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Lamellar Conjugated Polymers by Electrochemical Polymerization of Heteroarene-Containing Surfactants: Potassium 3-(3-Alkylpyrrol-1-yl)propanesulfonates

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A series of self-assembling monomers, potassium 3-(3-alkylpyrrol-1-yl)propanesulfonates, are electrooxidatively polymerized from micellar solution to afford lamellar phases of the substituted polypyrrole. The kinetics of electrochemical oxidation are quite sensitive to the concentration of the surfactant monomer and display the effects of solvent-induced molecular self-assembly. The films were characterized by low–angle X-ray diffraction, glancing angle infrared spectroscopy and X-ray photoelectron spectroscopy. The lamellar phase consists of a head-to-head packing of the surfactant repeat units. Consequently, the crystal repeat distance corresponds to approximately twice the extended length of the monomer. Infrared measurements indicate that lower homologs are conformationally less ordered, in accord with the observation that they also give rise to broadened X-ray diffraction lines, reflecting less positional order. The as-grown films are resistive ($<10^{-6}\ \Omega^{-1}\ cm^{-1}$). Upon treatment with aqueous $HClO_4$ the conductivity along the film is enhanced ($10^{-3}\ \Omega^{-1}\ cm^{-1}$) imparting anisotropic conductivity which is consistent with the lamellar structure.

Introduction

One of the underlying themes of recent research in the area of organic materials has been the use of self-assembly to form ordered arrays of functional molecules.[1] An area where this has attracted considerable attention, with some success, is that of inherently conductive polymers. The great potential of electronically conductive polymers as components in optical displays, sensors, rechargable batteries, membranes, electromagnetic interference shielding, nonlinear optics, and microelectronics is well recognized.[2] However, at present the intractibility[3] of these materials impedes their widespread employment[4] in these applications. Control of both microscopic and macroscopic structural homogeneity is desirable in the development of materials with enhanced electronic, optical, and magnetic properties. For example, although polymer morphology, crystallinity, and microstructure play important roles in electron transport and mechanical properties of conductive polymers, the relationships between these parameters have yet to be thoroughly elucidated. Small structural alterations often afford large changes in material properties that cannot necessarily be attributed to simple electronic or steric interactions. Recent developments in the synthesis of microscopically regular polymers (i.e., regiopure polyalkylthiophenes,[5] well-defined fused aromatic ladder polymers[6]) allow the realization of materials with enhanced optical and electronic properties which have been ascribed, in part, to an increase in macroscopic order.

The degree of crystallinity is an important factor in the conductivity of polyacetylene, and recent advances in synthesis and processing have led to the preparation of highly conductive materials.[7] This dependence arises from the increased degree of π-orbital overlap along the polymer chain, and the resulting decrease in the bandgap[8] (although a low bandgap alone is not sufficient for high conductivities[9]). Theoretical treatments clearly show that coplanarity of p orbitals along the chain should lead to enhanced optical properties[10] and conductivity.[11] The control or design or morphologies in other conducting polymers is largely unexplored. Diffraction studies are difficult to perform because large single crystals do not readily form. Chemically prepared polymers often show some order after annealing, and unit cells can be determined. Electrochemically deposited polymers are typically amorphous.[12]

Controlling the polymer chain packing of poly(arylenes) promises the possibility of (i) increasing the conjugation length along the backbone and (ii) imparting orientation

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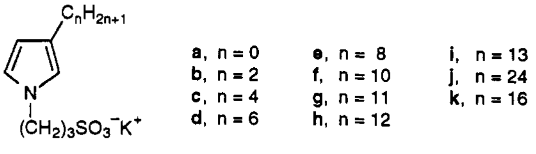
to the polymer. The first effect will increase charge carrier density and mobility. The decrease in conductivity of the polymers of *N*-alkylated pyrroles has been attributed to steric interactions between substituents on neighboring repeat units which prevent coplanarity of the rings and thus disrupt conjugation along the polymer chain.[13] An alkyl chain at the 3-position is sterically less demanding and accordingly affects the conductivity less.[14] Similarly, the twisting effect of alkyl substituents is smaller on a polythiophene backbone.[15] Orientation of polymer chains decreases the number of interchain hops required for long range charge transfer[16] and further reduces the bulk resistivity of the sample along the orientation axis. This is commonly realized by stretch orientation which leads to anisotropic conduction with enhanced conductivity along the stretch axis.[17]

Recently, the formation of layered heterostructures of conjugated polymers by sequential deposition of a substrate in solutions of polyanionic and polycationic polymers has been described.[18] Previous attempts to explore the effect of self-assembling monomers on conductive polymer morphology have concentrated on the study of Langmuir-Blodgett films. Two general approaches to layered conductive polymers by deposition of Langmuir–Blodgett films have been reported. A number of heterocycle-containing amphiphiles have been prepared which are deposited as Langmuir monolayers at an air–water interface and transferred to solid substrates. Polymerization is performed either before[19,20a] or after transfer.[20] The second approach entails dissolution of a soluble conductive polymer (i.e., a poly(3-alkylthiophene)) in an inert supporting Langmuir monolayer (i.e., arachadonic acid) followed by transfer.[21] These two methods require carefully controlled conditions for monolayer formation and transfer and afford only limited amounts of material for further use. These factors negate a number of experimental techniques which would provide valuable information about such lamellar phases, and impede use of thick or nonplanar films of these materials.

