reported at coarser range resolution than the DOW data: 75 m for the DOW, 250 m for KLTX. Furthermore, the DOW over-sampled azimuthally, calculating four beams per degree, whereas KLTX collected only one beam per degree. KLTX resolution was thus coarser than that of the DOW by a factor of 3.5 to 7. Because the roll wavelength was ~600 m with sub-roll peak wind speed regions with scales of ~100 m (Fig. 4), the rolls were less accurately characterized by KLTX and the peak wind intensity was underestimated. Peak-to-trough differences in wind speeds were near 10 m s⁻¹, only 30% of that observed by the DOW and lower than typical hurricane gust factors (16). An important consequence was that the KLTX data implied less severe peak low-level wind speeds than were observed at the ground or by the DOW (Fig. 6). Because the wind field sampled near KLTX had passed over ~40 km of land, some of the observed differences likely resulted from evolution of the near-surface wind field.

REFERENCES AND NOTES

4. ibid., p. 1287.
10. The DOW radar prototype described in (9) was upgraded to include a 2.44-m antenna, improved signal processing, and other hardware and software. The radar used a 40-kW transmitter operating at 9.375 GHz (21 cm). Pulses were 450 ns in duration, repeating every 500 μs, and sampled 500 times, resulting in range resolution of 75 m. The 2.44-m parabolic antenna produced a 0.95° beam, which spread to a width of 160 m at a range of 10 km from the radar. Radar beams were oversampled, resulting in 4 beams per degree.
11. This data collection mission was coordinated with the Hurricane Research Division (HRD) of the National Oceanic and Atmospheric Administration. F. Marks and S. Houston of HRD provided forecast guidance, other information, and coordination with the low-frequency weather forecast office in Wilmington, N.C. M. Biddle and C. Edwards, with J.W., crewed the DOW radar.
12. The Wilmington Weather Service Forecast Office provided real-time forecasting guidance and logistical support during the data collection. New Hanover International Airport provided the data site, logistics, and safety coordination during data collection. The tower was later removed from sources of airborne debris, particularly trees, tree limbs, and portions of damaged buildings. The tree line was generally 400 to 1000 m distant and blocked only the lowest radar beams, which were less than 1° above the horizon. The airport terminal building caused blockage up to several degrees above the horizon in the southern sector. Wetting of the antenna cover caused severe attenuation of both transmitted and received radiation, reducing sensitivity by 10 to 20 dB during periods of intense rainfall. Reflectivity and Doppler velocity data were collected in eight conical scans with inclinations ranging from 0° to 30° above the horizon, repeating every 300 s, to sample the volume of space surrounding the radar.
14. S. Houston, M. Powell, P. Dodge, ibid., p. 92.

Switching Supramolecular Polymeric Materials with Multiple Length Scales

J. Ruokolainen, R. Mäkinen, M. Torkkeli, T. Mäkelä, R. Serimaa, G. ten Brinke,* O. Ikkala*

It was demonstrated that polymeric supramolecular nanostructures with several length scales allow straightforward tailoring of hierarchical order-disorder and order-order transitions and the concurrent switching of functional properties. Poly(4-vinyl pyridine) (P4VP) was stoichiometrically protonated with methane sulfonic acid (MSA) to form P4VP/MSA,⁺, which was then hydrogen-bonded to pentadecyphenol. Microphase separation, re-entrant closed-loop macrophase separation, and high-temperature macrophase separation were observed. When MSA and pentadecyphenol were complexed to the P4VP block of a microphase-separated diblock copolymer poly(styrene-block-(4-vinyl pyridine)), self-organized structures-in-structures were obtained whose hierarchical phase transitions can be controlled systematically. This microstructural control on two different length scales (in the present case, at 48 and 350 angstroms) was then used to introduce temperature-dependent transitions in electrical conductivity.

During the past decade, methods to prepare nanosized structures have progressed greatly, stimulated by the continuing demand for miniaturization of devices and electronic components. Polymers offer a means to construct ordered nanoscale domains through self-organization, on the basis of competing interactions (1-7). Perhaps the most studied example is provided by block copolymers, where the repulsion between the chemically connected blocks leads to self-organization into lamellar, cylindrical, spherical, and other structures with length scales on the order of 100 to 1000 Å (1). Even more complicated structures have been created with block copolymers containing rigid moieties (4, 8). Recently, another concept to achieve mesomorphic structures at much smaller length scales (typically 30 to 40 Å) has been presented in which nonmesogenic amphiphilic oligomers are noncovalently bonded to homopolymers (5, 6, 9). In the case of hydrogen bonding between amphiphilic oligomers such as pentadecyphenol (PDP) and homopolymers such as P4VP, the competition between attraction and repulsion leads to a microphase-separated (often lamellar) morphology at low temperatures (6, 10, 11). Heating yields an order-disorder transition to a disordered phase (10, 11).

