(q), 38.46 (s), 40.61 (d), 119.79(d), 128.52 (s), 131.05 (d), 144.59 (s), 150.66 (s), 152.30 (s), 159.59 (s), a signal assignable to *ipso*-^{13}C of Bbt group was not observed.; ^{31}P NMR (121 MHz, C_6D_6): $\delta = 612.0$; UV/vis (*n*-hexane): λ_{max} (ε) = 455 (10000), 540 (sh, 1000), and 670 nm (300); high-resolution MS (FAB): *m*/*z*: 1109.5511([*M*+H]$^+$), calcd for $C_{48}H_{97}Si_7PBi$ 1109.5516. Slow evaporation of a hexane solution of the residue in a refrigerator at $-40\,^\circ$C fixed in a glovebox filled with argon gave green crystals of **1**·0.5 hexane.

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[12] Crystal data for **1**·0.5 hexane ($C_{51}H_{103}BiPSi_7$): $M_r = 1152.91$, $T = 93(2)$ K, triclinic, $P\bar{1}$ (no. 2), $a = 12.7372(2)$, $b = 14.6943(5)$, $c = 18.5933(5)$ Å, $\alpha = 107.5367(14)$, $\beta = 95.2385(15)$, $\gamma = 107.9837(5)^\circ$, $V = 3090.27(14)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.239$ g cm^{-3}, $\mu = 3.044$ mm^{-1}, $\lambda = 0.71070$ Å, $2\theta_{max} = 50.0$, 35164 measured reflections, 10813 independent reflections, 572 refined parameters, GOF = 1.034, $R_1 = 0.0201$ and w$R_2 = 0.0483$ ($I > 2\sigma(I)$), $R_1 = 0.0225$ and w$R_2 = 0.0489$ (for all data), largest difference peak and hole 1.106 and -0.476 e Å^{-3}. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-168594. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk). The intensity data were collected on a Rigaku/MSC Mercury CCD diffractometer. The structure was solved by direct methods (SHELXS-97) and refined by full-matrix least-squares procedures on F^2 for all reflections (SHELXL-97). All hydrogens were placed using AFIX instructions.

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Erodible Conducting Polymers for Potential Biomedical Applications**

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Electrically conducting polymers have been investigated for numerous applications, including organic substitutes for metals in electronic circuits,[1] coatings for electromagnetic shielding,[2] analytical and biological sensing devices,[3–5] and as substrates for the manipulation of mammalian cell growth and function.[6] From a separate standpoint, the development and application of biodegradable polymers has had a profound impact in numerous medical and surgical applications.[7] It occurred to us that the creation of biocompatible, degradable conducting polymers could open the door to a number of new biomedical applications.[8] Several groups have reported the synthesis and characterization of conducting poly(thiophene) derivatives containing hydrolyzable ester groups in the polymer backbone.[9] However, to our knowledge, the degradability and biocompatibility of these polymers has not been established, and the reduced environmental stability of oxidized polythiophenes could limit their application under physiological conditions.

Of the various electrically conducting polymers, polypyrrole (Ppy) has been the most widely studied material for potential biomedical applications because it is relatively stable to air and water and can be readily synthesized through chemical and electrochemical routes.[10] Additionally, Ppy is a suitable substrate for cell attachment and proliferation[6] and possesses excellent biocompatibility in vivo.[8, 11] Our attempts to synthesize biodegradable Ppy derivatives through the incorporation of backbone ester moieties (in analogy to the polythiophenes discussed above) have thus far been unsuccessful because of extensive side reactions accompanying pyrrole coupling chemistry and the generally poor oxidative stability of the requisite oligopyrrole intermediates. Herein, we report an alternative strategy for the design of *erodible* Ppy materials based on the chemical and electrochemical polymerization of β-substituted pyrrole monomers containing ionizable and/or hydrolyzable side groups [Eq. 1]. These polymers can be fabricated into conductive materials that erode slowly under physiological conditions and support the growth, proliferation, and differentiation of primary human cells in in vitro cell culture assays.

