Soluble Oligoimide Molecular Lines which have Persistent Poly(anion radicals) and Poly(dianions)

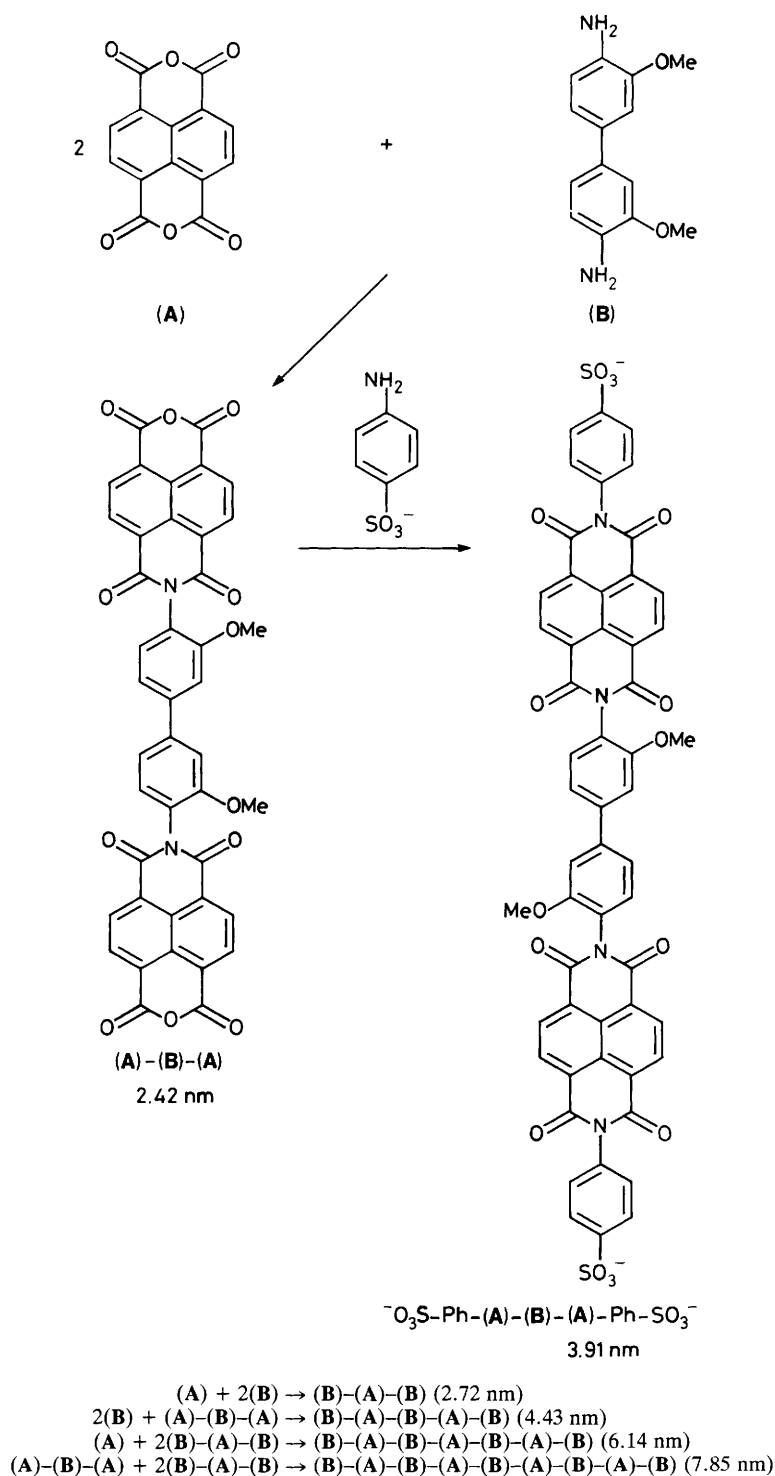**Timothy M. Dietz, Barbara J. Stallman, Wing Sum V. Kwan, Jean Francois Penneau, and Larry L. Miller***
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Linear oligoimides up to 7.85 nm long were prepared, solubilized in trifluoroacetic acid (TFA)/$CHCl_3$, assayed by HPLC, electrochemically reduced, and studied by EPR spectroscopy.

