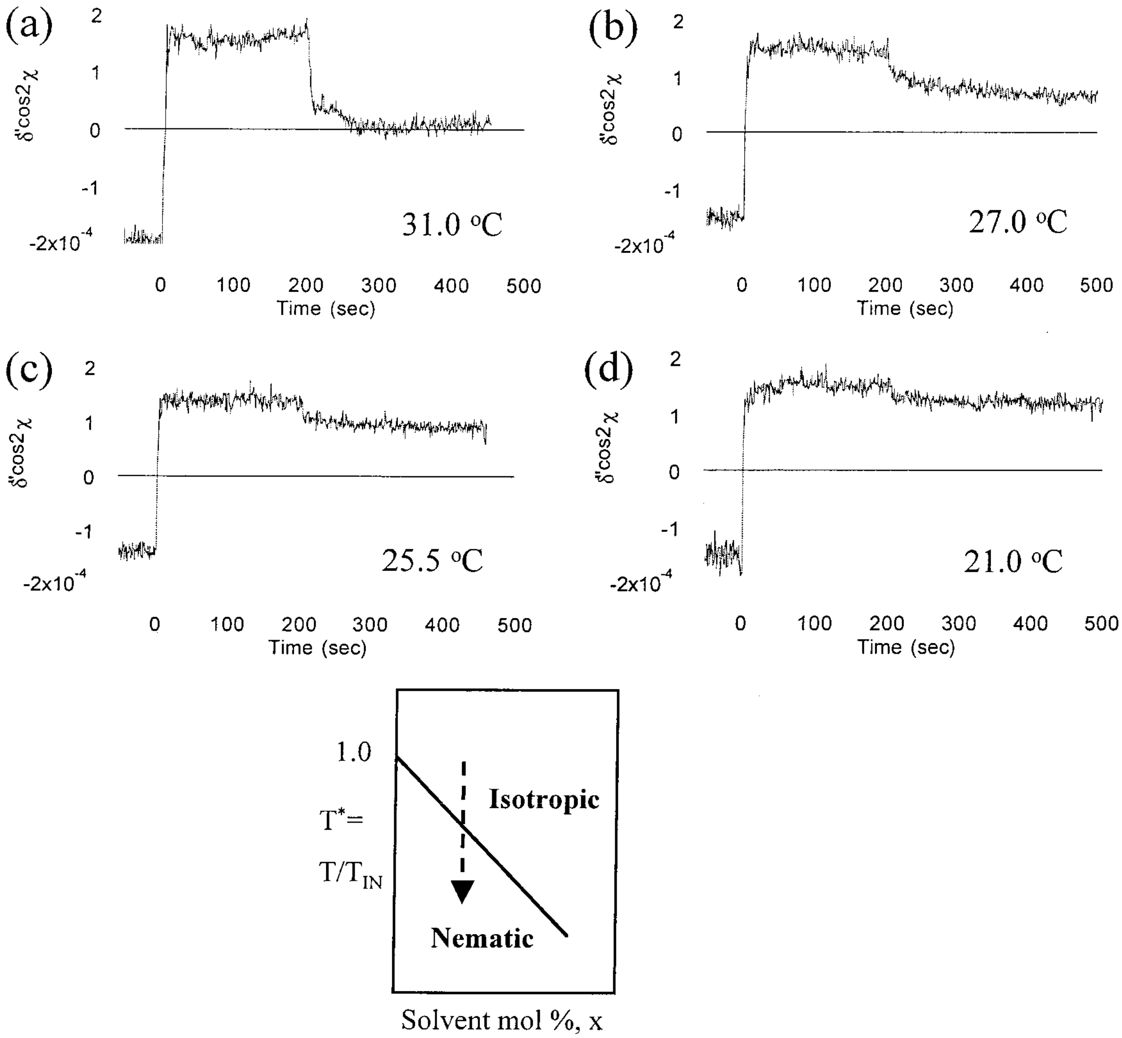


Figure 3. Thermotropic phase behavior: isotropic−nematic transition induced by change of temperature at 20 mol % PPPSH/SA. (a) 31.0, (b) 27.0, (c) 25.5, and (d) 21.0 °C. The inset represents schematically the transition in the phase diagram.

S, is obtained from the quantity δ''/δ''_{ss}, where δ''_{ss} is the steady-state anisotropy that corresponds to complete orientation of the polymer rods.

An interfacial stress rheometer was used to study the surface rheology of the monolayers.[17] This device utilizes a thin magnetized rod lying on the interface that is forced to glide upon the application of a magnetic field gradient at the air−water interface. The rod is situated between two parallel, solid boundaries that form a flow channel. As a result, a shear flow is generated, and the dynamic shear moduli can be determined by applying an oscillating force and measuring the resulting displacement of the rod.