Use of alkylsulfonate surfactant electrolytes for the deposition of polypyrrole gives materials with low degrees of supermolecular order.[22] It was postulated that the bulky surfactant anions in the doped polymers act as spacers between layers of conductive polymer backbone. However, the correlation length of these ordered polymers is short, as shown by the breadth of low-angle X-ray diffraction lines. Use of surfactants as electrolytes for electrochemical polymerization of pyrrole results in polymers which have particularly good material properties (in particular flexibility), conductivity, and stability.[23] Other approaches to control the spatial arrangement of polymer chains include preparation of conductive polymers in inorganic solids,[24] zeolites,[25] and ion-exchange polymers.[26] Self-assembled monolayers of monomers are also being studied to form aligned polymers.[27]

The directed synthesis of macroscopically ordered materials through molecular design serves to bridge the gap in understanding the relationship between various levels of structural features. By specifically inducing large changes in supramolecular packing by variation of molecular structure, changes in bulk properties might be attributed primarily to macroscopic features. This relies on the choice of well-defined macroscopic systems which are easily accessible.

We have previously reported that polymerization of monomer **1h** from micellar solutions affords a highly ordered lamellar phase of poly**1h**.[28] To gain a further understanding of the factors affecting supermolecular packing in polymers consisting of extended π-conjugated backbones, we now report the behavior of the series of homologs **1a–k**.



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Results and Discussion

Monomer Design and Synthesis. 3-(3-Alkylpyrrol-1-yl)propanesulfonates **1** possess amphiphilic character by virtue of the hydrophobic alkyl chain and hydrophilic ionic sulfonate head group. Others have shown that 3-alkylpyrroles are soluble in organic solvents[14] and that potassium 3-(pyrrol-1-yl)propanesulfonate is water soluble.[29] The resulting polymers retain this solubility.

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Other sulfonated polyheteroarenes are also water soluble.[30] Interest in these materials derives, in part, from the ionic change balance (compensation) provided by the anionic group. Monomers 1 are readily accessible. *N*-Tosylpyrrole was prepared by reaction of tosyl chloride with pyrrole under basic phase-transfer catalytic conditions.[31] Although the synthesis of this compound has been reported using potassium as a base to stoichiometrically deprotonate pyrrole,[32] we have found that the phase-transfer-catalyzed reaction is much more convenient to run on a several-hundred-gram scale. Friedel–Crafts acylation gave the crude *N*-tosyl-3-alkanoylpyrroles which were treated with aqueous sodium hydroxide to hydrolyze the sulfonamide.[33] The resulting 3-ketopyrroles were reduced with sodium bis(methoxyethoxy)aluminum hydride (RedAl, Aldrich Chemical Co.), although lithium aluminum hydride is also appropriate.[14] The corresponding alkylpyrrole was treated with potassium or potassium hexamethyldisilazide to afford a solution of the potassium salt, which upon treatment with 1,3-propanesultone[29] gave the corresponding potassium 3-(3-alkylpyrrol-1-yl)propanesulfonates 1. We could not avoid formation of potassium 3-hydroxypropanesulfonate, $HO(CH_2)_3SO_3K$, in the last step by hydrolysis of 1,3-propane sultone. Although addition of ether to the reaction mixture precipitated crude 1 in high yield (>80% yield, >90% pure), repeated recrystallization from ethanol–water afforded much lower yields of the pure monomer. The purified sulfonates 1 gave satisfactory proton magnetic resonance and infrared spectra, and elemental analysis.

Solubility and Assembly. The unsubstituted parent compound (**1a**) and short homologs of 1 are soluble in water and aqueous solutions of electrolyte. The 3-hexadecyl homolog **1k** is insoluble in water.[28] Compounds with intermediate alkyl chain lengths (**1d-j**, n = 6–14) form micellar solutions. Critical micelle concentrations (cmc) were determined colorimetrically using pinacyanol chloride.[34] A solution of this dye appears pink in the presence of surfactant above the cmc, and blue in solutions of surfactants below their cmc. Critical micellar concentrations are listed in Table 1. As expected, the cmc decreases with increased alkyl chain length (n) as the hydrophobicity of the amphiphile increases. The cmc is further depressed by addition of the electrolyte necessary for electrochemical polymerization. For example, the values of cmc for **1f** and **1h** are decreased to 1×10^{-4} and 2×10^{-5} M, respectively, in 0.1 M KNO_3. All of the electrooxidative polymerization experiments were conducted well above the cmc (in the 1–10 mM range).

Table 1. Critical Micellar Concentrations (cmc) of 1 and Interlayer Spacing (*c*) of Poly1

1	n	cmc/M[a]	c/Å[b]
a	0	∞[c]	*d*
b	2	∞[c]	*d*
c	4	$>5 \times 10^{-2}$	*d*
d	6	2×10^{-2}	25.3[e]
e	8	1×10^{-3}	30.9
f	10	8×10^{-4}	36.5
g	11	1.5×10^{-4}	38.9
h	12	1×10^{-4}	40.8
i	13	7×10^{-5}	42.7
j	14	5.5×10^{-5}	45.7
k	16	*f*	
h, M = H[g]	12		37.9
h, M = Li[g]	12		39.9

[a] ±20% in H_2O; determined colorimetrically according to method of Corrin et al.; see Experimental Section. [b] ±0.3 Å; polymer deposited potentiostatically from a 10 mM solution of 1, in 0.1 M KNO_3. [c] Soluble in H_2O (cmc > 0.1 M). [d] Soluble in H_2O, not deposited as thin film. [e] Deposited from 1.0 M aqueous KNO_3. [f] Insoluble in H_2O. [g] **1h** polymerized from 0.1 M $MClO_4$.