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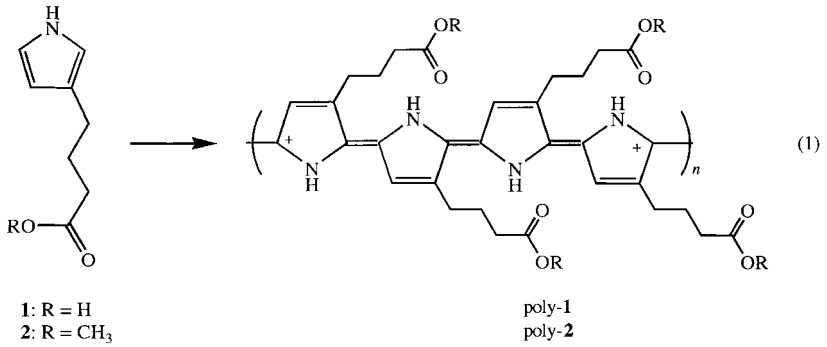

(1)

We recently reported the synthesis of carboxylic acid functionalized pyrrole monomer **1**.[12] Direct esterification of compound **1** by reflux in methanol in the presence of phenylsulfonic acid afforded methyl ester functionalized monomer **2** in 80% yield. Both monomers underwent oxidative electrochemical polymerization and ferric chloride mediated chemical polymerization to yield conductive thin films and colloidal dispersions [poly-**1** and poly-**2**, Eq. 1]. In contrast to the insoluble cross-linked polymer deposits typically obtained from the oxidative polymerization of pyrrole, poly-**2** was completely soluble in common organic solvents such as THF and chloroform. Poly-**1** was insoluble in organic solvents, but was sparingly soluble in water. The solubility of these polymers suggested that they were not extensively cross-linked, presumably because of the presence of the β-substituents that prevent the cross-linking at this position. The sheet resistance of thin films prepared from poly-**1** was 300 ($\pm$100) Ω, which is consistent with literature values for β-substituted polypyrroles.[10, 13]

In view of the low solubility of poly-**1** in water, we hypothesized that thin films formed from poly-**1** might undergo a gradual erosion process under physiological conditions in a manner approximating the behavior of conventional biodegradable polymer systems. To test this hypothesis, we incubated thin films of poly-**1** in acetate (pH 5.0), HEPES (pH 7.2 HEPES = 2-[4-(2-hydroxyethyl)-1-piperazinyl]ethanesulfonic acid) and TAE (pH 8.2; TAE = tris(hydroxymethyl)aminomethane acetate, 10 mM ethylendiaminetetraacetate) buffers and investigated their erosion/dissolution profile at 37 °C as a function of pH value. Thin films deposited on iridium tin oxide (ITO) glass dissolved within 24 hours at pH 8.2, but dissolved more slowly at pH 5. Intermediate dissolution rates were observed at pH 7.2. Unfortunately, the deterioration of film quality over time, coupled with the tendency of the films to detach from the ITO substrates and float, prevented a quantitative analysis of the erosion process over an extended period of time.

To facilitate a more quantitative analysis, we prepared pressed pellets of chemically polymerized poly-**1** (20 mg, diameter = 8 mm, thickness = 0.5 mm) and followed the erosion/dissolution of polymer by UV/Vis spectroscopy in acetate (pH 5.0), HEPES (pH 7.2), and TAE (pH 8.2) buffers (see Experimental Section). As shown in Figure 1, the erosion rate of pellets at pH 7.2 was twice the rate of erosion at pH 5.0, and the rate was dramatically enhanced under alkaline conditions. Pressed pellets formed from hydrophobic methyl ester functionalized poly-**2** eroded much more slowly than their acid-functionalized counterparts (50 mg, diameter = 8 mm, thickness = 1 mm) at pH 7.2. As shown in Figure 2, the mass loss from pellets of poly-**1** was 27% after 80 days of incubation at 37 °C, while the mass loss from pellets of poly-**2** was 6%. These results parallel an increase in pyrrole oligomer concentration in solution over time (as determined by UV/Vis spectroscopy, Figure 2). The disparity in the erosion/dissolution rates between poly-**1** and poly-**2** suggests a means of tailoring erosion rates through judicious copolymerization of both

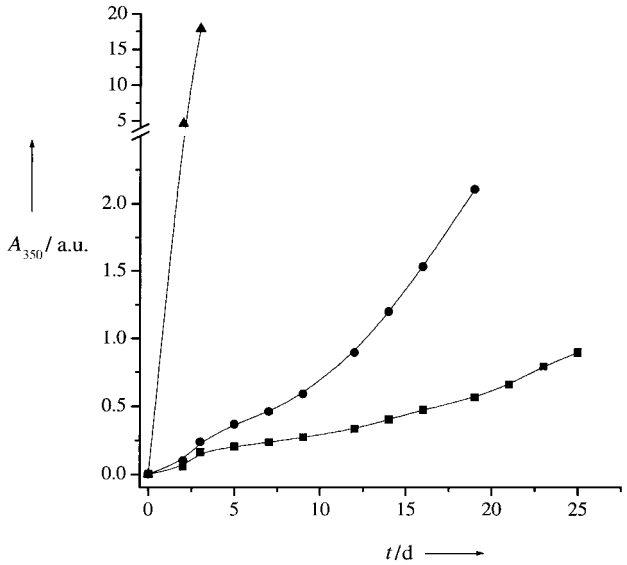

Figure 1. Dissolution of pressed pellets of poly-**1**, monitored by UV/Vis spectroscopy, at different pH: 8.2 (▲), 7.2 (●), and 5.0 (■)

