A Donor−Acceptor Conducting Copolymer with a Very Low Band Gap and High Intrinsic Conductivity

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Conducting polymers with very small band gaps have been prepared by the electrochemical copolymerization of 4-dicyanomethylene-4*H*-cyclopenta[2,1-*b*;3,4-*b'*]dithiophene (**1**) with 3,4-ethylenedioxythiophene (**2**). Strong evidence that the materials formed are true copolymers rather than polymer blends is obtained from Raman spectroscopy and cyclic voltammetry. Both of these techniques also show that the copolymer composition can be controlled by varying the polymerization potential, with the ratio of **1:2** in the copolymer increasing with increasing potential. In situ conductivity measurements as a function of potential clearly show that the copolymers have significantly higher intrinsic conductivities than either homopolymer. Band gaps estimated from these intrinsic conductivities range from 0.33 to <0.16 eV. Band gaps for the 3,4-ethylenedioxythiophene-rich copolymers are too low to be accurately estimated but appear to be close to zero. Cyclic voltammograms are consistent with such low band gaps.

The search for stable organic polymers with low band gaps has been progressing steadily other the past 15 years.[1] Among their many potential advantages,[2−4] such materials will be intrinsic conductors, eliminating the need for doping. A significant number of stable conducting polymers with band gaps below 1 eV are now known.[1]

We have recently reported a study of the in situ conductivity of the low band gap polymer poly(4-dicyanomethylene-4*H*-cyclopenta[2,1-*b*;3,4-*b'*]dithiophene)[5] (poly-**1**) as a function of its doping level.[6] A minimum in the conductivity, at a potential between the formal potentials for p- and n-doping, gave an intrinsic conductivity that was consistent with the optical band gap of ∼0.8 eV. We now report similar measurements on copolymers of **1** with 3,4-ethylenedioxythiophene (**2**).[7,8] Copolymerization with this electron-donating monomer can increase the intrinsic conductivity by more than 5 orders of magnitude to >10^{-3} S cm^{-1}, corresponding to a decrease in the band gap to <0.16 eV.

The rationale for the copolymerization of these two monomers arises from the postulation that copolymers with alternating donor and acceptor subunits will have lower band gaps than the homopolymers.[9] There are

1   **2**
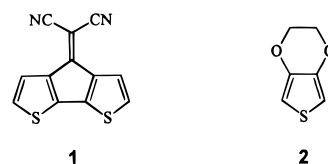
now a significant number of examples in the literature which appear to support this idea, e.g., refs 2, 10, and 11. The new example reported here supports the generality of this strategy for band gap reduction and produces the lowest band gap reported to date for an organic polymer.

