that expected for the separate components, perhaps due to energy migration from PS to N via the antenna effect.[18]

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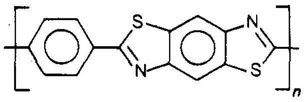
Conductive Polymers Based upon Rigid-Rod Ultrahigh-Modulus Macromolecules. Electrochemical Doping of Poly(*p*-phenylenebenzobisthiazole-2,6-diyl) (PBT)

Rigid-rod benzobisazole-based macromolecules, as exemplified by poly(*p*-phenylenebenzobisthiazole-2,6-diyl) (PBT, I), constitute some of the mechanically strongest



I

and most robust polymeric substances known.[1,2] Especially when processed into a highly ordered and crystalline microstructure, PBT exhibits impressive thermal and environmental stability as well as extremely high tensile strength and modulus.[1,2] In addition to these characteristics, the architecture of the PBT π-electron system suggests a possible pathway for delocalization and charge transport. We address here this latter issue and provide the first evidence that PBT can be electrochemically doped and undoped, either as thin coatings or as extruded, highly oriented free-standing films and fibers, to yield an electrically conductive polymer.[3]

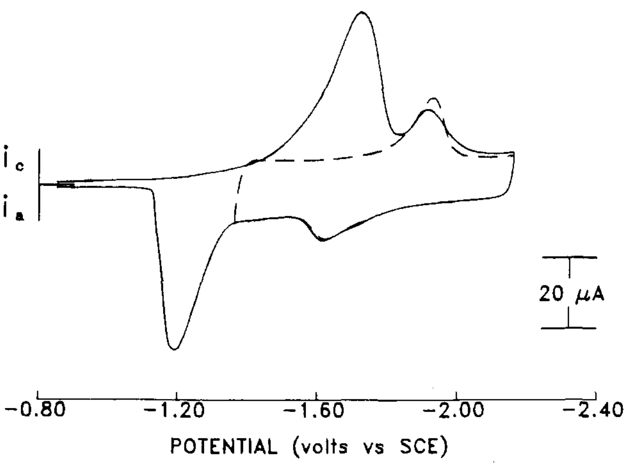


Figure 1. Cyclic voltammetry of a PBT (I) film on Pt in THF/0.1 M tetra-*n*-butylammonium tetrafluoroborate. Solid line: typical CV. Dashed line: CV when potential sweep direction for reoxidation is reversed at −1.35 V. The scan rate is 10 mV/s.

Table I
Electrochemical Data for Films of PBT (I) on a Platinum Electrode and for Dicapped Fragment Compound II in Solution (Volts versus SCE)

	wave	$E_{1/2}$	E_{pc}	E_{pa}
PBT (I)[a]	1	−1.47	−1.70	−1.23
	2	−1.78	−1.92	−1.64
fragment (II)[b]	1	−1.62	−1.66	−1.58
	2	−2.01	−2.06	−1.98

[a] Supporting electrolyte: 0.1 M tetra-*n*-butylammonium tetrafluoroborate in THF. [b] Supporting electrolyte: 0.5 M tetra-*n*-butylammonium tetrafluoroborate in THF.

Films containing known quantities of PBT were cast onto 0.5-cm^2 Pt flag electrodes from fresh 0.1% (w/w) isotropic solutions of PBT[4a] in trifluoromethanesulfonic acid. Films were coagulated with distilled water, soaked overnight in a large excess of distilled water to remove residual acid, and dried in vacuo. Typical dry film thicknesses were on the order of 0.5 μm.[4b] Electrochemical studies were performed under inert atmosphere using rigorously purified THF and tetra-*n*-butylammonium tetrafluoroborate (TBABF$_4$) as the supporting electrolyte. The measurements were made in the three-electrode configuration with a Ag wire quasi-reference electrode and a large-area Pt gauze counter electrode. Potential values were referenced back to the SCE potential by using the ferrocene/ferrocenium couple as an internal standard. As can be seen in Figure 1, the electrochemical reduction of thin PBT films on Pt is chemically reversible.[5] Indeed, repetitive cycling of the films evidences no degradation in current response. The reduction of PBT is accompanied by a change in color from yellow to black, which is completely reversed upon reoxidation.

Two readily identifiable and chemically reversible redox processes are evident in the PBT cyclic voltammogram of Figure 1. Peak potential and half-wave values versus SCE are compiled in Table I. The data exhibit a prominent cathodic peak at −1.70 V and a corresponding anodic peak at −1.23 V, with the difference in peak potentials (ΔE_p) thus being 470 ± 30 mV. This separation is virtually insensitive to IR compensation. Large ΔE_p values are commonly observed in the electrochemistry of conductive polymer films and are usually attributable to redox-related structural reorganization processes within the film.[6,7] This ΔE_p for PBT is one of the largest observed to date for a π-electron conductive polymer. Studies of peak current as a function of scan rate were also carried out and reveal direct proportionality between i_p and v for scan rates between 1.0 and 10 mV/s, as expected for a surface-anchored