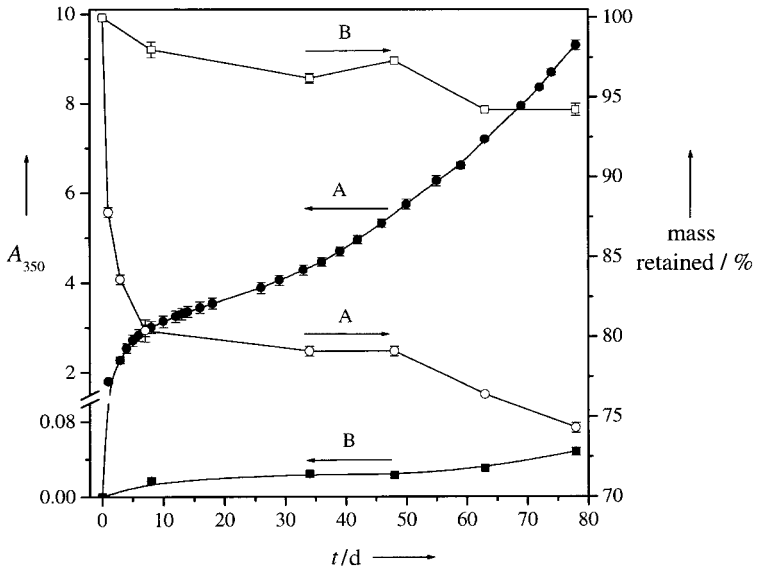

Figure 2. Dissolution of pressed pellets of poly-**1** (A) and poly-**2** (B), as monitored by solution UV/Vis absorbance (●, ■) and mass loss (○, □).

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hydrophilic and hydrophobic monomers.[14] Unfortunately, the surface roughness arising from erosion (scanning electron microscopy, data not shown), prevented a detailed study of the conductivity of the pellets as a function of degradation time; the design of a system to address this issue is currently underway. The sheet resistance of thin films prepared from poly-**1** rises slightly upon incubation in water, and reaches a plateau at approximately 700 ($\pm$200) Ω after two days. These data indicate that the films remain conductive under aqueous or water-equilibrated conditions. The resistance of these equilibrated films is similar to that of films formed from Ppy previously used for the stimulation of cells and tissue.[8]

We also carried out cytocompatibility studies on thin films of poly-**1** using primary human bone-marrow derived mesenchymal progenitor cells (MPCs) as a model cell system. All seeded cells attached to the substrate and proliferated at an average rate of 0.63 doublings per day, comparable to that measured for cells growing on tissue-culture-treated plastic.[15] MPCs cultured for nine days on the erodible Ppy substrate in medium promoting osteogenic differentiation progressed towards the osteoblast lineage, as assessed by the increased mRNA expression of collagen Type I (1.8-fold), bone sialoprotein (2.4-fold), and osteopontin (19.2-fold; Figure 3).

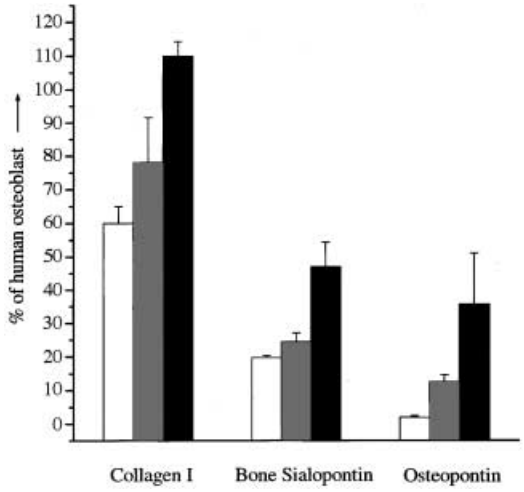

Figure 3. mRNA expression levels of osteoblast-related markers (collagen Type I, bone sialoprotein, and osteopontin) in mesenchymal progenitor cells grown on thin films of poly-**1**, before (white) and after exposure to soluble osteogenic stimuli for five (gray) or nine (black) days. The values, quantified and normalized to the amounts of 18-S rRNA (housekeeping gene) by using real-time reverse transcriptase polymerase chain reaction (RT-PCR), are expressed as a percentage of those measured in human osteoblasts.