Experimental Section

4-Dicyanomethylene-4*H*-cyclopenta[2,1-*b*;3,4-*b'*]dithiophene and 3,4-ethylenedioxythiophene were donated by Philips (The Netherlands) and Bayer Corp. (Pittsburgh, PA), respectively. Nitrobenzene (Fisher, ACS) was dried over CaCl$_2$ and distilled. Acetonitrile (Aldrich, HPLC Grade) and Bu$_4$NPF$_6$ (Fluka, puriss) were used as received.
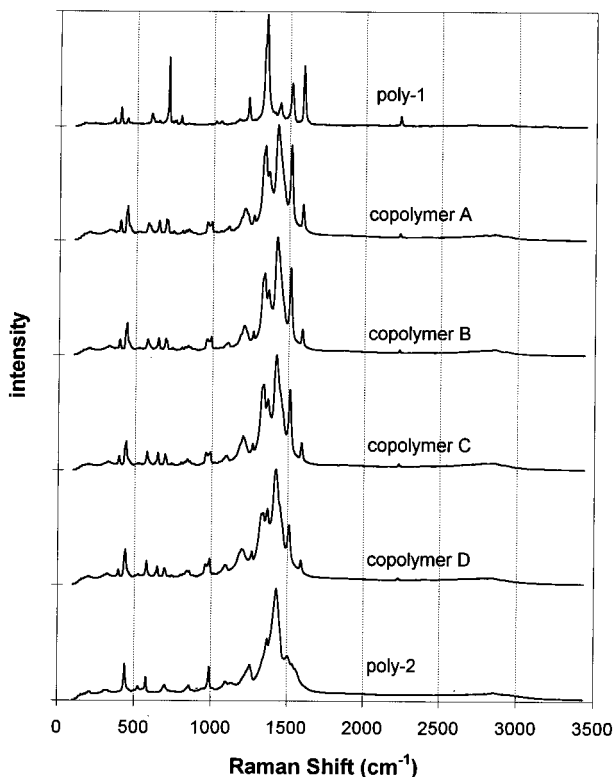
A Pine Instruments RDE4 Potentiostat and a conventional three-electrode cell were used for electrochemical experiments. Polished Pt disks (1.3×10^{-4} or 5.2×10^{-3} cm^2) sealed in glass were used as working electrodes. The dual electrode technique employed for in situ conductivity measurements has been described previously.[6] A fixed potential difference (ΔE_{Pt-Au} = 20 mV) was maintained between the polymer-coated Pt electrode and a gold film coating the polymer while the potential (vs SCE) was slowly scanned (1 mV s^{-1}).

Raman spectra of films on Pt electrodes were recorded using a Reneshaw Raman Imaging Microscope System 1000 using a CCD31 detector and the red line (633 nm) of an argon laser as the excitation source. Films were held at a potential corresponding to the current minimum in their voltammogram between n- and p-doping (see Figure 4) prior to Raman spectroscopy.

Electrochemical Copolymerization. The oxidation potentials for **1** and **2** are very close (E_{pa} = 1.44 and 1.43 V vs

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Figure 1. Raman spectra of poly-**1**, poly-**2**, and copolymer films synthesized at 1.28 (D), 1.30 (C), 1.32 (B), and 1.34 (A) V.
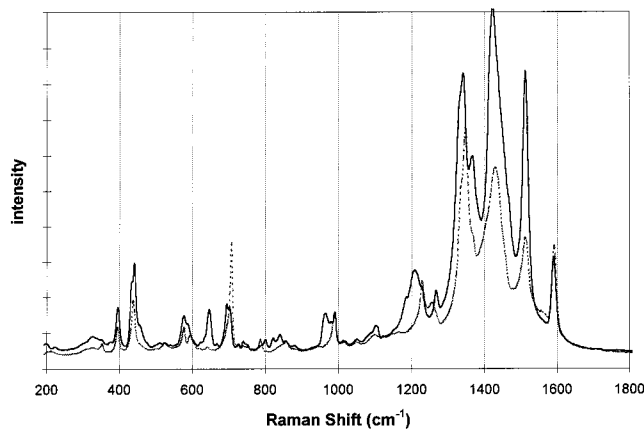
Table 1. Assignments of the Main Bands in the Raman Spectra of Poly-1, Poly-2, and Their Copolymers

poly-**1**		poly-**2**		poly(**1**-*co*-**2**)	
bond	wave-number (cm^{-1})	bond	wave-number (cm^{-1})	bond	wave-number (cm^{-1})
		ethyl C−H	2849	ethyl C−H	2848
C≡N	2230			C≡N	2230
C=C(CN)$_2$	1593			C=C(CN)$_2$	1590
C$_\alpha$=C$_\beta$	1438, 1514			C$_\alpha$=C$_\beta$ (**1**)	1512
		C$_\alpha$=C$_\beta$	1429, 1504	C$_\alpha$=C$_\beta$ (**2**)	1423
		C$_\beta$−C$_\beta$	1370	C$_\beta$−C$_\beta$ (**2**)	1369
C$_\beta$−C$_\beta$	1348			C$_\beta$−C$_\beta$ (**1**)	1341
C−S−C	708	C−S−C	702	C−S−C	695, 701