Here, we show that the two above-mentioned ordering principles can be combined with the use of diblock copolymers consisting of a coil-like block and a block consisting of a supramolecular polymer-amphiphile complex, allowing microstructural control on two length scales. The hierarchi-
cal nanostructures were imaged, and it is shown that functionalization of one block results in transitions in electrical conductivity that can be explained by dimensionality transitions.

P4VP was first protonated with methane sulfonic acid (MSA). Fourier transform infrared measurements (FTIR) indicate (12) that a nominally complete protonation was achieved once the number of MSA molecules equaled or exceeded the number of pyridine groups. The resulting polystyrene, denoted here as P4VP(PIIPAa)1.0, was then mixed with PDP, which forms hydrogen bonds to the sulfonate group. Because of the large absorption bandwidth of the sulfonate bonds to the sulfonate group, FTIR does not easily lend itself to calculation of hydrogen bonding strength. However, calculations of hydrogen-bonding strength (13) suggest that the hydrogen bonding between the phenolic hydroxyl group and the sulfonate group of MSA becomes energetically feasible once a proton has been transferred from MSA to P4VP. Thus, the expected supramolecular structure combines proton transfer and hydrogen bonding (Scheme 1). Alternatively, one PDP molecule is used for each sulfonate group, but the actual number of PDP molecules that are hydrogen bonded remains uncertain at present.

Scheme 1.

Optical microscopy shows a complex phase behavior for P4VP(PIIPAa)1.0(PDP)1.0 consisting of optically anisotropic, transparent, and cloudy phases (Fig. 1). To identify the phases, we conducted small-angle x-ray measurements (SAXS) as a function of temperature, using methods described elsewhere (11). Below 100°C, a distinct and relatively narrow SAXS peak at the scattering vector \( q_1 \approx 0.13 \text{ Å}^{-1} \) was observed, corresponding to a lamellar structure with a long period of \( L_0 \approx 48 \text{ Å} \) (14). Above 100°C, a steplike increase in the half-width of this Bragg reflection was observed. In close analogy with conventional block copolymers (15), a broad correlation hole peak remained visible, which upon further heating gradually decreased and shifted to a smaller angle, as a result of the reduction in the number of hydrogen bonds. Near 175°C, a strong forward scattering peak appeared, signaling macrophase separation. The intensity of this peak diminished again above 200°C. The phase separation at ~220°C could not be identified in the SAXS data.

Hence, supramolecular P4VP(PIIPAa)1.0(PDP)1.0 structures show mesomorphic order at a short length scale \( L_0 \) as well as a sequence of phase transitions. In a next step, we confined this system inside another nanostructure with a longer length scale \( L_0 \) by using diblock copolymers in which the P4VP chains form the minority blocks of microphase-separating diblock copolymers of polystyrene (PS) and P4VP, PS-block-P4VP.

The number-averaged molecular masses of the P4VP and PS blocks were selected to be 5600 and 40,000 daltons, respectively, resulting in a spherical morphology for the uncomplexed PS-block-P4VP system, as confirmed by SAXS and transmission electron microscopy (TEM) (16). This finding is in perfect agreement with the volume fraction of the P4VP blocks, \( f = 0.12 \). Classically, an increase of \( f \) yields a transition to the cylindrical \( (f = 0.16) \) and lamellar \( (f = 0.32) \) phases (17), MSA and PDP acting as selective solvents for the P4VP domains, and the complexation of MSA and PDP to the pyridine blocks introduces a simple way to control the phase morphology because the volume fraction of the P4VP-containing domains can be controlled effectively. In this way, supramolecular structures combining hydrogen bonding, proton transfer, and hydrogen bonding were obtained (Scheme 1).

Judicious selection of the block lengths \( (n \) and \( m \), the length of the phenolic alkyl group, and also the sulfonic acid thus allows a detailed tailoring of hierarchical self-organized structures, as will subsequently be discussed in one particular case.

The SAXS data (Fig. 2) for PS-block-P4VP(PIIPAa)1.0(PDP)1.0 as a function of temperature show three regimes:

1) Below ~100°C (Figs. 2 and 3A), the P4VP(PIIPAa)1.0(PDP)1.0 and PS blocks formed alternating layers with a long period \( L_0 \approx 350 \text{ Å} \). A lamellar morphology could be expected because the volume of P4VP(PIIPAa)1.0(PDP)1.0 divided by the two...
ordered P4VP(MSA)1.0(PDP)1.0 layers were further microphase separated into another lamellar structure with a long period $L_c \approx 48 \text{ Å}$. In a separate study involving a closely related system of PS-block-P4VP fully complexed with nonadecylphenol, which has a longer alkyl tail than PDP, we were able to resolve these mutually perpendicular lamellar structures by TEM (Fig. 4).