Although additional experiments in vivo will be required to more accurately determine the biocompatibility of the developed polymers, these results demonstrate the potential for erodible Ppy-based materials as cell substrates in biomedical applications. The conductive nature of Ppy has been shown to allow interactive control over cell shape, differentiation, and function.[8, 11, 16] Ongoing studies are aimed towards influencing the behavior of cells cultured on erodible Ppy substrates through the application of magnetic fields and/or electrical currents.

Experimental Section

4-β-pyrrolylbutyric acid (**1**) was prepared as previously described.[12] ^{1}H NMR (300 MHz, $CDCl_3$) $\delta = 1.9$ (m, 2H), 2.4 (t, 2H), 2.55 (t, 2H), 6.1 (s, 1H), 6.4 (s, 1H), 6.72 (s, 1H).

Methyl-4-β-pyrrolylbutyrate (**2**): **1** (2.0 g, 13 mmole) in methanol (25 mL) was heated under reflux overnight in the presence of catalytic amounts of phenylsulfonic acid. The reaction mixture was poured onto ice cold water (200 mL) and extracted with diethyl ether (5×25 mL), and the combined organic layers were dried over Na_2SO_4. Removal of the solvent followed by a silica column chromatography (eluent ethyl acetate:hexane = 1:3) and removal of solvents gave 1.6 g of a white solid. ^{1}H NMR (300 MHz, $CDCl_3$) $\delta = 1.9$ (m, 2H), 2.4 (t, 2H), 2.55 (t, 2H), 3,64 (s, 3H), 6.1 (s, 1H), 6.4 (s, 1H), 6.72 (s, 1H).

Chemical polymerization: Monomer **1** (2.52 g, 16.5 mmol) and tetrabutylammonium *p*-toluenesulfonate (6.8 g, 16.5 mmol) were dissolved in acetonitrile (25 mL) and mixed with an equal volume of acetonitrile charged with ferric chloride (5.36 g, 33 mmol). The mixture was stirred vigorously for 20 min, then poured onto ice-cold water (500 mL). The precipitate was collected, washed with water (5×50 mL), and dried under vacuum. Polymer **2** was synthesized in an analogous manner. Gel permeation chromatography (GPC) analysis of polymer **2** (THF, 0.1 M piperidine) showed that the sample primarily consists of oligomers ($M_n = 1700$, $M_w = 3200$ relative to monodisperse polystyrene standards). ^{1}H NMR (300 MHz, $CDCl_3$) $\delta = 1.9$ (m, 2H), 2.4 (t, 2H), 2.55 (t, 2H), 6.1 – 7.9. Elemental analysis of the polymers showed trace amounts of Cl (0.14%) and Fe (0.15%).

Electrochemical polymerization: **1** was electrochemically deposited onto indium tin oxide (ITO) coated glass slides from a 1M solution in acetonitrile containing 0.5 M of tetrabutylammonium tetrafluoroborate by passing 1 Coulomb of electrical current at a constant potential (1.0 V vs Ag/AgCl reference electrode).

pH Dependent degradation: Pressed pellets formed from poly-**1** were incubated at 37 °C in 2 mL of the media with the desired pH value (0.01 M acetate buffer, pH 5.0; 0.01 M HEPES buffer, pH 7.2; $1 \times$ TAE buffer, pH 8.2). Media was changed and subsequently analyzed with UV/Vis spectroscopy every 2 – 4 days.

Degradation of pressed pellets: Pressed pellets were placed into HEPES buffer (10 mL, 0.1M; pH 7.2) and incubated at 37 °C on an orbital shaker. For experiments employing poly-**1**, buffer media was removed for absorbance measurements and replaced with fresh media every 2 – 5 days. As pellets formed from poly-**2** degraded more slowly than poly-**1**, buffer media was collected and analyzed every 7 – 14 days. The mass loss of the pellets was analyzed at selected time points by removing the incubation media, washing the pellets with de-ionized water (3×5 mL), and subsequently freeze-drying each pellet. All experiments were performed in triplicate.