SCE, respectively), allowing their copolymerization to be achieved and controlled easily by electrochemical methods. Potentiostatic polymerization from a nitrobenzene + 0.1 M Bu$_4$NPF$_6$ solution containing 8 mM **1** and 2 mM **2**, at potentials ranging from 1.26 to 1.34 V, was employed for the synthesis of all copolymer films, unless otherwise stated. Film thicknesses (typically 0.3−0.8 μm) were estimated from the polymerization charge by assuming that 1 C cm^{-2} produces a 4.6 μm thick film. This is the measured relationship for poly-**1**.[6] It probably slightly overestimates the thickness of poly-**2** and copolymer films.

Results and Discussion

Raman Spectroscopy. Figure 1 shows Raman spectra of copolymer films prepared at different potentials together with spectra for films of the two homopolymers prepared under similar conditions. Assignments of the main bands are made in Table 1.[12]

(10) Pagani, G.; Berlin, A.; Canavesi, A.; Schiavon, G.; Zecchin, S.; Zotti, G. *Adv. Mater.* **1996**, *8*, 819.

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Figure 2. Raman spectrum of a copolymer film prepared at 1.34 V (solid, A from Figure 1) and a simulated spectrum of a blend of poly-**1** and poly-**2** (dashed, average of the poly-**1** and poly-**2** spectra from Figure 1).

It is clear from the spectra in Figure 1 that the films prepared from the mixture of monomers are true copolymers rather than simply blends of the two homopolymers. This is shown more clearly in Figure 2, where the spectrum of copolymer A is compared with a simulated spectrum for a blend, created by adding spectra of the two homopolymers (the spectra have been normalized to approximately match the heights of the peaks at 1593 and 2230 cm^{-1} due to the C=C(CN)$_2$ group, which are the least affected by copolymerization). The most notable differences are in the 1200−1300 cm^{-1} region, where C$_\alpha$−C$_\alpha$ inter-ring bands are found.[12] The new band at ∼1206 cm^{-1} in the copolymers can be assigned to the C$_\alpha$−C$_\alpha$ bond between monomer **1** and monomer **2** units.

The new band at 964 cm^{-1} in the copolymer spectra is probably due to the C$_\beta$−H bend of monomer **1** units that are adjacent to monomer **2** units. This band occurs at 990 cm^{-1} in the homopolymer. The new band at 648 cm^{-1} can probably be assigned to a C−S−C ring deformation, which would be expected to be significantly shifted in a copolymer. The corresponding bands in the homopolymers are presumably those at 596 cm^{-1} in poly-**1** and 578 cm^{-1} in poly-**2**. The 578 cm^{-1} band and the shoulder at ∼590 cm^{-1} are still seen in the copolymer spectra.

The observations described above and the shifts in other bands detailed in Table 1 are all consistent with the formation of a C$_\alpha$−C$_\alpha$-linked random copolymer. The relative intensities of the C≡N (2230 cm^{-1}) and C$_\alpha$=C$_\beta$ (**2**) (1423 cm^{-1}) bands show that the ratio of monomer **1** to monomer **2** in the copolymer increases as the polymerization potential is increased. This is consistent with the higher potential required to oxidize **1**.

Cyclic Voltammetry. Figure 3 shows cyclic voltammograms of the two homopolymers and a poly(**1**-*co*-**2**) film synthesized by potential scanning between 0 and 1.45 V (17 cycles at 100 mV s^{-1} in nitrobenzene containing 0.1 M Bu$_4$NPF$_6$, 8 mM **1**, and 2 mM **2**). The voltammogram of poly-**1** exhibits p-doping/undoping peaks at a formal potential (E°′) of ca. +0.9 V and n-doping/undoping peaks at E°′ ∼ −0.65 V, correspond-