2) Between 100° and 150°C (Figs. 2 and 3B), the P4VP(MSA)1.0(PDP)1.0 and PS blocks continued to form a lamellar structure, but the second layered structure had disappeared. Therefore, an order-disorder transition within the polymer-amphiphile complex layers took place at 100°C.

3) Above ~150°C (Figs. 2 and 3C), the disordered P4VP(MSA)1.0(PDP)1.0 (x \ll 1) domains formed hexagonal cylindrical lamellae with a long period $L_c = 550 \text{ Å}$. It is slightly larger than in the other samples of this work because of the higher molecular mass of this particular sample. The number-averaged molecular masses of the P4VP and PS blocks were 49,500 and 238,000 daltons, respectively. Thus, it is demonstrated that the control of the microstructure allows a means to control the macroscopic conductivity. Drastically larger anisotropic effects ac-

The local structures are indicated; macroscopically, the samples are isotropic. (A) Alternating PS layers and layers consisting of alternating one-dimensional slabs of P4VP(MSA)1.0 and PDP for $T < T_{ODT}$ (14). (B) Alternating two-dimensional PS and disordered P4VP(MSA)1.0(PDP)1.0 lamellae for $T_{ODT} < T < T_{OOT}$. (C) One-dimensional disordered P4VP(MSA)1.0(PDP)1.0 (with $x \ll 1$) cylinders within the three-dimensional PS-PDP medium for $T > T_{OOT}$.

Fig. 3. Schematic illustration of the self-organized structures of PS-block-P4VP(MSA)1.0(PDP)1.0. The local structures are indicated; macroscopically, the samples are isotropic. (A) Alternating PS layers and layers consisting of alternating one-dimensional slabs of P4VP(MSA)1.0 and PDP for $T < T_{ODT}$ (14). (B) Alternating two-dimensional PS and disordered P4VP(MSA)1.0(PDP)1.0 lamellae for $T_{ODT} < T < T_{OOT}$. (C) One-dimensional disordered P4VP(MSA)1.0(PDP)1.0 (with $x \ll 1$) cylinders within the three-dimensional PS-PDP medium for $T > T_{OOT}$.

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Fig. 4. Transmission electron micrograph of PS-block-P4VP(NPD)1.0, where nominally one nonadecylphenyl (NPD) has been hydrogen bonded with each pyridine group. The long period of the alternating PS (light grey) and P4VP(NPD)1.0 (dark grey) lamellae equals $L_c \approx 550 \text{ Å}$. It is slightly larger than in the other samples of this work because of the higher molecular mass of this particular sample. The number-averaged molecular masses of the P4VP and PS blocks were 49,500 and 238,000 daltons, respectively. Thus, it is demonstrated that the control of the microstructure allows a means to control the macroscopic conductivity. Drastically larger anisotropic effects ac-

No effort was made to orient the microscopic sample. The number-averaged molecular masses of the P4VP and PS blocks were 49,500 and 238,000 daltons, respectively. Thus, it is demonstrated that the control of the microstructure allows a means to control the macroscopic conductivity. Drastically larger anisotropic effects ac-

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Fig. 4. Transmission electron micrograph of PS-block-P4VP(NPD)1.0, where nominally one nonadecylphenyl (NPD) has been hydrogen bonded with each pyridine group. The long period of the alternating PS (light grey) and P4VP(NPD)1.0 (dark grey) lamellae equals $L_c \approx 550 \text{ Å}$. It is slightly larger than in the other samples of this work because of the higher molecular mass of this particular sample. The number-averaged molecular masses of the P4VP and PS blocks were 49,500 and 238,000 daltons, respectively. Thus, it is demonstrated that the control of the microstructure allows a means to control the macroscopic conductivity. Drastically larger anisotropic effects ac-

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Fig. 5. Electrical conductivity $\sigma$ during heating at 5°C/min, on the basis of ac impedance measurements extrapolated to zero frequency. Similar data are observed during cooling. PS-block-P4VP(MSA)1.0 showing the classical thermally activated conductivity. PS-block-P4VP(MSA)1.0 showing thermally activated behavior up to ~160°C, at which the first signals of imminent macrophase separation appear. Further increase in temperature results in a decrease in $\sigma$. The conductivity starts to increase again above ~195°C. PS-block-P4VP(MSA)1.0 showing the classical thermally activated conductivity. PS-block-P4VP(MSA)1.0 showing thermally activated behavior up to ~160°C, at which the first signals of imminent macrophase separation appear. Further increase in temperature results in a decrease in $\sigma$. The conductivity starts to increase again above ~195°C.
competing the dimensionality transitions are expected, eventually approaching on-off switching, once efforts are taken to orientate the nanostructures.