Cell culture: Culture medium (CM) was Dulbecco's modified Eagle medium with 10% fetal bovine serum (LOT 40G2470J, Gibco BRL Life Technology, Basel, CH), D-glucose (4.5 mg/ml), nonessential amino acids (0.1 mM), sodium pyruvate (1 mM), HEPES buffer (100 mM), penicillin (100 U/ml), streptomycin (100 μg/ml), and L-glutamine (0.29 mg/ml). Bone marrow aspirates were obtained during routine orthopedic surgical procedures involving exposure of the iliac crest, after informed consent. Nucleated cells were isolated using a density gradient solution (Histopaque, Sigma Chemical, Buchs, CH), plated at a density of 3,000 cells cm^{-2} in CM supplemented with fibroblast growth factor-2 (5 ng/ml; R&D Systems, Wiesbaden, D) and dexamethasone (10 nM; Sigma) and cultured in a humidified 37 °C/5% CO_2 incubator.[15] MPC were selected on the basis of adhesion and proliferation on the plastic substrate. After about 10 days, upon reaching subconfluency, MPC were detached using 0.25% trypsin/1 mM EDTA (EDTA = ethylendiaminetetraacetate) and plated on glass slides coated with the polymer **1**, at a density of 6,000 cells cm^{-2}. Cells were cultured in medium known to promote MPC osteogenic differentiation, which consisted of CM supplemented with dexamethasone (10 nM), L-ascorbic acid-2-phosphate (0.1 mM), and β-glycerophosphate (10mM).[17] Cultures were harvested at timed intervals (5 and 9 days) and assessed for DNA content and mRNA analysis as described below.

Cell proliferation: The DNA content of MPC cultures was assessed using the CyQuant kit (Molecular Probes, Eugene, Oregon). MPC proliferation

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rate was defined as the number of doublings between day 5 and day 9 (determined as the logarithm in base 2 of the increase in the DNA amount) divided by the elapsed time (4 days).

Real-Time quantitative RT-PCR: RNA was extracted from cell layers using Trizol (Life Technologies, Basel, CH) according to the single step acid-phenol guanidinium method,[18] treated with DNAse I using the DNA-free kit (AMS Biotechnology Ltd, CH) and transcribed into cDNA by using random hexamers (Catalys AG, CH) and Stratrascript reverse transcriptase (Stratagene, NL). Real-time RT-PCR reactions were performed and monitored using an ABI Prism 7700 sequence detection system (Applied Biosystems, Rotkreuz, Switzerland). In the same reaction, cDNA samples were analyzed both for the gene of interest and the reference housekeeping gene (18-S rRNA), by using a multiplex approach (Perkin Elmer User Bulletin No. 2). The probe for 18-S rRNA was fluorescently labeled with VIC and TAMRA (Applied Biosystems), whereas probes for the genes of interest were labeled with 6-carboxy-fluorescein (FAM) and TAMRA. The efficiency of each set of primers and probes, assessed as previously described,[19] was always higher than 90%. Primers were purchased from Microsynth (Balgach, CH) and probes were from Perkin-Elmer or Eurogentech (Seraing, B).

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Characterization of C_2 (C_xH_y) Intermediates from Adsorption and Decomposition of Methane on Supported Metal Catalysts by in situ INS Vibrational Spectroscopy**

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Conversion of methane into higher hydrocarbons is a process of enormous technological importance, which would benefit from a better understanding of the nature of the surface intermediates formed during methane activation. Currently methane is converted into hydrocarbons mainly by an indirect route[1, 2] via syn gas[3] as the intermediate. Alternative routes, such as oxidative coupling of methane[4–7] over metal oxide catalysts and methane homologation[8–10] on transition metal catalysts have also been extensively investigated. In a previous study we[11] have observed the formation of various C_xH_y surface intermediate species after methane decomposition on single-crystal Ru(0001) and Ru(1120) model catalysts, observed by high-resolution electron energy loss spectroscopy (HREELS). In this study we used INS to investigate the surface intermediate species formed during the decomposition of methane on Ru/Al_2O_3 and Ni/SiO_2 catalysts. We relate these findings to our previous work on idealized single-crystal model catalysts. The present work represents a step in the effort to bridge the gap between surface science and real-world catalysts in terms of the type of material and pressure used. Inelastic neutron scattering (INS)[12–14] vibrational spectroscopy is a technique that can be directly applied to high surface-area catalysts from ambient to high pressures. This method can also provide accurate quantitative information, has high sensitivity to hydrogenous species, and is not limited by the selection rules of other vibrational spectroscopies.

Herein we report the first experimental evidence of the formation of ethylidyne, vinylidene, and methylidyne (C_xH_y) species from methane on supported metal catalysts. Shown in Figure 1 is the difference INS vibrational spectrum after methane decomposition on Ru/Al_2O_3. The rather modest resolution, especially at higher frequencies, and poor statistics are the result of having to use a difference spectrum and of the relatively small amount of H in the sample. Nonetheless, the

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