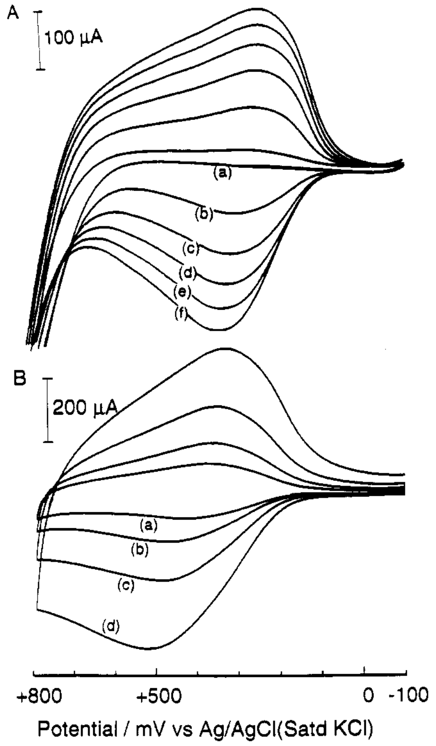

Figure 1. Cyclic voltammograms of poly**1h**. A, polymerization of **1h** (10 mM **1h** in 0.1 M aqueous KNO_3, 100 mV s^{-1}): deposition cycle (a) 5, (b) 10, (c) 15, (d) 20, (e) 25, (f) 30. B, reversible redox wave of poly**1h** (prepared by procedure in Figure 1A) in 0.1 M aqueous KNO_3 at (a) 25, (b) 50, (c) 100, and (d) 200 mV s^{-1}.

Electrochemistry. Thin layers of polymer were deposited by cyclic voltammetry on gold electrodes with a positive switching potential of +840 mV (all potentials are referenced to Ag/AgCl (saturated KCl)). The wave corresponding to reversible redox of the deposited polypyrrole at ca. +250 mV grew during repeated potential cycling (Figure 1A). Electrodes bearing thin layers of polymer give relatively sharp polymer redox waves. Thicker layers give broader responses, typical for a process in which diffusion of the charge compensating ion becomes rate limiting for redox switching. In these anionic (sulfonate) polymers charge balance is presumably provided by cation (K^+) migration. When polymers were polymerized potentiostatically and subject to cyclic voltammetry, only ca. 20% of the deposition charge was apparent in the reversible wave corresponding to redox switching of the polypyrrole backbone. Assuming a two-electron oxidative polymerization mechanism, this implies that the polymer is 10% doped, corresponding to one cationic charge for each 10 pyrrole repeat units. The wave corresponding to

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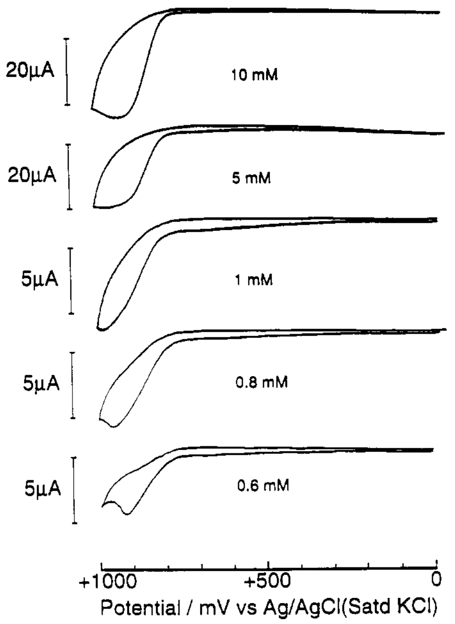

Figure 2. Effect of concentration of monomer on the appearance of cyclic voltammograms. First cycle of cyclic voltammograms of **1e** in 0.1 M aqueous KNO_3 at 10, 5, 1, 0.8, and 0.6 mM at 50 mV s^{-1} on gold (area = 3.14 mm^2).

the redox of the polymer layer persisted after transfer of the electrode to a monomer-free solution of electrolyte (Figure 1B). Proceeding to higher potentials led to a loss of electrochemical response due to overoxidation of the polymer.

Self-assembling monomers **1e–j** were polymerized at lower concentrations than can be used for efficient film growth of pyrrole or 3-alkylpyrroles (typically pyrrole is polymerized from >25 mM aqueous[35] or organic solutions[36]). We failed to electrooxidatively polymerize pyrrole from a 10 mM aqueous solution (0.1 M KNO_3). Attempts to electrooxidatively deposit polymers from solutions containing monomers below their cmc failed. Radical cation coupling is a slow process, which relies on the presence of a relatively high concentration of reactive species. At lower concentrations, the radical cations of monomers and oligomers diffuse from the electrode without precipitation. When monomers are present above their cmc, there is a high local concentration in the assembly at the electrode surface resulting in efficient polymer deposition.

The rate of polymerization of self-assembling homologs of 1 is quite insensitive to the concentration of monomer above the cmc. The cyclic voltammograms of monomers **1d–j** display features that can be qualitatively attributed to molecular assembly (Figure 2). In general, when monomer is present in solution above the cmc, the cyclic voltammetric oxidation waves are sharper and occur at lower peak potentials than the case of lower concentrations of monomer. We assign these features to the surface activity of the monomers. Above the cmc, the voltammetric wave is a consequence of oxidation of the adsorbed, surface-confined monomer. Diffusion of additional monomer from solution to replenish the concentration at the interface is slow. As polymerization proceeds, further monomer is adsorbed such that an admicelle or multilayer is maintained on the growing film of conductive polymer. Film growth proceeds by polymerization of monomers in this assembly. Below the cmc, the monomer is not adsorbed at the interface and the voltammetric wave is dominated by diffusional processes. A plot of anodic peak current versus monomer concentration for **1e** (Figure 3A) takes the form of two straight lines intersecting at a concentration approximately equal to the cmc. The slope of the curve below the cmc is greater than that above the cmc, indicating the change in kinetics for polymerization. This pattern of behavior is not observed in the case of monomers which do not self-assemble (at least over appropriate concentration ranges). A plot of peak current versus monomer concentration for monomer **1a** affords a straight line over a large concentration range (Figure 3B). Lower homologs, with high cmc (i.e., **1a–c**), undergo anodic oxidation but the polymer is not deposited on the electrode surface. This is presumably due either to lack of radical ion coupling or to the solubility of the polymers in water. Oxidation of **1a** in acetonitrile solutions affords a thin insulating film of the polymer on the first oxidative potential sweep, which results in passivation of the electrode.[28]