(12) Louarn, G.; Buisson, J. P.; Lefrant, S.; Fichou, D. *J. Phys. Chem.* **1995**, *99*, 11399−11404.
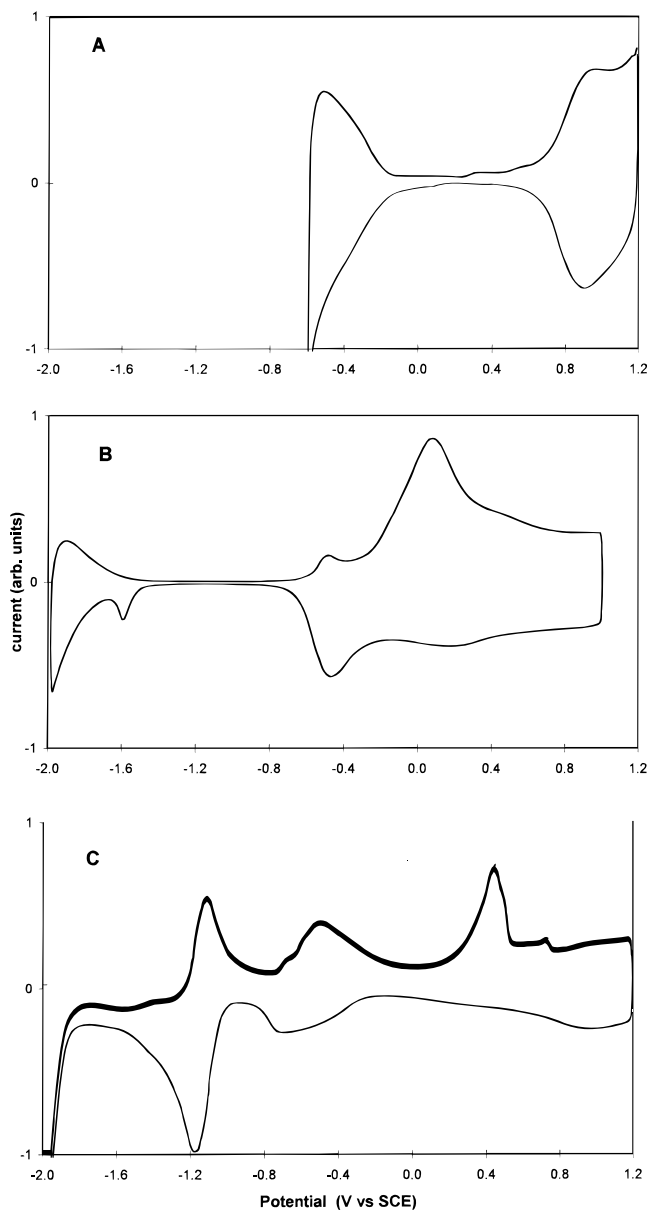
Figure 3. Cyclic voltammograms at 100 mV s^{-1} of poly-**1** (A), poly-**2** (B), and poly(**1**-*co*-**2**) (C) films in acetonitrile containing 0.1 M Bu$_4$NPF$_6$.

ing to a band gap of ca. 0.8 V between the onsets of p- and n-doing. p-Doping/undoping of poly-**2** occurs over a broad potential range (ca. from −0.7 to > +1.2 V) encompassing both the p- and n-doping regions of poly-**1**. Suitable overlap of the orbitals of **1** and **2** might therefore be expected to produce a material with no band gap. n-Doping of poly-**2** begins at ca. −1.6 V, corresponding to a band gap of ca. 1.2 eV.[13]

Cyclic voltammograms of copolymers of **1** and **2** (e.g. Figure 3 (solid line)) show p-doping/undoping over a wide potential range, coinciding with that observed for poly-**2**, and relatively narrow n-doping peaks at E°′ ∼ −0.6 V, approximately coincident with those of poly-**1**. A second n-doping/undoping wave appears at E°′ ∼ −1.1 V. The onsets of p- and n-doping overlap significantly, indicating that the band gap is very small or that there is no band gap.

