Piezoelectricity in Polar Supramolecular Materials**

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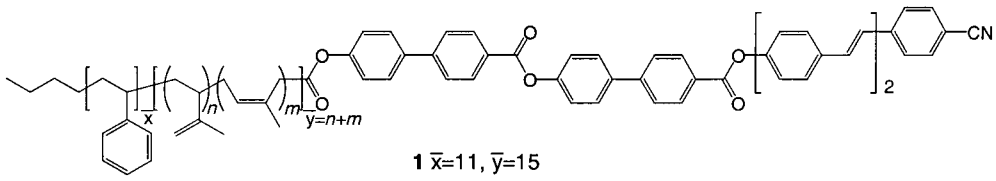
The great potential of supramolecular materials is the possible discovery of properties that are characteristic of molecular clusters and not of individual molecules. Simple changes in the chemistry of building blocks in such clusters enhance further our ability to target specific properties in supramolecular materials. Designing for polar order in organic systems has long been a goal in materials chemistry because of its implications in surface properties, nonlinear optics, piezo-, ferro-, and pyroelectricity. The approaches to polar organic materials include the poling of host–guest systems[1] self-assembled host–guest systems,[2] the poling of polymer films,[3] Langmuir–Blodgett film multilayers,[4–6] grafted polymer brushes,[7] multilayer growth,[8] or the spontaneous assembly of triblock rodcoil molecules into polar supramolecular films[9] discovered in our laboratory.

This spontaneous polar self-assembly provides potentially a direct pathway to the creation of polar domains with a minimum number of processing steps.[9] These hierarchical structures begin with the aggregation of rodcoil molecules into a mushroom-shaped nanostructure lacking a center of inversion. This structure forms as a result of the crystallization of identical rodlike segments but long-range order is disrupted in the system by steric and entropic effects involving the oligomeric coils grafted to rod segments. The supramolecular objects arrange parallel to each other and form sheets and their head-to-tail stacking leads to polar three-dimensional (3D) domains. The self-assembly of these domains on a substrate generates a macroscopic material with net polarization.[9] Recent work has shown that this polar structure is not highly specific to a certain chemical composition of rodcoil molecules. Instead, the structure seems to be a direct consequence of molecular architecture.[10] This finding implies that many rodcoil molecules could be synthesized to target specific properties.

We reported previously on the synthesis of **1** in a stepwise fashion starting with the sequential anionic polymerization of styrene and isoprene and continuing with esterification steps



1 $\bar{x}$=11, $\bar{y}$=15

to build the rod segment.[10] The cyano-substituted phenylene vinylene chromophore imparts fluorescent properties[10] to these molecules and increases drastically their dipole moment.[11] Our previous characterization of this family of molecules has included fluorescence studies, nonlinear optical experiments, small-angle X-ray scattering, as well as transmission electron microscopy (TEM) and electron diffraction.[10–12] We showed that these materials form mushroom-shaped supramolecular aggregates consistent with previous work on triblock rodcoil molecules. Triblock structure **1**, with an average of 11 units of styrene and 15 units of isoprene, forms the most regular nanostructures of this particular family of molecules. Furthermore, we have observed in this family of molecules the polar stacking of molecular layers by cross-sectional TEM.[12]

In this work we have measured piezoelectricity and electrostriction in films of **1** using interferometric experiments described elsewhere.[1, 7, 13] Piezoelectricity is an electromechanical transduction observed exclusively in polar materials, thus resulting in electrical signals as a consequence of a mechanical deformation. Electrostriction, on the other hand, is observed in all materials and refers to deformation in materials as a result of an applied electric field. Samples were prepared on glass substrates coated with a 30-nm aluminum electrode. The films of **1** were deposited from a 2.5 wt.% toluene solution by dip coating at a controlled rate (ca. 1 cm s^{-1}) resulting in films with a uniform thickness of 110 nm. The dip-coating process left a droplet of solution at the bottom edge of the substrate, leading to a thicker region near that edge. However, care was taken to ensure measurements were carried out within the film regions that had uniform thickness. Films were annealed above their relaxation temperature[14] ($T \approx 100\,^{\circ}$C) for 2 h and then a top aluminum electrode was deposited by evaporation to a thickness of 50 nm. Leads were silver painted to the aluminum in such a way as to prevent the shorting of the device.

The sample configuration described above can be considered as a dielectric in a parallel plate capacitor and therefore it can be shown that Equation (1) holds[1] and for an alternating current Equation (2) is valid, where h is the film thickness, a and d are the electrostriction and piezoelectric tensors, respectively, and E is the applied electric field. In this sample configuration the tensor notation can be suppressed and using a lock-in amplifier a and d are measured independently.