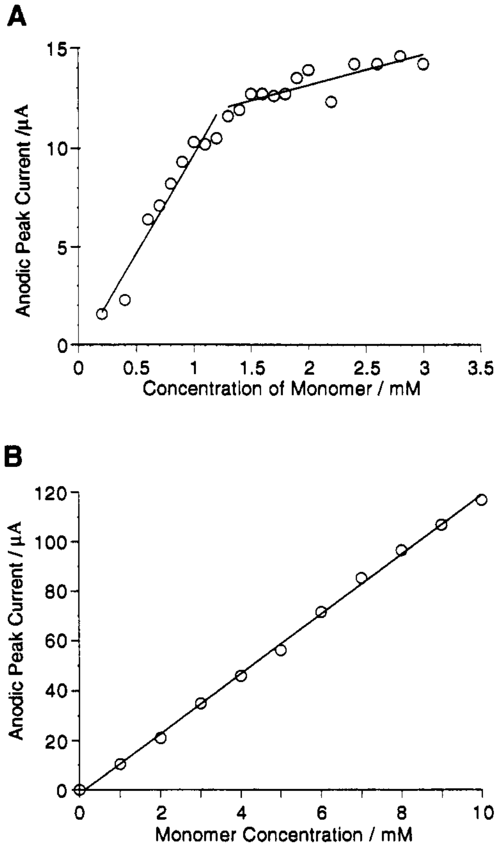

Figure 3. Plot of anodic peak current versus concentration of monomer: A, octyl homolog **1e**, currents recorded from voltammograms in Figure 2; B, unsubstituted monomer **1a**. Cyclic voltammetric peak currents obtained for first positive scan at 50 mV s^{-1} on a polished gold electrode.

Under conditions where higher homologs are successfully polymerized, the hexyl homolog, **1d**, gives brittle polymer films which flake from the electrode surface as a fine powder which could not be recovered for X-ray diffraction. However, a more robust polymer was deposited upon increasing the electrolyte concentration to 1.0 M.

Polymer Film Structure. Thick layers of poly1 were deposited by potentiostatic polymerization at +700 mV

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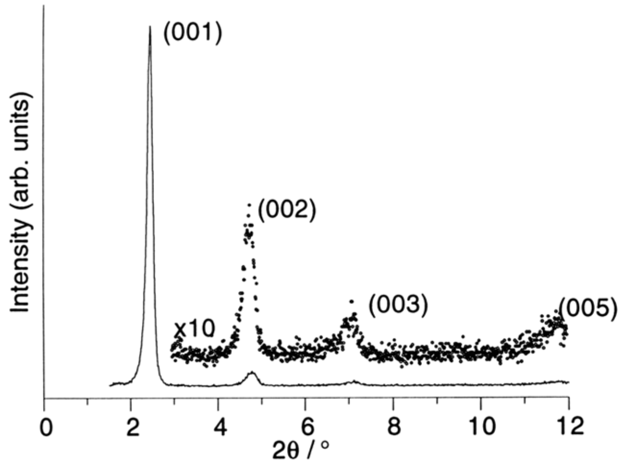

Figure 4. X-ray diffraction pattern of poly**1f** (ca. 0.3 C cm^{-2} on Au).

in gently stirred reaction mixtures. Electropolymerization affords polymers in their doped states. They were rinsed gently under a stream of water, and allowed to dry slowly in air. Attempts to dry the films quickly under reduced pressure, or by immersion in methanol, ethanol or acetonitrile resulted in cracking and peeling. The resulting dry, smooth films were further dried in a vacuum desiccator. Typically 0.5 C cm^{-2} of charge was passed to deposit thick films, affording layers approximately 7–10 μm thick. Profilometry measurements on films of poly**1h** gives the rate of film growth as approximately 15 $\mu m/(C\ cm^{-2})$. Since each molecule extends approximately 21 Å in a layer (i.e., the interlayer spacing from X-ray diffraction, see later), the area per molecule is approximately 25 $Å^2$.

The monomers **1** display three pyrrole C–H out-of-plane bending vibrations in the 700–800-cm^{-1} range of the infrared spectrum. After electrooxidative deposition the vibrations at 680 and 645 cm^{-1} are greatly diminished as the 2- and 5-positions of the ring are incorporated into the polymer backbone.

X-ray photoelectron spectroscopy was used to determine the composition of the thin films. The ratio of signal intensities for **1h** correspond to the predicted elemental composition of the polymer (±2%).[28] XPS indicated the absence of nitrate from the polymerization solution in the polymer. The thin films are electrochromic, undergoing a reversible transition upon oxidation from pale green (λ_{max} <350 nm) to red. The intrinsic bandgap, from the π–π^* transition in the UV–vis spectrum, is approximately 3 eV. Upon oxidation two new transitions appear below the bandgap at λ_{max} = 470 nm, and a broad onset to a peak at approximately 820 nm.