(13) Fu, Y. P.; Cheng, H. T.; Elsenbaumer, R. L. *Chem. Mater.* **1997**, *9*, 1720−1724.
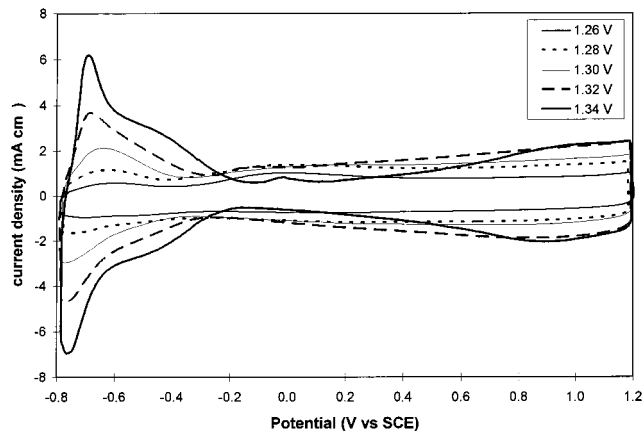
Figure 4. Cyclic voltammograms (at 100 mV s^{-1} in acetonitrile containing 0.1 M Bu$_4$NPF$_6$) of poly(**1**-*co*-**2**) films prepared at various potentials (100 s polymerization time) as indicated.

Figure 4 shows voltammograms of copolymer films prepared at different potentials. As the polymerization potential is increased, the peaks a ca. −0.6 V due to n-doping of polymer segments rich in **1** increase relative to the p-doping region. This reflects the increasing **1:2** ratio indicated by the Raman results (Figure 1). Interestingly, the potential of these peaks does not shift significantly with changing composition (although they do appear to split into two separate waves), indicating that the n-type charge carriers formed by **1** are not extensively delocalized. This conclusion is supported by the fact that the reduction wave of **1** shifts very little with polymerization.[5]

Only the films with the highest **1:2** ratio (solid lines in Figures 3 and 4) show a significant feature at ca. +0.9 V that could be attributed to p-doping of poly-**1**. This provides further strong evidence that we are dealing with true copolymers, rather than polymer blends. On the basis of the size of the −0.6 V peaks in Figure 4 and the similar heights of the p- and n-doping waves of poly-**1** (Figure 3), all of the copolymer films would have shown significant peaks at ca. +0.9 V, if they were mixtures of poly-**1** and poly-**2**.

The p- and n-doping/undoping processes observed in the voltammograms in Figures 3 and 4 were stable over many cycles (>30 between −1.5 and +1.2 V). Peak currents were linear with scan speed over the 20−100 mV s^{-1} range employed.

The cyclic voltammograms in Figure 4 were used to estimate the compositions of the films as follows. The charge under the p-undoping wave from +1.2 V to ∼ −0.2 V was separated into components for **1** and **2** in the copolymer, $Q_{p,1}$ and $Q_{p,2}$, by assuming that $Q_{p,1}$ is the same as the n-undoping charge from −0.6 V to ∼ −0.2 V. This assumption is based on the approximate equality of these two charges for the homopolymer of **1** under similar conditions. The mole ratio of **1:2** was then obtained by using eq 1

$$\text{mol } \mathbf{1}/\text{mol } \mathbf{2} = (Q_{p,1}/Q_{p,poly-1})/(Q_{p,2}\ Q_{p,poly-2}) \quad (1)$$