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$$h(E) = h_0(1 + dE + aE^2 + \ldots) \quad (1)$$

$$\frac{\Delta h(E)}{h_0} = \left(\frac{1}{2}aE_0 + dE_0\cos\omega t + \frac{1}{2}aE_0^2\cos 2\omega t + \ldots\right) \quad (2)$$

Figure 1 is a plot of the piezoelectric response as a function of voltage. The data points are an average of multiple scans to ensure that the observed response is reproducible and not due

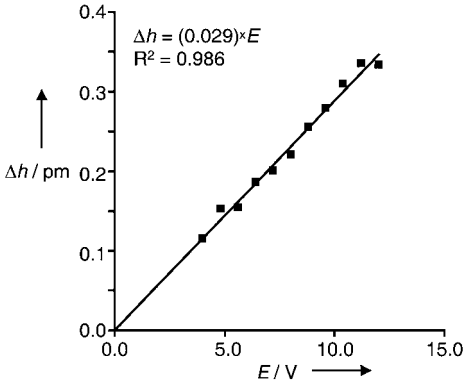

Figure 1. Plot of the piezoelectric response of an annealed film of **1**; the piezoelectric coefficient is equal to 0.029 CN^{-1}.

to thermal fluctuations.[1, 7, 13] The field-induced extensions observed yield a piezoelectric coefficient of $d = 0.029\ CN^{-1}$. Figure 2 shows a plot of polarization in self-assembled films as a function of temperature. This sample was not annealed prior to the experiment such that changes in the film could be

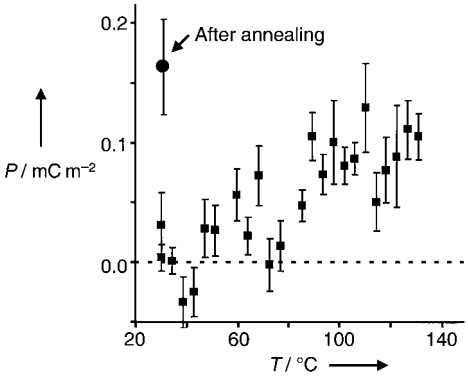

Figure 2. A net polarization develops during annealing of a film of molecules **1**. The circular data point (●) represents the stable net polarization remaining after cooling to room temperature.

observed during the annealing process. In order to obtain these data, the sample was sequentially heated to various temperatures for 30 min before recording piezoelectric and electrostrictive responses. The polarization, P, at each temperature was calculated using Equations (3) and (4),[1] where β is the plate compliance for uniaxial compression normal to the

$$d = -\beta P\frac{\varepsilon + 2}{3}\left(\frac{\varepsilon + 2}{3}\right) \quad (3)$$

$$a = \frac{-\beta\varepsilon_0}{2}\left(\varepsilon + \frac{(\varepsilon + 2)(\varepsilon - 1)}{3}\right) \quad (4)$$

layer[1] and ε is the dielectric constant. Specifically a, d, and ε were measured at each temperature, and the above system of equations was solved for P. A measurable polarization is not detected in as-cast samples, but above the relaxation temperature of 80 °C a positive polarization is observed. Further increments in temperature result in higher polarization, and most importantly when samples are cooled to room temperature the net polarization is retained. The scatter in data is a consequence of compounded errors associated with each experimentally measured value, however, the error bars clearly demonstrate the statistically significant change after annealing. This thermally activated reorganization demonstrates that a polar structure is indeed stable in this material. Polar order was previously suggested by second harmonic generation experiments and these piezoelectricity measurements confirm a net polar arrangement in the self-assembled films. Furthermore, the samples with piezoelectric activity had been annealed above their relaxation temperature ($T \approx 100$ °C) without an applied field prior to the measurements. This should have allowed the system to equilibrate indicating that the spontaneous polarization is an inherent characteristic of the material.