Results and Discussion

The films considered in this study can be thought of as two-dimensional analogues of lyotropic liquid crystals. The isotropic−nematic transition in such systems is influenced both by the temperature and the concentration of the rods. This transition can be identified in two ways. The first method uses UV dichroism measurements of the order parameter and a protocol of extensional flow reversals followed by flow cessation. The responses of the isotropic and nematic phases will be qualitatively different. Isotropic monolayers will show no dichroism in the absence of flow, and any flow-induced orientation will ultimately relax to zero once the flow is removed. Nematic layers, however, show long-range order at rest.

The second way to monitor the transition is to follow the interfacial rheology (surface viscosity, for example) as either temperature or concentration is changed. This strategy is used in bulk systems where the transition to a nematic phase is accompanied by a sharp maximum in viscosity.

Figure 2 shows the lyotropic phase transition induced by varying the stearic acid solvent concentration in PPPSH/SA monolayers at a constant temperature of 31 °C. As explained earlier, the monolayers were subjected to a sequence of flow reversals. First, the monolayer was subjected to an extensional flow with the orientation angle at $\chi = 90°$ (see Figure. 1). At zero time, the rotation direction of the rollers was reversed, and the PPPSH reoriented toward $\chi = 0°$. At 200 s, the flow was stopped. Figure 2a shows the results for a 20 mol % PPPSH solution that is able to fully relax following flow cessation, indicating that it is an isotropic system. The same is true for the sample with a concentration of 40 mol %. At this concentration, transitional fluctuations are observed before the final recovery to an isotropic state, which indicates enhanced repulsive interactions between polymer molecules. Increasing the concentration of the polymer to 65 mol % leads to a nematic phase, which has long-range order in the absence of flow. Evidently the isotropic−nematic transition occurs between 40 and 65%.