The implications of the present work on nanotechnology seem manifold. The present methods to construct zero-, one-, and two-dimensional nanostructures suggest controllable nanostructures in conjugated electronically conducting polymers. P4VP is a semiconducting side-chain–conjugated polymer. In this case, conductivity appears to proceed through a protonic mechanism (19); this mechanism is not a serious limitation to the generality of the concepts, which are based on a control of the morphology. Chemically, P4VP resembles in several ways main-chain–conjugated polymers such as polyaniline, poly(p-phenylene), poly(p-phenylene vinylene) (20, 21), and possibly even polyprrole. These materials are inherently difficult to process because of their rigidity. However, in polyaniline, for example, methods have been demonstrated to introduce processibility by the use of amphiphilic dopants (22) or amphiphilic oligomers capable of molecular recognition with the polyaniline chain (23). Such concepts easily provide the short length scale discussed above.

REFERENCES AND NOTES

12. The ioninc bonding of pSA to P4VP can be monitored by the use of the characteristic FTIR absorption band at 1637 cm\(^{-1}\) of the quaternized pyridine ring as compared with the corresponding free pyridine ring at 1597 cm\(^{-1}\) [J. Ruokolainen et al., Macromolecules 29, 6621 (1996)].
14. The two levels of structure are distinguished by their subscripts. For example, the long period for the semiconducting polymer-amphiphile structure is denoted as \(L_s\) and the long period for the block copolymer length scale as \(L_p\). Similarly, the order-disorder transition for the polymer-amphiphile complex is denoted as \(ODT_s\) and the order-disorder transition in block copolymer length scale as \(ODT_p\).
19. The motivation to protonate side-chain–conjugated P4VP by MSA originates from previous studies: The main chain–conjugated polyaniline can be doped to yield electronic conductivity by protonating the imine nitrogens with stoichiometric amounts of strong acids (J.-C. Chiang and A. G. MacDiarmid, Synth. Met. 13, 193 (1986)). The amine of polyethylene can be protonated by stoichiometric amounts of sulfuric or phosphoric acid to yield protonic conductivity (18).
26. We thank E. L. Thomas for collaboration in electron microscopy at the early stage of this work and M. Saariaho, J. Tanner, and H. Isotalo for experimental assistance and discussions. The Institute of Technology/Electron Microscopy Unit is acknowledged for the privilege of using their facilities. Supported by the Finnish Academy, Technology Development Centre (Finland), and Nestle Foundation.

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Platinum Catalysts for the High-Yield Oxidation of Methane to a Methanol Derivative

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Platinum catalysts are reported for the direct, low-temperature, oxidative conversion of methane to a methanol derivative at greater than 70 percent one-pass yield based on methane. The catalysts are platinum complexes derived from the biacizene ligand family that are stable, active, and selective for the oxidation of a carbon-hydrogen bond of methane to produce methyl esters. Mechanistic studies show that platinum(II) is the most active oxidation state of platinum for reaction with methane, and are consistent with reaction proceeding through carbon-hydrogen bond activation of methane to generate a platinum–methyl intermediate that is oxidized to generate the methyl ester product.

More efficient methods for the oxidation of low-value, light alkane feedstocks, such as natural gas, to the corresponding alcohols or other useful liquid products would accelerate the use of natural gas feedstocks as a complement to petroleum. Current technologies for the conversion of natural gas to liquid products proceed by generation of carbon monoxide and hydrogen (syn-gas) that is then converted to higher products through Fischer-Tropsch chemistry (1).

The initial formation of syn-gas in these processes is energy intensive and proceeds at high temperatures, typically 550°C. In contrast, direct methods partially oxidize the alkane molecule, functionalizing one C–H bond, and in principle can proceed more efficiently and cost-effectively through lower temperature routes.

Given the potential for high payoff, the goal of direct, selective alkane oxidation has been the focus of substantial effort since the 1970s (2, 3). Despite these extensive efforts, very few selective alkane oxidation processes are known. Except in a few special cases (4), the basic chemistry for the selective, low-temperature, direct, oxidative conversion of alkane C–H bonds to useful functional groups in high one-pass yield (5) has not yet been developed. Such development is challenging, because alkane C–H bonds are among the least reactive known and the desired products of oxidation are typically more reactive than the starting alkanes and are consumed before recovery. Consequently, only uneconomically low one-pass yields can be obtained with direct alkane oxidation chemistries available today without prohibitively expensive separations and recycle.

We developed a catalytic system for the direct, low-temperature, selective oxidation of methane to generate an ester of methanol in 72% one-pass yield at 81% selectivity based on methane (5). Recently, we reported the selective oxidation of methane to an ester of methanol in ~43% one-pass yield catalyzed by mercuric salts (6). We now show that selected Pt complexes are more effective catalysts for this reaction. These Pt complexes are stable and selectively activate (7) and oxidize a C–H bond of methane at temperatures as low as 100°C to generate a methyl ester product that is chemically “protected” from overoxidation.