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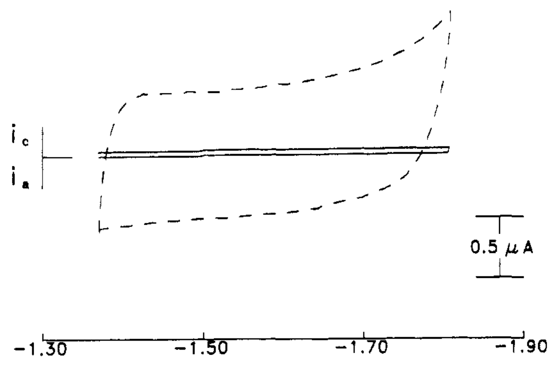


Figure 2. Comparison of the "capacitive" current of a reduced 0.05-μm PBT film on Pt to background current. The Pt electrode is a disk of 0.15-cm diameter. For both voltammograms, the scan rate is 20 mV/s and the supporting electrolyte is THF/0.1 M tetra-*n*-butylammonium tetrafluoroborate. Dashed line: PBT film on Pt. After the first reduction process, the potential sweep direction is reversed at −1.80 V and again at −1.35 V (before oxidation of the film). Solid line: Background current exhibited by a bare Pt disk electrode of the same area.

species.[6,7] Also evident in the PBT cyclic voltammogram is a smaller cathodic peak with $E_{pc} = -1.92$ V and $E_{pa} = -1.64$ V versus SCE. This feature is reproducibly present in all films, is unchanged upon cycling, and appears to arise from a defect, impurity, or second redox process (vide infra) in the polymer.

Figure 1 also reveals substantial background "capacitive" currents[8] for PBT in the reduced state. By reversing the scan direction prior to reoxidation of reduced PBT, it is possible to isolate these effects. They are compared to the background current for a bare Pt electrode of equal area in Figure 2. Such currents are typical of electronically conductive surface-anchored assemblies and are observed in voltammograms of polypyrrole, polythiophene, and many other electroactive polymers.[6-8] As expected,[6,7] the magnitude of the PBT "capacitive" current is also found to be directly proportional to the scan rate.

The number of electrons transferred per PBT repeat unit in the aforementioned cathodic processes can be estimated via eq 1 where Γ = electrode coverage (mol/cm²),

$$\Gamma = Q/nFA \qquad (1)$$

Q = Coloumbs passed (excluding background and "capacitive" currents[8,9]), n = number of electrons, A = electrode area, and F = Faraday's constant.[7a] In order to fix the value of Γ, a film containing a measured quantity of PBT was cast onto a Pt flag electrode by applying 2.0 μL of a 0.1% (w/w) solution of PBT in trifluoromethanesulfonic acid. As already noted and in contrast to many conductive polymers, the "capacitive" features can be readily separated for doped PBT due to the large ΔE_p. The charge associated with each cathodic peak in the cyclic voltammogram can then be related to the respective peak area with exclusion of the "capacitive" effects.[9] The value of n for the first cathodic process is then determined to be ca. 0.6 electron/repeat unit. The calculated n for the smaller cathodic feature at more negative potentials is ca. 0.2 electron/repeat unit.

It is also possible, by using controlled potential techniques,[10] to electrochemically dope highly ordered/crystalline free-standing PBT films and fibers which have been processed[2a,b] for maximum modulus. For example, a 1.5 × 0.75 × 0.002 cm strip of heat-treated uniaxial PBT film[11] can be reversibly doped within two hours at −2.10 V versus SCE (in $TBABF_4$/THF using pressure contacts) to yield a flexible, coppery-black, air-sensitive film. As doping proceeds, the black coloration is observed to spread most rapidly in the orientation parallel to the fiber extrusion (chain axis) direction. Similar observations obtain for heat-treated PBT fibers.[11] For the doped film, an inert atmosphere four-probe dc conductivity measurement in the extrusion direction yields $\sigma = 20 \pm 10\ \Omega^{-1}\ \mathrm{cm}^{-1}$ at room temperature. This result represents a 10^{13} increase in conductivity over undoped[12] PBT. EPR spectra of the undoped PBT film at room temperature reveal a single isotropic signal near the free electron value, having g = 2.0033 and a line width of 3.0 G, typical of a mobile, primarily carbon/nitrogen-centered radical ion.[13] Preliminary X-ray diffraction measurements indicate that the doping process is accompanied by a substantial dimunition in polymer crystallinity.

