COOH), 3.50 (t, 8 H, alkyl chain H (P-(*meso*-Ph)-NHCOC-$(CH_3)_2(CH_2)_{17}CH_2O$–), 5.90 (s, 8 H, side-chain CH_2 of itaconic acid group (P-(*meso*-Ph)-NHCOC$(CH_3)_2(CH_2)_{17}CH_2OCOCH_2C({=}CH_2)COOH$), 7.10–7.90 (m, 24 H, phenyl H), 8.70 (s, 4 H, amido H), 8.80 (s, 8 H, β-H of porphyrin ring); ^{13}C NMR ($CDCl_3$, Me_4Si standard, ppm δ_C 24.2 (2′,2′-dimethyl C), 24.8 (alkyl chain C (P-(*meso*-Ph)-NHCOC$(CH_3)_2CH_2CH_2$–), 29.2–31.6 (alkyl chain C (P-(*meso*-Ph)-NHCOC$(CH_3)_2CH_2CH_2(CH_2)_{15}$–), 40.5 (alkyl chain C (P-(*meso*-Ph)-NHCOC$(CH_3)_2CH_2$–), 42.4 (tertiary C of pivaloyl group (P-(*meso*-Ph)-NHCOC$(CH_3)_2$–), 62.4 (alkyl chain C of itaconic acid group (P-(*meso*-Ph)-NHCOC$(CH_3)_2CH_2CH_2(CH_2)_{15}CH_2OCOCH_2$–), 65.5 (alkyl chain C (P-(*meso*-Ph)-NHCOC$(CH_3)_2CH_2CH_2(CH_2)_{15}CH_2$–), 114.9 (*meso* C of porphyrin ring), 121.3, 123.6, 130.2, 131.3, 134.1, 138.5 (3-, 5-, 4-, 1-, 6-, and 2-C's of phenyl group), 122.2 (side-chain vinylidene C of itaconic acid group (P-(*meso*-Ph)-NHCOC$(CH_3)_2CH_2CH_2(CH_2)_{15}CH_2OCOCH_2C({=}CH_2)COOH$), 130.9 (inner vinylidene C of itaconic acid group (P-(*meso*-Ph)-NHCOC$(CH_3)_2CH_2CH_2(CH_2)_{15}CH_2OCOCH_2C({=}CH_2)COOH$), 131.8 ($\beta$-C of porphyrin ring), 146.2 (α-C of porphyrin ring), 167.9 (top carbonyl C of itaconic acid group (P-(*meso*-Ph)-NHCOC$(CH_3)_2CH_2CH_2(CH_2)_{15}CH_2OCOCH_2C({=}CH_2)COOH$), 168.9 (inner carbonyl C of itaconic acid group ($-OCOCH_2C({=}CH_2)COOH$)), 175.5 (carbonyl C of pivaloyl group (P-(*meso*-Ph)-NHCOC$(CH_3)_2$–); IR (KBr pellet, cm^{-1}) 1640 ($\nu_{C=C}$), UV–vis (chloroform, nm) 228, 417, 512, 544, 588, 643; elemental anal. C, H, N; (found: C, 84.5; H, 9.8; N, 5.7; calcd ($C_{152}H_{214}N_8O_{20}$) C, 84.8; H, 10.0; N, 5.2.

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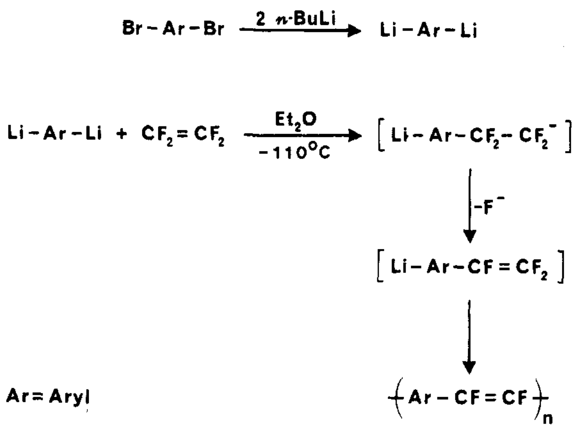
The Synthesis of New Poly(arylenedifluorovinylenes) from Aromatic Dianions and Tetrafluoroethylene

Conjugated organic polymers recently have been shown to exhibit dramatic increases in electrical conductivity when oxidized or reduced by electron acceptors or donors.[1] Since the conductivity varies from insulating to conducting depending on the structure of the polymer and the nature of the dopant, there is much interest in elucidating the structure–property relationships that give rise to the observed electrical properties. Poly(phenylenevinylene) is among the conjugated organic polymers that have received attention as promising conducting materials, and a number of structure–conductivity studies of this polymer recently have appeared.[2-4] In this communication, the synthesis of new fluorinated poly(arylenevinylene) via a novel polymerization reaction is reported.