A poled sample was prepared by applying a DC field of 45 MV m^{-1} to the sample at temperatures above the relaxation temperature for 30 min and cooling it to room temperature under an applied field. Then, the sample was heated and the piezoelectric response in the absence of the poling field was monitored with increasing temperature. Plotting piezoelectric coefficient and plate compressibility versus temperature one can observe the decay of the piezoelectric response down to the nominal value for the unpoled sample. At the same time the softening of the material is observed (Figure 3). We note

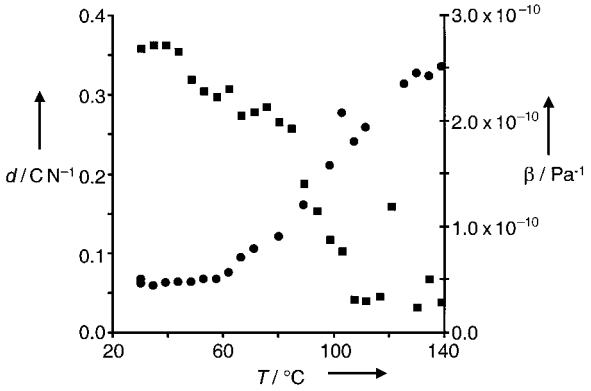

Figure 3. Loss of piezoelectric response, d, (■, left axis) in a poled sample with increasing temperature, and corresponding increase in plate compliance, β (●, right axis).

the values of β at low and high temperatures are comparable to those measured for amorphous polymers below and above the glass transition temperature, respectively. This suggests the observed changes in the self-assembled films must be controlled by the glass-forming oligostyrene block.[13] The fact that the piezoelectric signal returns to a value similar to that measured in a film annealed but never exposed to a poling field offers support for the possibility that net polarization in these systems is thermodynamically stable.

The calculated maximum value of polarization one would expect if all nanostructures were perfectly aligned would be $P = 3.2\ \mathrm{mC\,m^{-2}}$,[15] an order of magnitude larger than the maximum value measured. This discrepancy is presumably due to the fact that polar grains point in different directions and also to the existence of inverted stacks of polar layers. However, unlike conventional ferroelectric materials where the global spontaneous polarization is canceled by polydomains, here macroscopic net polarization can be simply achieved by casting and annealing without the use of an external electric field. It is possible that the substrate on which the material is cast as well as the air/solid interface on top align nanostructures in a preferred direction thus generating net polarization in the film.

It was suggested above that the discrepancy between theoretical and observed polarization was due to inversions in the system. The poled sample, however, should eliminate these inversions and, as expected, the polarization of this sample was $1.46\ \mathrm{mC\,m^{-2}}$, much larger than that of the unpoled sample. A value of $3.2\ \mathrm{mC\,m^{-2}}$ is not achieved in the sample because of the aligning field used ($45\ \mathrm{mV\,m^{-1}}$ is not large enough. A maximum value of $3.19\ \mathrm{mC\,m^{-2}}$ can be obtained at higher poling fields from these materials (see Figure 4). This poling experiment strongly supports our hypothesis that a polydomain structure prevails in the as-cast film. The value of the piezoelectric coefficient for this soft self-assembling films is on the order of that observed for quartz. The system studied here contains oligostyrene and oligoisoprene segments which obviously dilute the overall dipole density of the system. Since we have shown that it is not the specific chemistry that is critical for the observed self-organization of triblock molecules,[10] it should be possible in principle to design systems to maximize the piezoelectric character. This of course requires both mechanical as well as polar design of the system and may require combinatorial approaches for optimization.

Figure 4 is a plot of polarization versus electric field for both positive and negative bias. The saturation values of polarization lie in the range expected for complete alignment of dipolar species. This observation is strong evidence for the polar nature of domains in this self-assembled material. Interestingly, the data show a slight hysteresis with a remnant polarization similar to that observed just after annealing the film without an applied field. This suggests that the polar order is stabilized in the self-assembled state, similar to what is observed in ferroelectric materials.[16] It is of course an open question whether these self-assembling systems indeed fall within the broader class of materials known as ferroelectrics. The fitted curves on the graph were calculated based on different models for dipoles in an applied field. One is a simplistic two-state model (solid curve), allowing only two antiparallel molecular orientations, and the other is a Langevin model (dotted curve) where dipoles orient with some average angle relative to the field orientation. The mathematical expression for the two-state model is given in Equation (5) where $x = \mu E/kT$, and for the Langevin model it is given in Equation (6).