Recent work from this laboratory has demonstrated the unusual properties of 'molecular lines'; rigid rod molecules with defined lengths in the nm range.[1a] It has been shown that these compounds, which are typically polyacene quinones, form organized monolayers,[1] can be imaged using STEM,[2] and form stable anions.[3] The long wavelength (1—2 μm) absorption bands[3] and high conductivity (1 S cm^{-1}) of simple salts of these anions[4] are of considerable interest and suggest that some of the anions can be considered to have mixed valence.[3b] Another laboratory has reported molecular rods in which bicyclobutane groups were used to form small oligomers.[5] We also draw attention to rigid, aliphatic 'spacers' used to study electron transfer rates.[6]

In the present work we set out to develop an alternative set of molecular lines which could be more readily prepared. We chose oligoimides. These compounds are of special interest because of the importance of polyimides as dielectric materials in microelectronics. However, they were unattractive candi-

(A)

(B)

(A)-(B)-(A)
2.42 nm

$^-$O$_3$S-Ph-(A)-(B)-(A)-Ph-SO$_3$$^-$
3.91 nm

(A) + 2(B) → (B)-(A)-(B) (2.72 nm)
2(B) + (A)-(B)-(A) → (B)-(A)-(B)-(A)-(B) (4.43 nm)
(A) + 2(B)-(A)-(B) → (B)-(A)-(B)-(A)-(B)-(A)-(B) (6.14 nm)
(A)-(B)-(A) + 2(B)-(A)-(B) → (B)-(A)-(B)-(A)-(B)-(A)-(B)-(A)-(B) (7.85 nm)

Scheme 1

dates because of the well known insolubility of oligoimides and polyimides. Fortunately, it proved possible to develop a very effective hydrogen-bond donating solvent for dissolution of rigid oligoimides. This allowed spectroscopic characterization and purity determination by HPLC and, therefore, electrochemical and EPR studies.

The synthesis, outlined in the following scheme, utilized 1,4,5,8-naphthalenetetracarboxylic dianhydride (A) and 3,3'-dimethoxybenzidine (B). Compound (A) was chosen in part

for its anticipated electroactivity, while (B) was chosen because it is less toxic than benzidine. Reactions were typically performed in N,N-dimethylacetamide (DMA) as solvent, heating first at 90 °C for a few min, then at 135 °C for 12 h. After cooling, ether was added and the product was filtered then purified by recrystallization. By carefully controlling the stoicheiometry, trimers (A)-(B)-(A) and (B)-(A)-(B) were prepared. Reaction of (A)-(B)-(A) with sulphanilic acid at 135 °C in DMA gave the capped product $^-$O$_3$S-Ph-(A)-(B)-

Table 1. HPLC and electrochemical data.

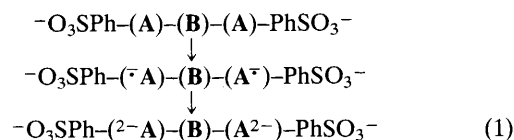| Compound	Retention time^a/min	$E°$ DMF^c /V vs. SCE	$E°$ MeCN^d /V vs. SCE
(A)	5.25	—	—
(B)	3.60	—	—
(A)–(B)–(A)	18.00	0.54, 1.05	—
(B)–(A)–(B)	4.07	0.64, 1.19	—
^-O_3SPh–(A)–$PhSO_3^-$	3.49	0.63, 1.12	0.62, 1.03
^-O_3SPh–(A)–(B)–(A)–$PhSO_3^-$	12.98	0.64, 1.15	0.63, 1.05
(B)–(A)–(B)–(A)–(B)	6.54	0.64, 1.18	—
(B)–(A)–(B)–(A)–(B)–(A)–(B)	3.79^b	0.62, 1.13	—
(B)–(A)–(B)–(A)–(B)–(A)–(B)–(A)–(B)	10.63^b	0.62, 1.14	—

^{a} Column: V_{ydac} 218 TP (5 μ, 4.6 × 150 mm). Eluant: 0.08% TFA in 50% MeCN/50% H_2O. Flow rate: 0.5 ml min^{-1}. ^{b} Flow rate: 0.9 ml min^{-1}. ^{c} ($E_p{}^a$ + $E_p{}^c$)/2, DMF, Bu_4NBF_4 (0.1 M). Sweep rate 100 mV s^{-1}. ^{d} MeCN, Et_4N tosylate (0.1 M).