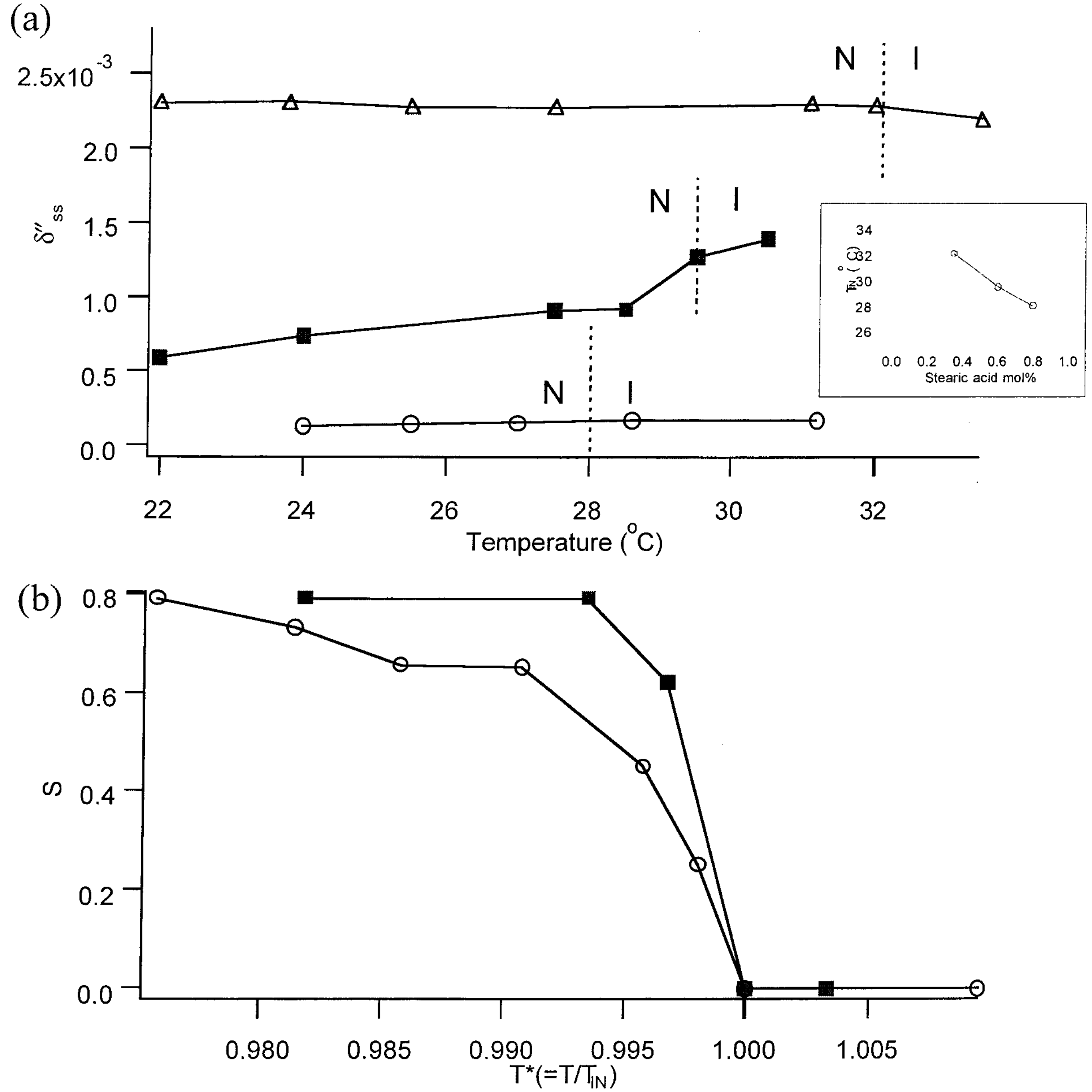


Figure 4. (a) Temperature dependence of the steady-state anisotropy for the mixed monolayers of PPPSH and SA. △, 20 mol % PPPSH/SA; ■, 40 mol % PPPSH/SA; ○, 65 mol % PPPSH/SA. The vertical lines represent the isotropic–nematic transition temperature, T_{IN}. The inset shows the changes in the transition temperature, T_{IN}, with change in the solvent mole fraction x. The parameter $\beta = dT_{IN}/dx$ indicates the destabilization of a nematic phase by a solvent. (b) Order parameter as a function of reduced temperature, $T^* = T/T_{IN}$; ■, 20 mol % PPPSH/SA; ○, 40 mol % PPPSH/SA.

The thermotropic phase transition induced by lowering the temperature at a fixed polymer concentration of 20 mol % is shown in Figure 3. At 31.0 °C, a complete relaxation of orientation is observed (Figure 3a). Decreasing the temperature creates long-range orientational order and a nematic phase (Figure 3b–d).

In Figure 4a, the steady-state anisotropy, δ''_{ss}, is plotted against temperature for three monolayers of different compositions. Located on each trace is the location of the isotropic–nematic transition. As expected, the solution with the higher concentration of PPPSH resulted in the higher anisotropy under the flow because it has the largest absorption coefficient. The isotropic–nematic transition temperature, T_{IN}, decreases with the addition of stearic acid, which suggests that the addition of solvent destabilizes the nematic phase. It is known that this change of T_{IN} depends on the size and shape of the solvent molecule, as well as the solvent concentration. The perturbing influence of different sizes of solvent amphiphiles on T_{IN} for two-dimensional nematics should be studied.

A sensitive measure of the destabilization of the nematic phase through the addition of solvent is the slope of the transition temperature, T_{IN}, with change in the solvent mole fraction x, defined as $\beta = dT_{IN}/dx$. Positive values of β indicate an ability of solvent molecules to facilitate order, whereas negative values are linked to systems that disrupt long-range orientational order. The inset graph in Figure 4a shows that stearic acid disturbs nematic ordering in these particular lyotropic systems.

The order parameter for PPPSH/SA solutions of different concentrations is plotted as a function of reduced temperature ($=T/T_{IN}$) in Figure 4b. In general, the order parameter weakly depends on temperature until the vicinity of the transition and then continuously

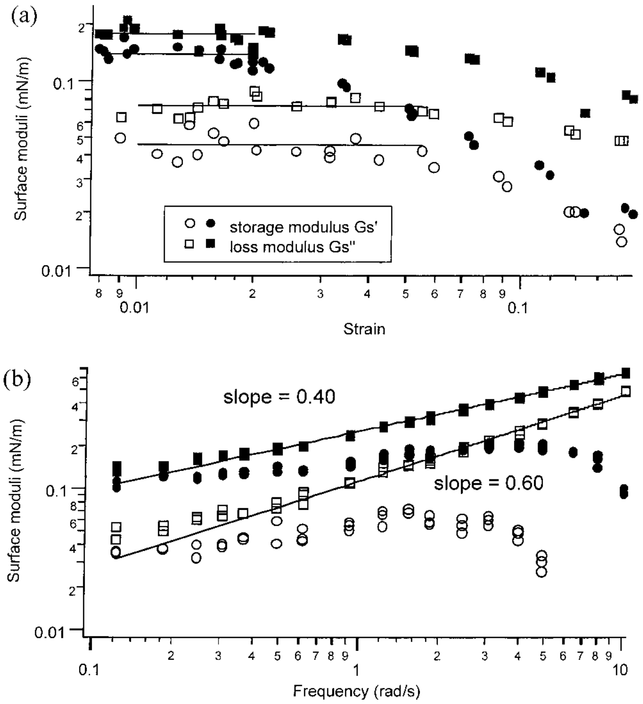


Figure 5. Dynamic surface moduli as a function of (a) shear strain and (b) frequency for 20 mol % PPPSH/SA monolayers: isotropic phase of 32 °C (□, ○) and nematic phase of 24 °C (■, ●). Circles are surface storage modulus, and squares are surface loss modulus.

decreases to zero at the transition temperature. A higher concentration of solvent reduces the order parameter, indicating that the presence of the solvent disturbs polymer–polymer van der Waals interactions. Unlike for the three-dimensional bulk phase, a rapid jump in the order parameter is not observed.

