Synthesis and Properties of an n-Self-Doped Conducting Polymer

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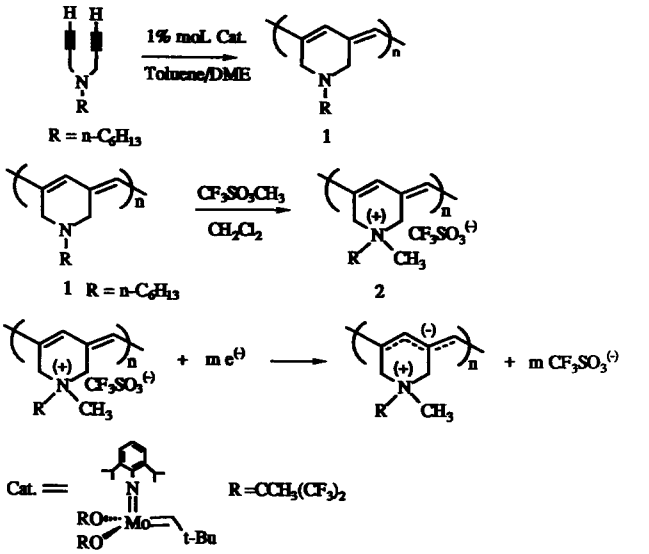
Since self-doped conducting polymers were first reported,[1] several analogous materials were synthesized.[2] In these unusual conjugated polymers, the potential counterions are convalently bound to the polymer. Charge injected into the π-electron system of the polymer is compensated by proton (or Li^+, Na^+, etc.) migration, leaving behind the oppositely charged counterion.[3]

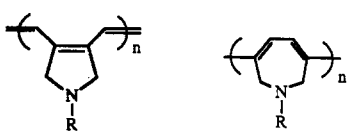
To our knowledge, all previous self-doped conducting polymers contain only negatively charged counterions. In this paper, we report a new self-doped conjugated polymer, shown in Scheme I, in which the dopant (cationic site) is incorporated into the polymer.

As shown in the scheme, the preparation of the polymer is based on the cyclopolymerization reaction of *N*-hexyldipropargylamine (DPHA), which occurred rapidly at −30 °C with 1% of Mo(CH-*t*-Bu)(NAr)[OCMe$(CF_3)_2]_2$[4] as initiator to give poly(dipropargylhexylamine), PDPHA, in good yield. Ziegler–Natta catalysts such as $MoCl_5$, $MoCl_5$–Bu_4Sn, $MoCl_5$–Et_3Al, and Cp_2TiCl_2–Bu_4Sn failed to polymerize the monomer, although these catalysts gave good yields in the polymerization of a variety of dipropargyl derivatives.[5]

PDPHA was fully characterized spectroscopically and by elemental analysis.[6] Close examination of the ^1H NMR spectrum (peaks at 5.8, 3.7, and 2.6 ppm) suggested that the polymer did not contain only a single repeat unit (six-membered ring). In addition to structure 1, structures 3 and 4 are also possible for PDPHA due to different cyclopolymerization pathways. As already suggested,[4,7] of these structures, 1 may be the most favorable from the viewpoint of its stability and the cyclopolymerization mechanism by alkylidene complexes.[4,7] On the basis of NMR spectroscopy, PDPHA consists of a random distribution of 80% 1 and 20% 3 formed through head-to-tail and tail-to-tail copolymerization of the two acetylenic bonds in the monomer.[8]

Scheme I





3 4

Treatment of PDPHA with methyl trifluoromethanesulfonate in methylene chloride affords the corresponding poly(dipropargyl-*N*-hexyl-*N*-methylammonium triflate), PDPHMAT, in 92% yield (Scheme I). PDPHMAT was fully characterized.[9,10] A broad ^1H NMR peak at 3.43 ppm was assigned to the methyl protons on nitrogen. Due to the positive charge on nitrogen, all the peaks shifted down field relative to PDPHA. The infrared spectrum of PDPHMAT exhibits strong bands at 1256 and 1163 cm^{-1}, characteristic of asymmetric and symmetric sulfonate SO_2 stretching vibrations. The UV–visible spectrum of PDPHMAT shows the characteristic broad band of a conjugated polyene π–π^* absorption in the visible region (300–