X-ray diffraction of these films gives rise to four or five diffraction lines in the range of 2θ = 2–15°, e.g., Figure 4. These lines can be assigned Miller indices (*hkl*) of (001), (002), (003), and (005). The lines for odd values of *l* are more intense than those with even values, in accord with observations on Langmuir–Blodgett multilayers.[37] Consequently, the (004) reflection is so weak that it is not always observed. Interlamellar spacings for poly**1d–j** are given in Table 1. Smaller peak widths and higher relative intensities of the higher order reflections were observed for higher homologs, indicating an increase in the relative order (or correlation length) of these phases. The (001) diffraction lines of poly**1d**, **e**, **f**, and **h** are shown in Figure 5.

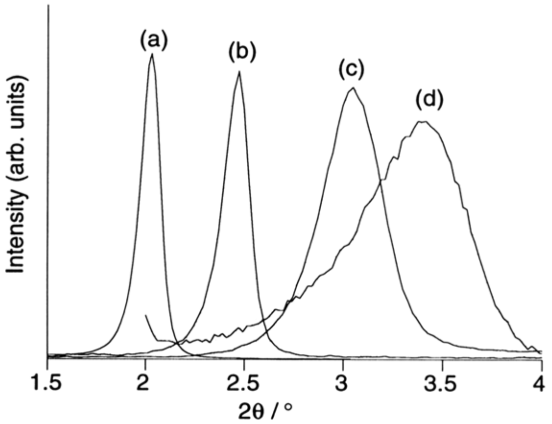

Figure 5. X-ray diffraction patterns for: (a) poly**1d**, (b) poly**1e**, (c) poly**1f**, and (d) poly**h1h**. Only the (001) peak is shown. The *y* axis is X-ray intensity in arbitrary units, and the peak heights do not represent the observed relative intensities.

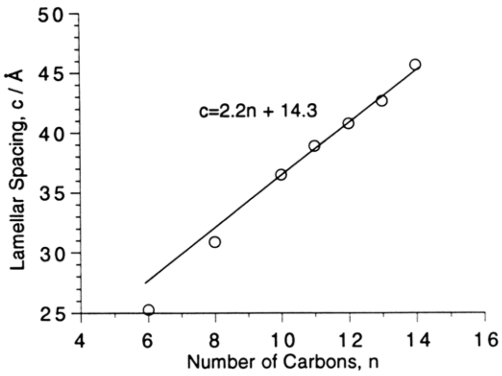

Figure 6. Plot of interlamellar unit cell spacing of poly(potassium 3-(3-alkylpyrrol-1-yl)propanesulfonate)s, poly**1**, versus the number of carbons in the 3-alkyl substituent.

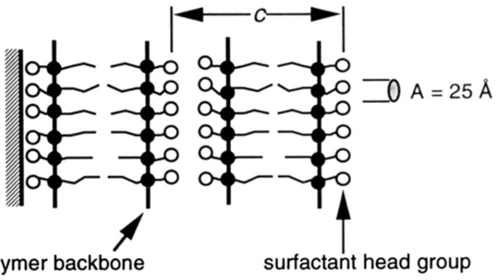

Figure 7. Schematic for lamellar phase of poly**1** deposited from micellar phases.

The observed spacings correspond to approximately twice the extended length of the appropriate monomer. A plot of lamellar spacing versus the number of carbons in the 3-alkyl substituent is shown in Figure 6. The straight line fit through the values for the higher homologs indicates that each additional methylene in the alkyl chain contributes approximately 2.2 Å to this spacing. Accordingly, we propose that the lamellar structure is a consequence of a head-to-head bilayer type packing (corresponding to a Y-type Lagnmuir–Blodgett film) (Figure 7) with a contribution of 1.1 Å by each methylene unit to the unit-cell dimension, *c*. Extrapolation of the straight line to *n* = 0 gives a distance of 14.3 Å which accounts for the space occupied by the potassium 3-(pyrrol-1-yl)propane sulfonate and any water of hydration. The spacings for lower homologs (poly**1d** and -**e**) fall below the best fit line in Figure 6, indicating either that the alkyl substituents are

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[37] Banerjie, A.; Lando, J. B. *Thin Solid Films* **1980**, *68*, 67.

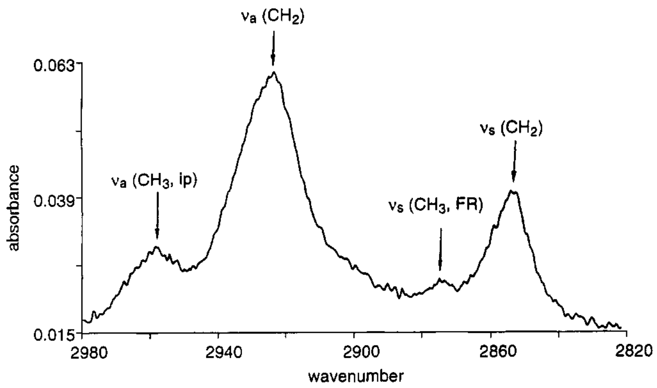

Figure 8. C–H Stretch region of the glancing angle reflection infrared spectrum of **1h**.

Table 2. Band Positions[a] for Alkyl C–H Stretching Modes in Polymer Multilayers of Poly1

structural group	C–H stretching mode	band position, cm^{-1} poly1**h**, $n = 12$	band position, cm^{-1} poly1**e**, $n = 8$
–CH$_2$–	ν_a[b]	2923	2927
	ν_s[c]	2853	2856
–CH$_3$	ν_a(ip)	2958	2957
	ν_s(FR)	*d*	*d*
	ν_s(FR)	2873	2872

[a] Mean of four samples, ±1 cm^{-1}. [b] Polyethylene ν_a: crystalline, 2920; liquid, 2928 cm^{-1}. [c] Polyethylene ν_s: crystalline, 2850; liquid, 2856 cm^{-1}. [d] Obscured by asymmetric methylene stretch.

interdigitated or that they are not in an extended conformation.