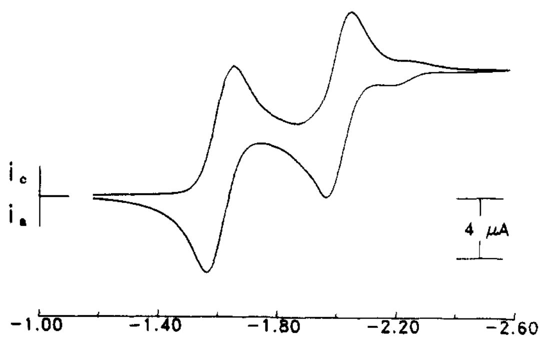
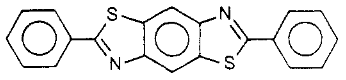


Figure 3. Cyclic voltammetry of the PBT model compound 2,6-diphenylbenzo[1,2-*d*:4,5-*d*′]bisthiazole (II, 3.0 mM) in THF/0.20 M tetra-*n*-butylammonium tetrafluoroborate; the scan rate is 20 mV/s, and the working electrode is a Pt disk.

Cyclic voltammetry of the dicapped PBT fragment molecule 2,6-diphenylbenzo[1,2-*d*:4,5-*d*′]bisthiazole (II)[14]



II

in solution provides an informative contrast to the polymer solid results (Figure 3, Table I). Two reversible faradaic processes are evident, with ΔE_p = 80 mV and i_p <<λdn $\upsilon^{1/2}$ inferring unexceptional, solution-phase one-electron redox processes. Comparison of $E_{1/2}$ values (Table I) indicates somewhat greater thermodynamic stability for the reduced states of the polymeric solid.

These results demonstrate that a rigid-rod, ultrahigh-modulus macromolecule such as PBT can be electrochemically doped and that the resulting electronic structure can support facile charge transport. Equally noteworthy is the observation that the doping process can be effected for such a polymer in a highly ordered and closely packed crystalline microstructure.[2] Further investigations of this and related systems are in progress.

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Extremely High Molecular Weight Polymer Formation Using a Photoinitiation System of Xanthate Fixed at an Oriented Bilayer Surface

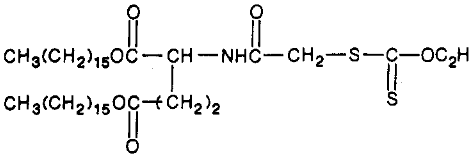
In this paper we present a new polymerizable bilayer system in which a photoinitiator containing two long alkyl chains is fixed at the adjacent polymerizable groups in a bilayer matrix. In such a bilayer system, photopolymerization proceeds smoothly in a bilayer state and the formation of super high polymer is observed under a mild condition.

Polymerizable bilayer membrane is useful for the modification of bilayer physical properties, e.g., increasing mechanical stability and decreasing membrane permeability. Extensive investigations[1] on polymerization behaviors of such polymerizable bilayer membranes have been carried out. In most of such cases, UV irradiation and/or appropriate initiators were employed for initiation of polymerization. However, the position of those initiators resulting from solubilization into bilayer matrix, adsorption on bilayer membrane surface, and so on were not readily fixed near the polymerizable groups and was not always suitable for initiation.

Synthetic bilayer membranes are two-dimensional arrays of molecules and are useful tools for ordering of molecules. The molecular ordering produces various interesting properties. It was found that J-aggregates of anionic cyanine dyes were formed at the charged surface of cationic bilayer membranes[2] and that macroscopic orientations of electron spins were achieved by using anionic Cu^{II} chelates embedded into cationic membrane surfaces.[3] It seems that the well-defined charged surface of bilayer membranes is a suitable vehicle for the regulation of the polymerization of a monomer containing an opposite charge. Regen et al.[4] built "polymer-encased vesicles" by the photopolymerization of dioctadecyldimethylammonium with methacrylate as a polymerizable counterion. Extracted polymer material had an IR spectrum identical with that of an authentic sample of poly(methacrylic acid). They also report data on $\bar{M}_w$ (85 000 in 0.002 M HCl) and tacticity of the poly(methacrylic acid) obtained.

We have reported that bis(isopropylxanthogen) disulfide and xanthate-terminated polymers are useful for a design of well-defined block copolymer because they serve as effective photonitiator and primary radical terminator.[5]

In the present study, we show a new polymerizable bilayer system in which a photoinitiator (1)[6] consisting of two long alkyl chains and a xanthate group which are coupled via a glutamate connector is fixed near polymerizable groups in a bilayer matrix (2).[6]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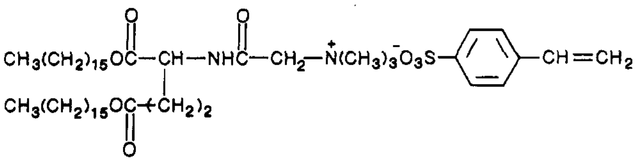
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Clear solution was obtainable when the polymerizable amphiphile (60 mM) was dispersed in water by sonication (Branson Sonifier 250). Kunitake et al. showed that amphiphiles derived from dialkyl glutamate give well-developed bilayer structures.[8] It is expected that 2 would also give a bilayer structure even though styrene sulfonate were used in place of chloride as the counteranion. The aggregation morphology of this new polymerizable amphiphile will be described elsewhere. Differential scanning calorimetry (DSC) gives an endothermic peak at 35.2 °C due to the gel-to-liquid crystal-phase transition (T_c), which

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