Theoretical considerations suggest that fluorine is a particularly desirable substituent for conducting polymers.[5,6] LCAO–SCF–MO calculations[5] predict that poly(fluoroacetylene) and poly(difluoroacetylene) should have decreased band gaps relative to poly(acetylene) due to lowering of the levels of the LUMO's as a result of the high electronegativity of fluorine and raising of the levels of the HOMO's due to electron donation through fluorine's lone pairs. It also has been proposed that fluorine substitution in poly(acetylene) may afford greater oxidative stability.[5] Furthermore, steric effects should be minimal with fluorine substitution and thus, fluorination should not interfere with coplanarity of a conjugated π-network.[1a,7] A preliminary account of the synthesis of the fluorinated analogue[8] of poly(1,6-hexadiene)[9] lends support to these predictions.

Scheme I



Poly(arylenevinylenes) for structure–conductivity studies have been prepared by the Wittig reaction,[2] by dehydrohalogenation of *p*-xylylidene dihalides,[2] via coupling of dibenzoylarylenes,[3] or, recently, from bis(sulfonium chloride) intermediates.[4] The route to new fluoro-substituted poly(arylenevinylenes) reported here employed polymerization of tetrafluoroethylene with aryl dianions. We envisioned that the reaction of aryl dianions with tetrafluoroethylene would afford poly(arylenedifluorovinylene) via an addition–elimination[10] step-growth polymerization, with the dianion and tetrafluoroethylene serving as difunctional monomers in the polymerization reaction (Scheme I). The model reaction for this polymerization, nucleophilic vinylic substitution of tetrafluoroethylene with aryl monoanions to give aryl-substituted trifluoroolefins and 1,2-diaryl-1,2-difluoroolefins, is well-established.[11]

Two aromatic monomers, *p*-dilithiobenzene and 4,4′-dilithiobiphenyl, were considered for the preparation of fluorinated analogues of poly(phenylenevinylene). The attempted preparation of *p*-dilithiobenzene by halogen–metal exchange[12,13] of *p*-dibromobenzene in ethyl ether at 0 °C with 2 equiv of *n*-butyllithium afforded predominantly monolithiobromobenzene (analyzed by gas chromatography after methanol quench). Efforts to optimize the formation of dilithiobenzene in ethyl ether were complicated by reactions with solvent and by loss of stoichiometric equivalency as a result of coupling of *n*-butyllithium with butyl bromide, the byproduct of the exchange reaction (characterized by GC–MS). The reaction of 2 equiv of *n*-butyllithium with *p*-dibromobenzene in refluxing petroleum ether (15 h) gave primarily dilithiobenzene (85%), but subsequent reaction with tetrafluoroethylene afforded only a low yield of uncharacterized product. Dilithiation was much more facile with 4,4′-dibromobiphenyl. Halogen–metal exchange of 4,4′-dibromobiphenyl in ethyl ether with 2 equiv of *n*-butyllithium proceeded smoothly and gave a quantitative yield of the desired dianion (0 °C, 1 h).

For the preparation of poly(biphenyldiyldifluorovinylene), tetrafluoroethylene was condensed into a stirred mixture of 4,4′-dilithiobiphenyl in dry, distilled ethyl ether at –110 °C. The reaction mixture was maintained at –110 °C under a nitrogen atmosphere for 3 h at which time it was allowed to warm slowly to room temperature. The resulting bright yellow solid was extracted (Soxhlet) for 6 days with ethanol, water (to remove LiF), ethanol, and ether and then dried at 80 °C under reduced pressure to

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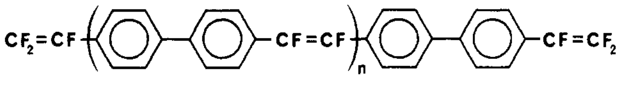
Table I
Elemental Analysis of 1

	% C	% H	% F
found	76.55	4.04	18.99
calcd for n = 10	76.28	3.61	20.11
calcd for n = 20	77.31	3.68	19.00

afford poly(4,4′-biphenyldiyl-1,2-difluoroethenyl), 1 (90%, based on the repeat unit).