Grazing angle infrared spectroscopy was used to further evaluate the structure of electrochemically deposited monolayers of poly1, e.g., Figure 8. Spectra were obtained using p-polarized light incident at 80° to the normal of films deposited by cyclic voltammetry (approximately 15 layers thick on average, but visually heterogeneous). The vibrational frequencies of the C–H stretching modes are collected in Table 2. Since vibrations parallel to the substrate surface do not give rise to adsorption of p-polarized light, the methylene symmetric (ν_s) and asymmetric (ν_a) stretches of all-trans alkyl chains oriented perpendicular to the substrate are not observed.[38] These vibrations are infrared active for poly1, clearly indicating that the stretching modes are not parallel to the substrate. The shift to higher frequencies for the methylene stretches upon decreasing the length of the alkyl chain is in good agreement with the findings of Porter et al.[39] for monolayers of alkanethiols spontaneously adsorbed on gold. From the work of Snyder et al.[40] reporting the frequency changes occuring at the crystal to liquid transition for polyethylene, these results can be interpretted in terms of lower conformational order in the alkyl chains of the lower homologs. This observation of conformational disorder is in accord with the results of X-ray diffraction which indicate that lower homologs are positionally less ordered than higher ones.

Effect of Electrolyte Cation. The other simple structural variation that we have studied is the counterion for the anionic monomer. Rather than carrying out a cation metathesis on the potassium salt we simply chose to polymerize the monomers in appropriate electrolytes. The dodecyl homolog **1h** is soluble in aqueous 0.1 M LiNO$_3$ and HNO$_3$ but insoluble in NaNO$_3$. Polymerization from these electrolytes was unexceptional. X-ray diffraction of the polymers deposited from either acidic or lithium-containing solutions indicate unit cell spacing which reflect the smaller size of these cations relative to potassium (Table 1).

Conductivity. The as-grown polymers are resistive, with conductivities less than 10^{-6} Ω^{-1} cm^{-1}. To further oxidize the polymer, a film of **1h** was immersed in 1.0 M aqueous perchloric acid. After extensive washing with water, rinsing, and drying, the film shows a higher conductivity, 10^{-3} Ω^{-1} cm^{-1} along the film but remains an insulator $\sigma < 10^{-6}$ Ω^{-1} cm^{-1} through the film. This treatment resulted in the exchange of the potassium cation for protons, as observed by the loss of the potassium signal from the X-ray photoelectron spectrum. No changes were observed in the UV–visible spectrum upon treatment with perchloric acid. The anisotropic conductivity is in accord with the proposed lamellar structure. The dc conductivity remains constant over long time periods, indicating an electronic conduction mechanism rather than a protonic conduction, since the latter case would lead to a rapid polarization and a decrease in conductivity over time. However, either ionic or electronic conduction could impart a higher conductivity along the film (parallel to the polymer chains or ion channels) than through the film, when migration of a charge carrier through a bilayer of densely packed hydrophobic alkyl chains is required.

Although we have shown that the use of self-assembling monomers affords control of polymer morphology, the electronic properties of the resulting materials are poor. There are a number of possible explanations. A primary concern is that we may be forcing the polymer backbone to adopt a nonplanar conformation. Evidence for this might include the low level of doping found (10%, versus 25–35% for polypyrrole). N-substituted pyrroles typically suffer from low conductivity owing to sterically induced twisting of the conjugated backbone. Although self-assembly might be expected to orient the chain in the case of these surfactant polymers, the structural anisotropy incurred in satisfying the amphiphilic packing requirements could induce an all-syn conformation in the polymer with a corresponding decrease in the effective conjugation length. The resulting curvature might be relieved to some extent by disordering of the aliphatic side chains.

Conclusion. We have shown that the crystallinity of electrochemically deposited conductive polymers can be controlled by preorganization of amphiphilic monomers by molecular self-assembly. Lamellar phases of poly1 are conveniently prepared by electropolymerization of the appropriate monomer from a micellar solution. This avoids the need for Langmuir–Blodgett monolayer film transfer. These phases are highly ordered compared to polypyrrole with non-covalently bound amphiphilic sulfonate counterions.[22] Our future efforts are directed towards polymers which make use of a defined morphology to induce highly anisotropic conductivity, and a particularly high conductivity in one (or more) dimensions. The design of polymer systems with ordered supramolecular packing *and* a planar, all-anti polyarylene backbone is the subject of ongoing studies.

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(39) Porter, M. D.; Bright, T. B.; Allara, D. L.; Chidsey, C. E. D. *J. Am. Chem. Soc.* **1987**, *109*, 3559.

(40) Snyder, R. G.; Hsu, S. L.; Krimm, S. *Spectrochim. Acta* **1978**, *34A*, 395.

Experimental Section

Determination of Critical Micellar Concentration. Critical miicellar concentrations were determined by the method of Corrin,[34] whereby the effect of surfactant concentration on the color of a dilute solution of pinacyanol chloride is monitored. The measured values of cmc were reproducible to within ±20% and the test solutions remained stable overnight. The value determined for SDS by this method compares well with that determined by other techniques (8.1×10^{-3} M).[41]

Electrochemistry. Electrochemical polymerizations and analyses were performed on a Bioanalytical Systems BAS 100B. Polymerizations were performed on 0.1–10 mM solutions of **1** in 0.1 M aqueous KNO_3 prepared with water obtained from a Barnstead Nanopure System (resistivity >18 MΩ cm^{-1}). Owing to poor polymer adhesion, poly**1d** was prepared from 1.0 M aqueous KNO_3. Polymers were prepared on polished gold (area = 2.01 mm^2), evaporated gold on a glass microscope slide (area ≈ 1 cm^2), or ITO glass working electrodes. A gold counter electrode and a Ag/AgCl (saturated aqueous KCl) reference electrode were used for all experiments.