where $Q_{p,poly-1}$ and $Q_{p,poly-2}$ are the p-undoping charges for films of the two homopolymers prepared using equal charges (40 mC cm^{-2}). The results are given in Table 2.
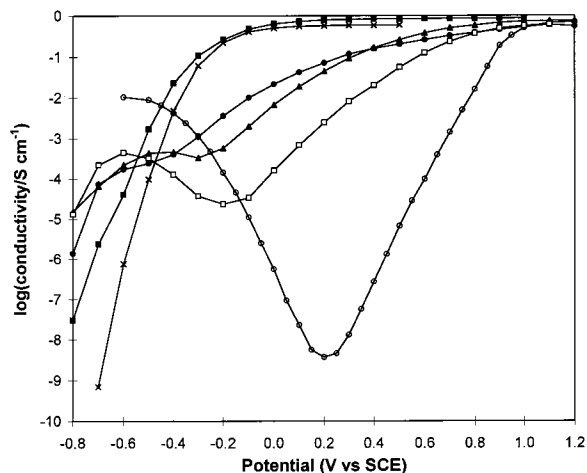
Figure 5. In situ conductivity vs potential profiles for poly-**1** (○), poly-**2** (×), poly(**1**-*co*-**2**) films prepared at 1.31 (■), 1.32 (●), 1.33 (▲) and 1.34 (□) V.

Table 2. Estimated Compositions [*x* in Poly(1ₓ-*co*-2)] from the Cyclic Voltammograms Shown in Figure 4.

synthesis potential (V vs SCE)	1:2 ratio in copolymer
1.26	0.31
1.28	0.46
1.30	0.96
1.32	1.2
1.34	2.5

Electronic Conductivity. Figure 5 shows plots of in situ electronic conductivity vs potential for poly-**1**, poly-**2**, and various poly(**1**-*co*-**2**) films. Despite the low potential scan rate (1 mV s⁻¹) used during collection of these data, there was hysteresis between conductivities obtained from cathodic and anodic scans, particularly for poly-**2** and the copolymer prepared at 1.31 V. The data shown in Figure 5 are for cathodic scans. Similar trends with changing composition were observed in data from anodic scans.

The in situ conductivity of poly-**1** has been discussed in detail elsewhere.[6] The intrinsic conductivity measured close to the minimum (∼0.2 V) between the regions of n- and p-type conductivity is consistent with the spectroscopic and electrochemical band gap of ∼0.8 eV. The p-conductivity of poly-**2** (Figure 5, ×) extends to much lower potentials than that of poly-**1** and overlaps considerably with the n-type conductivity of poly-**1**. At potentials below ca. −0.3 V, it decreases rapidly, reaching values far below the intrinsic conductivity of poly-**1** at potentials below −0.7 V. The intrinsic conductivity of poly-**2** is too low to be measured by our technique, but can be estimated to be ca. 10⁻¹² S cm⁻¹ from the band gap of 1.2 eV estimated above.[6]

The conductivity profiles of the copolymers (Figure 5) are in most cases intermediate between those of the two homopolymers. Both homopolymers and all of the copolymers have a maximum conductivity (p-type) of ca. 0.5 S cm⁻¹. The decrease in conductivity as the potential is decreased begins earliest for poly-**1** and latest for the copolymer prepared at 1.31 V. It is intermediate for the other copolymers, moving to lower potentials as the content of **2** is increased (lower polymerization potential). Like poly-**1**, all of the copolymers exhibit higher conductivity than poly-**2** at potentials below ca. −0.4 V. This indicates that they develop n-type con-

ductivity in this potential region due to reduction of sites rich in **1**. The maximum n-type conductivity (at ca. −0.7 V) increases with an increasing ratio of **1:2**. The three copolymers with the largest **1:2** ratios exhibit a conductivity minimum between the n- and p-doping regions that can be used to estimate the band gap (see below). The position of this minimum occurs at more negative potentials as the **1:2** ratio is decreased