(A)–Ph–SO_3^-. Larger oligomers resulted from the reactions shown in Scheme 1. An excess of the majority reagent was used to force the reaction to completion and avoid polymerization.

After experimentation with a variety of solvents, including m-cresol and trifluoroethanol, it was found that mixtures of 0.1—10% TFA in methylene chloride or chloroform were the solvents of choice for these compounds. Oligomers as large as (B)–(A)–(B)–(A)–(B)–(A)–(B)–(A)–(B)–(A)–(B)–(A)–(B)–(A)–(B) were soluble with 10% TFA/$CHCl_3$ and it is suggested that this solvent will be widely applicable due to its strong hydrogen-bond accepting character. Using this solvent it was possible to purify these compounds, as ascertained using HPLC (Table 1), and to obtain NMR and IR spectra.

It was anticipated that these materials would be reduced electrochemically,[7,8] and we were interested in the interaction, if any, between units. Surprising to us was the observed stability of the anions. As an example, consider the reduction of Bu_4N^+ $^-SO_3Ph$–(A)–(B)–(A)–$PhSO_3^-$ Bu_4N^+ in MeCN, Et_4N^+ TOS$^-$ (0.1 M), at Pt. Cyclic voltammetry shows two reversible processes (60 mV peak separation and E_p independent of sweep rate) with $E° = -0.63, -1.05$ V vs. standard calomel electrode (SCE). Preparative electrolysis in dimethylformamide (DMF) using a reticulated carbon cathode at -0.8 V gave 1.9 electrons per molecule.† At -1.3 V another 1.8 electrons per molecule were consumed. Thus, the two 60 mV couples in the cyclic voltammogram are each due to $2e^-$/molecule[9] (leading eventually to a hexa-anion!). Thus it is indicated that the two (A) moieties are reduced at nearly identical potentials and that there are negligible interactions between them (equation 1). The thirteen line EPR spectrum of ^-O_3SPh–($^{\cdot}$A)–(B)–(A$^{\cdot}$)–$PhSO_3^-$ has intensities appropriate for coupling to two nitrogens, a_N 0.95 Gauss, and four hydrogens, a_H 1.90 Gauss. This spectrum showed that on the EPR time scale the electron is localized on one (A) group. Further reduction gave the same spectrum until the diamagnetic hexa-anion was obtained. This ion could be reoxidized to starting material. The striking stability of these ions is emphasized by the observation that a reversible $2e^-$ plus $2e^-$ reduction was obtained in the protic medium 20% H_2O/80% MeCN.

$$^-O_3SPh–(A)–(B)–(A)–PhSO_3^-$$
$$\downarrow$$
$$^-O_3SPh–(^{\cdot}A)–(B)–(A^{\cdot})–PhSO_3^-$$
$$\downarrow$$
$$^-O_3SPh–(^{2-}A)–(B)–(A^{2-})–PhSO_3^- \tag{1}$$

The voltammograms of the other compounds in Scheme 1 were quite similar in shape and $E°$ to those described above. In each case studied, the EPR spectrum showed a thirteen line pattern with a_N 0.93 ± 0.02 and a_H 1.87 ± 0.04. Thus, e.g., in the case of (B)–(A)–(B)–(A)–(B)–(A)–(B)–(A)–(B), it is possible to produce a molecular line 7.85 nm long which has four anion radicals or four dianions spaced precisely along its chain.

In conclusion, these preliminary studies have shown that molecular lines with lengths in the range of 2—10 nm can be easily produced and solubilized. Thus the purity can be assured by HPLC, NMR and IR spectroscopies. Electrochemically, the oligomers are well behaved, adding one electron to each naphthalene unit and then at a more negative potential, adding another electron to each unit, giving rather stable polyanions, even in protic media. These materials will allow a variety of studies to be performed which are otherwise not possible, e.g., studies with relevance to microelectronics.

References

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† Most compounds were insoluble in MeCN. Cyclic voltammetry in DMF typically gave ΔE_p ~80 mV. This may result from adsorption of the poorly soluble materials, giving some broadening of the peak.