Polymer Film Analysis. X-ray diffraction patterns were obtained on a Philips automated powder 2θ diffractometer using Cu Alα irradiation. Grazing angle infrared spectra were recorded on a Nicolet 60SX using 1-cm^{-1} resolution with a mirror velocity of 1.4 cm s^{-1} and a mercury–cadmium–telluride detector. A SpectraTech FT-80 spectral reflectance accessory equipped with a ZnSe polarizer was used to provide p-polarized light with an 80° angle of incidence. All spectra were referenced against a freshly cleaned gold mirror.

Synthesis. 1-(4-Methylphenylsulfonyl)pyrrole (80% yield recrystallized from MeOH, mp 97–99 °C, lit.[32] 104.5 °C) was prepared according to the method of Havinga et al. for the preparation of the corresponding *N*-phenylsulfonamide.[31] 3-Acetylpyrrole was prepared using acetic anhydride (46% yield, sublimed), whereas other 3-acylpyrroles were prepared using the corresponding acyl chloride, as illustrated by the procedure given below for tridecanoylpyrrole. All starting materials were purchased from Aldrich Chemical Co. 1,3-Propane solutone was distilled from CaH_2 and stored over molecular sieves under argon. **Caution:** 1,3-propane sultone is a potent carcinogen: appropriate handling precautions are required. Tetrahydrofuran and diethyl ether were distilled from sodium benzophenone ketyl immediately prior to use. The syntheses of potassium 3-(3-alkylpyrrol-1-yl)propanesulfonates followed the same general route from 1-(4-methylphenylsulfonyl)pyrrole. The procedures are illustrated here for the tridecyl homolog. Yields for the preparation of alkanoyl and alkyl pyrroles are uniformly good. Although crude sulfonates, **1**, could be isolated in high yield (ca. 80%), repeated crystallization to remove traces of potassium 3-hydroxypropanesulfonate led to low yields of isolated pure product. The synthesis of the tridecyl homolog **1i** is provided to illustrate the route to the entire series of monomers **1**.

3-Tridecanoylpyrrole. A solution of 1-(4-methylphenylsulfonyl)pyrrole (7.0 g, 32 mmol) in CH_2Cl_2 (50 mL) was added to a solution containing tridecanoyl chloride (8.15 g, 35 mmol) and $AlCl_3$ (5.1 g, 38 mmol) in 25 mL of CH_2Cl_2 under argon at 0 °C. The mixture was stirred at room temperature for 18 h, and ice water was added slowly. The mixture was extracted with CH_2Cl_2 (4 × 40 mL), organic portion was washed with water, dried ($MgSO_4$), and filtered, and the solvent was removed under reduced pressure. The resulting dark oil was added to 50 mL of MeOH and 50 mL of 10% aqueous NaOH, and the mixture was heated to reflux for 3 h. The solution was cooled, diluted with 100 mL of H_2O, and extracted with CH_2Cl_2 (3 × 60 mL). The organic extracts were washed with water and dried ($MgSO_4$), and the solvent was removed. The residue was recrystallized from 50/50 $EtOH/H_2O$, to give 3-tridecanoylpyrrole (5.96 g, 65% yield) as a colorless solid: mp 66–67 °C. ^1H NMR (300 MHz, $CDCl_3$) δ 0.88 (t, J = 6.7 Hz, 3H), 1.2–1.4 (m, 18H), 1.71 (p, J = 7Hz, 2H), 2.75 (t, J = 7Hz, 2H), 6.65–6.70 (m, 1H), 6.75–6.81 (m, 1H), 7.42–7.45 (m, 1H), 8.4–8.65 (br s, 1H). IR (KBr) 3203, 3089, 2972, 2919, 1629, 1508, 1433 cm^{-1}.

Melting points for other previously unreported 3-acylpyrroles: butanoyl, 46–48 °C; undecanoyl, 52–53 °C; tridecanoyl, 56–57 °C; tetradecanoyl, 69–70 °C; hexadecanoyl, 67–68 °C; all gave satisfactory ^1H NMR and IR spectra. The following 3-acylpyrroles have been reported previously: acetyl, 109—111 °C, (lit.[14] 109–110 °C); hexanoyl, 49–50 °C (lit.[14] 46–47 °C); octanoyl, 68–70 °C (lit.[14] 67–68 °C); decanoyl, 58–60 °C (lit.[14] 58–59 °C); dodecanoyl, 54–55 °C (lit.[14] 56–57 °C).

3-Tridecylpyrrole. A solution of 3-tridecanoylpyrrole (2.55 g, 9.68 mmol) in THF (25 mL) was added to a solution of sodium bis(2-methoxyethoxy)aluminum hydride, Red-Al (7.1 mL of 3.4 M solution in toluene, 24.2 mmol) in THF (60 mL) under argon. The reaction mixture was stirred at room temperature for 18 h and poured carefully onto ice. The solution was extracted with EtOAc (3 × 20 mL), and the organic portion was washed with water, dried, and the solvent was removed. The resulting brown oil was chromatographed on silica gel (5% ethyl acetate in hexanes), to give 3-tridecylpyrrole (2.38 g, 99% yield) as a clear oil. ^1H NMR (300 MHz, $CDCl_3$) δ 0.88 (t, J = 6.6 Hz, 3H), 1.22–1.44 (m, 20H), 1.57 (p, J = 7 Hz, 2H), 2.48 (t, J = 7 Hz, 2H), 6.07–6.13 (m, 1H), 6.54–6.59 (m, 1H), 6.69–6.74 (m, 1H), 7.85–8.10 (br s, 1H). IR (neat) 3390, 2953, 2916, 2848, 1464, 1067, 777, 709 cm^{-1}.