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(6) Proton NMR (500 MHz, 25 °C, CD_2Cl_2) δ 6.28 (m, 2H RC*H*=CR_2, six-membered ring), 5.81 (m, RC*H*=CR_2, five-membered ring), 3.69 (m, 4H, R_2C=CHCH_2NR, six-membered ring), 3.28 (m, 4H, R_2C=CHCH_2-NR, five-membered ring), 2.62 (br, 2H, NCH_2R, five-membered ring), 2.48 ((br, 2H, NCH_2R, six-membered ring), 1.52 (br, 2H, NCH$_2$CH_2R), 1.32 (br, 8H, NCH$_2$(CH_2)$_4$CH$_3$), 0.88 (br, 3H, N(CH$_2$)$_5$CH_3). $^{13}C\{^1H\}$ NMR (125.7 MHz, 25 °C, CD_2Cl_2) δ 136.85 (br, C=C), 57.54 (br, NCH$_2$C=C), 56.22 (NCH$_2$R), 31.78 (NCH$_2$CH$_2$R), 27.13 (N(CH$_2$)$_3$CH$_2$R), 27.04 (N(CH$_2$)$_3$CH$_2$R), 22.59 (N(CH$_2$)$_4$CH$_2$CH$_3$), 13.82 (N(CH$_2$)$_5$CH$_3$). IR (film, cm^{-1}) 2927 (vs), 2855 (vs), 1597 (w, C=C), 1463 (s), 1377 (s), 1161 (s), 938 (s), 896 (s). UV–vis λ_{max} = 550 nm (film) (536 nm, in THF). Anal. Calcd $(C_{12}H_{19}N)_n$: C, 81.30; H, 10.80; N, 7.90. Found: C, 78.62; H, 10.56; N, 7.74. 1.08% catalyst residue was found in the polymer.

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(8) While the existence of small amounts of 4 cannot be ruled out, it is difficult to see how it could be formed by the known cyclopolymerization mechanism (see ref 7).

(9) Proton NMR (500 MHz, 25 °C, CD_3CN) δ 6.31–7.09 (br, 2H, RC*H*=CR_2), 4.05–4.88 (br, 4H, NCH_2CR=CR_2), 3.43 (s, 3H, NCH_3), 3.15 (br, 2H, NCH_2R), 1.78 (br, 2H, NCH$_2$CH_2R), 1.35 (br, 8H, NCH$_2$(CH_2)$_4$-CH$_3$), 0.86 (br, N(CH$_2$)$_5$CH_3). IR (film, cm^{-1}) 2958 (s), 2862 (s), 1636 (s, C=C), 1466 (s), 1256 (vs), 1225 (s), 1163 (vs), 1030 (vs), 638 (s). UV–vis λ_{max} = 520 nm (in DMF), 5.02 nm (in CH_3CN). Anal. Calcd $(C_{14}H_{22}F_3NO_3S)_n$: C, 49.26; H, 6.50; N, 4.10. Found: C, 48.99; H, 6.54; N, 4.09.

(10) A similar poly(dipropargylammonium) salt was reported by: Kang, K.-L.; Kim, S.-H.; Cho, H.-N.; Choi, K.-Y.; Choi, S.-K. *Macromolecules* **1993**, *26*, 4539. The material was of much lower molecular weight and was prepared from an ammonium monomer.

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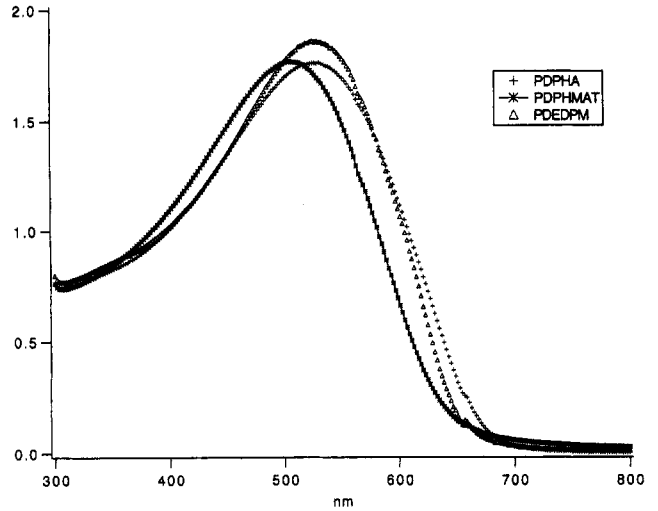

Figure 1. UV–vis spectra of PDPHA, PDPHMAT, and PDEDPM [poly(2,2-dipropargyl diethyl malonate)] in benzonitrile.

650 nm; see Figures 1 and 2A). Unlike PDPHA, PDPHMAT is thermally and environmentally stable; there is no observable change in the IR and UV spectra of a PDPHMAT solution upon exposure to air for 2 weeks. The fact that the polymer resists air oxidation is borne out by the elemental analysis results.

The oxidation and reduction process for films of the two polymers in acetonitrile are working-electrode-material-dependent. Results for both polymers are given below and are relative to Ag/AgCl with 0.1 M $TEAClO_4$ as electrolyte.

PDPHA

On glassy carbon (GC), both oxidation (E_{pa} = +305 mV vs) and reduction (E_{pc} = −1500 mV) processes are chemically and electrochemically irreversible. On Pt, a chemically reversible (electrochemically irreversible; $E_{pa} - E_{pc}$ = 157 mV) reduction (E_{pc} = −1509 mV, return = −1352 mV; $E_{1/2}$ = 1430 mV) is observable only in the first cycle but oxidation (E_{pa} = +402 mV) is irreversible. On Au, the polymer could not be reduced (up to −1700 mV) but could be oxidized with chemical reversibility but electrochemical irreversibility at (E_{pa} = +474, E_{pc} = +184 mV; $E_{pa} - E_{pc}$ = 290 mV). Finally on ITO, no electrochemical process was observable in the range +1000 → −1700 mV.