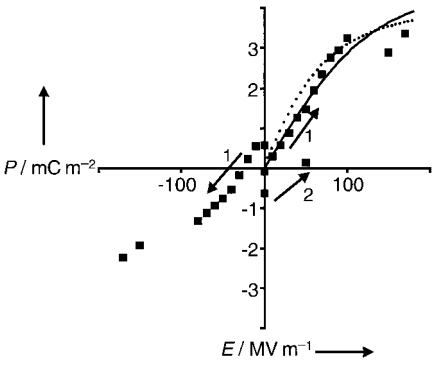

Figure 4. Plot of polarization versus electric field (■) showing a small hysteresis. The fitted curves correspond to a two-state model (solid curve) and a Langevin model (dotted curve). The arrows indicate the *E*-field path during cycle 1 and cycle 2.

$$P = \frac{N}{V}\mu \tanh x \tag{5}$$

$$P = \frac{N}{V}\mu \left(\coth x - \frac{1}{x}\right) \tag{6}$$

Given the error bars in Figure 2, it is clear that the error bars in Figure 4 are comparable to the size of the data points in this graph and therefore not visible. Neither of these models accurately describes the system but might provide upper and lower boundaries for estimating the dipole moments of the system's components. In fact, as revealed by the graph, the data do not precisely agree with either model but rather appear to have characteristics of both. Remarkably, both models yield an effective dipole which is larger than that of a single rodcoil molecule. The two-state model yields a μ_{eff} value of 8.5 D, while the Langevin model yields a μ_{eff} value of 33 D. Since the dipole of one molecule is roughly 4.2 D, both models suggest cooperative dipole interactions and thus imply that groups of molecules rather than single molecules realign in the applied field. The data suggest that at elevated temperatures supramolecular entities remain in the system. Our laboratory has obtained other evidence for this by showing that it is possible to thermally crosslink the interior of mushroom-shaped aggregates containing oligobutadiene segments without forming gels at temperatures as high as 250 °C.[17] This can only be possible if the reactive sites in supramolecular nanostructures are spatially isolated within one aggregate at such temperatures. We have also observed a small-angle X-ray peak that appears to correspond to the characteristic size of nanostructures at elevated temperature.[10] These observations and the data presented here would support the retention of supramolecular structure in the molten state.

Interestingly, a discrepancy is observed when a sample is poled in the opposite direction under the same conditions for the same amount of time. The piezoelectric constant of the reverse-poled sample is only 60 % of the value of the forward-poled sample. The reason for this difference can be attributed to the resistance of the material to reorganize at the substrate/material interface. As was mentioned earlier, the films formed by rodcoil molecules must order with the substrate during solvent casting and subsequent annealing. The reverse field might thus be forcing the mushroom-shaped nanostructures to reorder in a thermodynamically unfavorable orientation with respect to the substrate.

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We have shown here that supramolecular films composed of dipolar rodcoil molecules self-organize into polar macroscopic materials showing piezoelectric activity. Most importantly, the state with net polarization appears to have thermodynamic stability and to involve interactions between polar domains in the film and the substrate. Furthermore, our experiments strongly suggest that molecular aggregates present in these materials are important for the observed properties. This observation supports the concept that great potential exists in the supramolecular design of materials.

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Unusual Smectic Ordering of Unlocked Copper Bis-(terpyridine) Complexes**

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Supramolecular liquid crystals have now been engineered by way of hydrogen bonding, donor-acceptor interactions, or by cation complexation; the latter leading to the formation of metallomesogens.[1] Individual molecules within these organized networks act cooperatively to fulfill a useful function, such as thermochromism, ferroelectricity, nonlinear optical effects, or gelation. The anticipation that such structures might be used to construct molecular devices has been augmented by many examples of complex supramolecular architectures, such as discrete and infinite helices, hydrogen-bonded or π-π interacting networks, three-dimensional assemblies with defined channels, cucurbituril and similar molecules, highly symmetric coordination clusters, and organometallic polymers.[2] Increasing the extent of molecular ordering, however, to form organized macroscopic structures has proven difficult. Two important examples include silver complexes, constructed from polycatenar scaffolds, forming columnar liquid-crystalline mesophases,[3] and the description of the macroscopic ordering of a metallo-helicate (**B**).[4] It has also been shown that various pyridino-functionalized Schiff-base ligands coordinated to a tetrahedral copper(I) center assemble into columnar liquid-crystalline materials (**A**).[5] These latter structures, being rather rigid, appear to lack useful physical or catalytic properties.

We have sought to improve this situation by introducing more flexibility into the supermolecular structure but without detracting from its ability to assemble into organized networks. This delicate operation can be achieved by using a central core constructed from a terpyridine (terpy) ligand bearing two imino appendages equipped with phasmidic tails (long chains bound to the ends of a rodlike core). Complexation to copper(I) cations gives the first thermotropic terpy-based metallomesogens. Metallomesogens formed from tridentate ligands are rare, but lyotropic mesophases have been generated from ruthenium(II)-terpy complexes,[6] while the related terdentate (C,N,N) ligands cyclometalated to palladium(II) centers[7] are known to display a monotropic nematic phase.

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