Other previously unreported 3-alkylpyrroles all gave satisfactory ^1H NMR and IR spectra: tetradecyl, mp 39–31 °C; hexadecyl, mp 45–47 °C. Other 3-alkylpyrroles have been reported previously as liquids,[14] except dodecyl, mp 20–21 °C (lit.[14] 20 °C).

Potassium 3-(3-Tridecylpyrrol-1-yl)propanesulfonate (1h). Potassium hexamethyldisilazide (14.9 mL of 0.5 M solution in toluene, 7.46 mmol) was added to a solution of 3-tridecylpyrrole (1.86 g, 7.46 mmol) in THF (70 mL) under argon and the mixture as stirred for 30 min. 1,3-Propane sultone (0.654 mL, 7.46 mmol) was added via volummetric pipet. The mixture was heated to reflux under argon for 18 h and cooled to room temperature, and the solvent was removed under reduced pressure. Dry Et_2O was added, and the mixture was cooled to −20 °C overnight. The solid was filtered and washed with Et_2O to afford 2.22 g (78%) of **1h** as a colorless crude product. The major byproduct (<10%) was potassium 4-hydroxypropanesulfonate (^1H NMR (DMSO-d_6) δ 1.71 (p, J = 7 Hz, 2H, C-2 CH_2), 2.45 (t, J = 7 Hz, 2H, C-1 CH_2), 3.41 (t, J = 7 Hz, 2H, C-3 CH_2)). The crude mixture was recrystallized from 25:1 $EtOH/H_2O$ three times before satisfactory ^1H NMR and elemental analysis were obtained. ^1H NMR (300 MHz, DMSO-d_6) δ 0.86 (t, J = 6.5 Hz, 3H), 1.20–1.30 (m, 20H), 1.46 (br p, 2H), 1.90 (p, J = 7 Hz, 2H), 2.27–2.37 (m, 4H), 3.86 (t, J = 7 Hz, 2H), 5.77–5.82 (m, 1H), 6.44–6.49 (m, 1H), 6.55–6.60 (m, 1H). IR (KBr) 2955, 2918, 2851, 1502, 1192, 1056 cm^{-1}. Anal. Calcd for $C_{20}H_{36}KNO_3S$: C, 58.64; H, 8.86; N, 3.42; S, 7.83. Found: C, 58.47; H, 8.82; N, 3.36; S, 7.74.

All 3-(3-alkylpyrrol-yl)propanesulfonates gave satisfactory ^1H NMR and IR spectra and decomposed at temperatures greater than 200 °C. **1b**: Anal. Calcd for $C_9H_{14}KNO_3S$: C 42.33; H, 5.53; N, 5.48; S, 12.55. Found: C, 42.12; H, 5.48; N, 5.42; S, 12.56. **1c**: Anal. Calcd for $C_{11}H_{18}KNO_3S$: C, 46.62; H, 6.40; N, 4.94; S 11.31. Found: C, 46.71; H, 6.43; N, 4.93; S, 11.45. **1d**: Anal. Calcd for $C_{13}H_{22}KNO_3S$: C, 50.13; H, 7.12; N, 4.50; S, 10.29. Found: C, 50.22; H, 7.14; N, 4.47; S, 10.21. **1e**: Anal. Calcd for $C_{15}H_{26}KNO_3S$: C, 53.06; H, 7.72; N, 4.13; S, 9.44. Found: C, 53.31; H, 7.76; N, 4.17; S, 9.45. **1f**: Anal. Calcd for $C_{17}H_{30}KNO_3S$: C, 55.55; H, 8.23; N, 3.81; S, 8.72. Found: C, 55.66; H, 8.24; N, 3.76; S, 8.65. **1g**: Anal. Calcd for $C_{18}H_{32}KNO_3S$: C, 56.65; H, 8.45; N, 3.67; S, 8.40. Found: C, 56.53; H, 8.49; N, 3.63; S, 8.32. **1h**: Anal. Calcd for $C_{19}H_{34}KNO_3S$: C, 57.67; H, 8.66; N, 3.54; S, 8.10. Found: C, 57.67; H, 8.61; N, 3.42; S, 8.28. **1j**: Anal. Calcd for $C_{21}H_{38}KNO_3S$: C, 59.53; H, 9.04; N, 3.31; S, 7.57. Found: C, 59.6; H, 9.03; N, 3.30; S, 7.50. **1k**: Anal. Calcd for $C_{23}H_{40}KNO_3S$: C, 61.43; H, 8.96; N, 3.11; S, 7.13. Found: C, 61.02; H, 9.02; N, 3.15; S, 7.24.

Poly(potassium 3-(3-alkylpyrrol-1-yl)propanesulfonates): Bulk Polymerization. Potassium 3-(3-alkylpyrrol-1-yl)propanesulfonates were electrochemically polymerized at constant applied potential (+700 mV) from a gently stirred 10 mM solution

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in 0.1 M aqueous KNO_3. The polymer film was rinsed with water and allowed to dry slowly in air and then in a vacuum desiccator. IR (film transmission): 2980–2840 (s, C–H str), 1186, 1043 (s, RSO_3^- asym and sym str) cm^{-1}.

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