Estimation of Band Gaps. As discussed in ref 6, the intrinsic conductivity is somewhat higher than the minimum conductivity in a conductivity vs potential plot because the p-type charge carriers are more mobile than the n-type carriers. Since $\mu_p \gg \mu_n$ (μ = mobility), the intrinsic conductivity of the polymer (when $C_n = C_p$; C = concentration of charge carriers) is dominated by p-type carriers. The potential at which $C_n = C_p$ ($E_{intrinsic}$) can be estimated from:[6]

$$E_{intrinsic} = E_{min} - 0.038 \log(\mu_n/\mu_p) \qquad (2)$$

where E_{min} is the potential of the conductivity minimum. The band gap (E_g) can be estimated from the intrinsic conductivity ($\sigma_{intrinsic}$) by using[14]

$$C_{p,intrinsic} = \sigma_{intrinsic} C_{p,max}/\sigma_{p,max} \sim 4.2 \times 10^{-5} \exp(-E_g/2kT) \quad (3)$$

where $C_{p,max} \sim 8.5 \times 10^{-4}$ mol cm⁻³.[6] Data for these calculations and estimated band gaps are shown in Table 3 for the copolymers which exhibited a conductivity minimum between the n- and p-doping regions. From these data, it can be seen that the band gap decreases with increasing content of **2**. This is to be expected since the onset of n-doping is relatively insensitive to composition (see Figure 4) while the onset of p-doping shifts to lower potentials as the content of **2** is increased. By extrapolation, the copolymers prepared at potentials below 1.32 V would be expected to have band gaps below the minimum value of 0.19 eV reported in Table 3. The conductivity profile for the film prepared at 1.31 V is consistent with this hypothesis in that it exhibits significantly higher conductivities than poly-**2** in the expected n-doping region (ca. from −0.3 to −0.8 V) but no conductivity minimum. Unfortunately, the absence of a conductivity minimum makes it difficult to estimate the band gap for this film. However, if we assume that $E_{intrinsic} = -0.34$ V, as for the film prepared at 1.32 V, then we obtain an estimated band gap of zero for data from a cathodic scan and 0.16 eV for data from an anodic scan (note that the hysteresis in the conductivity profile was largest for this copolymer). Since we have almost certainly assumed an $E_{intrinsic}$ that is too anodic, we can conclude that the band gap of the film prepared at 1.31 V was significantly lower than 0.16 eV and probably close to zero. The absence of a significant band gap is consistent with the voltammetric results shown in Figure 4.

The mobility ratios for the copolymers [$\mu_n/\mu_p \sim 0.002$ (Table 3)] are significantly less than for poly-**1** ($\mu_n/\mu_p \sim 0.025$).[6] This is presumably because the n-doped sites are diluted and therefore less mobile.

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Table 3. Conductivity Data and Band Gaps for Selected Copolymers

$E_{polymerization}$ (V vs SCE)	$\sigma_{p,max}$ (S cm^{-1})	$\sigma_{n,max}$ (mS cm^{-1})	$C_{n,max}/C_{p,max}$	η_n/η_p	$E_{intrinsic}$ (V)	$\sigma_{intrinsic}$ (mS cm^{-1})	band gap (eV)
1.32	0.6	0.22	0.2	0.0018	−0.34	0.69	0.19
1.33	0.74	0.48	0.3	0.0022	−0.19	0.68	0.21
1.34	0.62	0.44	0.4	0.0018	−0.11	0.052	0.33

Conclusions

Copolymerization of **1** with **2** appears to have little influence on the potential at which the dicyanoethene-bridged bithiophene moiety is reduced. This presumably arises because the n-type charge carriers thus generated are not significantly delocalized beyond the bithiophene unit. This leads to facile n-doping of all of the copolymers.

In contrast, p-type charge carriers are more delocalized so that the potential at which they begin to form is strongly dependent on the composition of the copolymer. As the ratio of the electron-rich 3,4-ethylenedioxythiophene moiety to the electron-deficient dicyanoethene-bridged bithiophene moiety is increased, p-doping becomes easier and the band gap of the polymer decreases. The mobility of the p-type carriers remains high because the electrons are delocalized.

As a consequence of these effects, copolymers with vanishingly small band gaps and high intrinsic conductivities can be produced. The low mobility of the n-type carriers in such materials is of little consequence since their intrinsic conductivities are dominated by the more mobile p-type carriers.

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