PDPHMAT

On both GC and ITO glass, the polymer showed only irreversible processes; the oxidation E_{pa} was +1398 and 1371 mV, respectively. The reduction E_{pc} was −835 and −902, respectively. The methylated polymer is clearly more easily reduced and more reluctantly oxidized as compared to the parent polymer. This polymer (polyelectrolyte) was too rapidly soluble from metal surfaces, making it difficult to reproducibly obtain cyclic voltammograms.

Spectroscopic modifications as a function of n-doping (Figure 2A) and changes in conductivity (Figure 2B) as a function of n-doping clearly support the notion of n-self-doping. Doping, in both cases, was carried out with the very mild reducing agent, sodium sulfide, on a film cast from solution onto a quartz plate which had gold contacts evaporated onto it. The *in situ* four-probe conductivity measurement indicates that the conductivity of the sample ($\sigma_{undoped} < 10^{-6}$ S/cm) increases rapidly upon dipping it into a solution of Na_2S in THF and saturates in a few

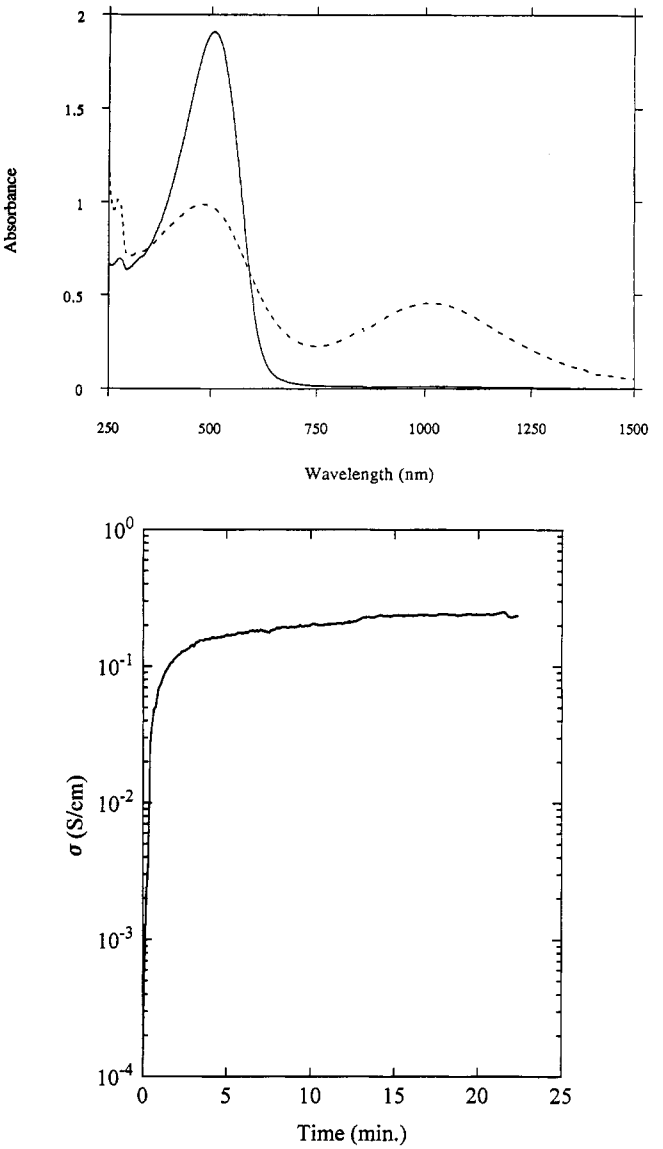

Figure 2. (A, top) UV–vis spectrum of a film of PDPHMAT on quartz immersed in acetonitrile (solid line) and the same film after addition of excess Na_2S. (B, bottom) Plot of the conductivity of a film of PDPHMAT as a function of doping time. Dopant, Na_2S suspension in THF.

minutes. Control experiments showed that the contribution of ionic conduction to the conductivity is negligible ($R_{ionic} \approx 10^3$–10^4 Ω cm; $R_{sample} \approx 5$ Ω cm).

We have shown above that one can prepare an n-dopable conjugated polymer which is amenable to reduction by much milder reducting agents than those used previously (Na, Li) and that the concept of self-doped polymers can be extended to n-dopable polymers. We have also shown that conjugated polymers carrying a positive charge in the neighborhood of the conjugated backbone exhibit increased electron affinity with a concomitant increased stability to the atmosphere. Also consistent with higher electron affinity is a reluctance for the backbone toward oxidation. The electrochemically determined energy gap scales well with the spectroscopically determined π–π^* gap. We have no simple explanation for the observation that unlike the p-self-dopable polymers, the n-self-dopable polymer described above exhibit irreversible redox.

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