The surface moduli of both isotropic and nematic phases of 20 mol % PPPSH/SA solution are shown as functions of the strain amplitude in Figure 5a and of the frequency in Figure 5b. The isotropic phase at a temperature of 32 °C has a linear viscoelastic plateau, where the rheological properties are not a function of the applied strain, that is observed up to a strain of 0.06. The nematic phase at a temperature of 24 °C has a smaller linear viscoelastic region, which is followed by a nonlinear response of the rheological properties. A similar strain dependence of dynamic properties has also been found in three-dimensional liquid crystalline melt systems.[18] From the frequency sweeps in Figure 5b, it is found that the loss moduli are linear on log–log scales with powers of 0.60 and 0.40 for the isotropic and nematic phases, respectively. These values are in contrast to that of a Newtonian fluid, where the slope is unity. The surface storage modulus of the nematic phase is approximately three times higher than that for the isotropic phase, indicating higher polymer–polymer interactions between aligned molecular conformations.

The temperature dependence of the dynamic surface viscosity for the 20 mol % PPPSH/SA solution is plotted in Figure 6. Above the transition temperature of 28 °C, the surface viscosity is a monotonically decreasing function of temperature in the isotropic phase. At the transition, however, the surface viscosity shows a local maximum, and in the nematic phase, the surface viscosity first decreases with temperature and then increases as the transition temperature is approached. The location of the local maximum of 28 °C corresponds to the temperature separating the isotropic and nematic phases identified using dichroism relaxation measurements shown in Figure 4a. Local maxima in viscosity at the transition temperature are also found in three-dimensional nematics,[18,19] but they are generally much stronger than the maximum reported here for the PPPSH/SA monolayer.

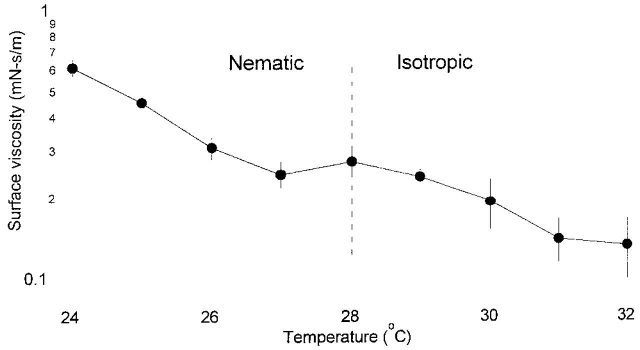


Figure 6. Temperature dependence of surface viscosity for 20 mol % PPPSH/SA monolayers. The vertical line represents the isotropic–nematic transition temperature, T_{IN}.

Activation energies, *E*, were measured by fitting the regions of decreasing viscosities to the Arrhenius equation for the isotropic and nematic phases, yielding values of 170 and 232 kJ/mol, respectively. These values are similar to values of 350 kJ/mol recently reported for dendrimer monolayers[20] but are much higher than the 23 and 50 kJ/mol values reported for isotropic and nematic phases in 3D lyotropic liquid crystals, respectively.[21] The larger activation barriers for two-dimensional systems are possibly a reflection of the limited mobility of monolayer molecules caused by confinement to the interface. However, the ratio $E_{\mathrm{nematic}}/E_{\mathrm{isotropic}} = 1.36$ found here is smaller than that of 1.8–2.0 measured for 3D liquid crystals.[21,22] This is further experimental evidence that the reduction in dimensionality lowers the strength of the transition between the isotropic and nematic phases.

Conclusions

We have investigated the isotropic–nematic transition in two-dimensional lyotropic nematics. The effects of varying both temperature and concentration have been studied. The isotropic–nematic transition temperature, T_{IN}, decreases as the concentration of amphiphilic solvent is increased, indicating that the addition of nonmesogenic solvents destabilizes long-range orientational order. Above T_{IN}, complete relaxation of molecules is observed following flow cessation, which indicates isotropic phases, whereas nematic phases are obtained below T_{IN}. From surface rheological measurements, it is found that nematic phases are more non-Newtonian in their behavior, showing stronger shear thinning and nonlinear viscoelasticity. The surface viscosity shows a local maximum at the isotropic–nematic transition, which corresponds to the point separating the sotropic and nematic phases identified using dichroism relaxation measurements. It is worth noting that the results presented in this paper provide a new experimental approach for the investigation of the isotropic–nematic transition in two-dimensional systems. Our study also provides insight into the influence of a reduction in spatial dimensionality on the transition in the polymer–solvent mixture system.

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