1

Characterization of 1 by infrared spectroscopy, CP-MAS ^{13}C NMR spectroscopy, and elemental analysis was consistent with the assigned structure. Infrared spectroscopy (KBr pellet) showed aromatic absorptions at 3040, 1605, 1500, and 820 (para substitution) cm^{-1} and absorptions associated with fluorine substitution at 1755 ($CF_2{=}CF{-}$ end groups), 1680 ($-CF{=}CF-$), and 1275 and 1105 (s, C—F) cm^{-1}. For NMR analysis, solid-state techniques were employed due to the intractable nature of 1. $^1H-^{13}C$ cross polarization magic angle spinning (CP-MAS) NMR spectroscopy at 62.9 MHz showed carbon-13 chemical shifts for the biphenyl moiety at 128 and 139 ppm (relative to Me_4Si).[14] Good agreement between elemental analysis and the proposed structure of 1 was obtained (Table I). The degree of polymerization was estimated to be 10–20, assuming that all chains were terminated with trifluorovinyl end groups (a slight excess of tetrafluoroethylene was used in the polymerization reaction).

Differential scanning calorimetry (DSC) of 1 revealed no T_g or T_m over the temperature range 40–500 °C. While the polymer was stable at room temperature for several months, heating in air resulted in oxidation of the trifluorovinyl end groups (DSC exotherm at 225 °C). Infrared spectroscopy after heating in air showed the absence of the trifluorovinyl absorption at 1755 cm^{-1} and the appearance of a new absorption at 1810 cm^{-1}. Oxidation apparently resulted in conversion of the trifluorovinyl end groups to acid fluorides. This was consonant with a previous observation[15] that oxidation of trifluorostyrene in moist air afforded the corresponding carboxylic acid, probably by hydrolysis of the acid fluoride intermediate.

The electrical conductivity of a pressed powder pellet of 1 was 5×10^{-9} (Ω cm)$^{-1}$. The conductivity increased to 1.7×10^{-4} (Ω cm)$^{-1}$ by exposing the powder to 250 Torr of AsF_5 for 1 h prior to pressing (unoptimized single-point determination). Further conductivity evaluation and the preparation of other poly(arylenedifluorovinylenes) will be examined in an effort to elucidate the structure–conductivity relationships of these fluorinated polymers.

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Registry No. 1 (SRU), 106213-30-3; (copolymer), 106213-31-4; AsF_5, 7784-36-3.

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Synthesis of Liquid Crystalline Side-Chain Polyacrylates by Solid–Liquid Phase-Transfer Catalysis without Added Solvent

During the last decade, the chemical and physical properties and potential applications of liquid crystalline side-chain polymers have been widely investigated.[1,2] A variety of synthetic approaches have been utilized to prepare these mesomorphic side-chain polymers. These include free-radical polymerization of mesogenic methacrylates,[3] acrylates,[4] and chloroacrylates;[5] anionic[6] and group-transfer[7] polymerizations of methacrylates; ring-opening polymerizations of glycidyl esters to side-chain poly(ethylene oxides);[8] polycondensations to give side-chain polyesters;[9] and transformation of "reactive polymers" by reaction with terminally functionalized mesogens to give mesomorphic polysiloxanes,[1,10-13] polyacrylates,[14] polymethacrylates,[15] poly(methyl vinyl ether comaleates),[16] and polyitaconates.[17]

The last of these methods has the advantage that known polymers are used to prepare the liquid crystalline polymers. It also permits the preparation of such nonclassical mesomorphic polymers as poly(methyl vinyl ether comaleates)[16] and polyitaconates,[17] which are not easily accessible by other routes. We have used this procedure to devise a simple synthesis of mesomorphic polyacrylates by reaction of sodium polyacrylates with ω-bromoalkyl esters

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