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# Conductivity and Third-Order Nonlinear Optical Measurements of Polymers with Distyrylbenzene and Diphenylbutadiene Segments

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New polymers were synthesized with discrete conjugated hydrocarbon segments alternating with flexible spacer groups. These processable polymers were designed for third-order nonlinear optical and conductivity studies for comparison with "fully-conjugated" polymers. The present materials contain distyrylbenzene or diphenylbutadiene units and have the advantages of solubility and melt processibility over "fully-conjugated" systems such as poly(acetylene). They were found in degenerate four-wave mixing experiments to have third-order optical susceptibilities in the range of $3 \times 10^{-12}$ esu. These values are within an order of magnitude of the $\chi^{(3)}$ value reported for unaligned poly(phenylenevinylene). Electrical conductivity measurements using $I_2$ and $H_2SO_4$ dopants, however, provided materials with conductivities from $2 \times 10^{-5}$ to $7 \times 10^{-5}$ $\times\ 10^{-5}$ S/cm, far lower than poly(phenylenevinylene).

## Introduction

Conjugated organic materials are unique in having both large optical nonlinearities and subpicosecond response times (in the nonresonant regime). Fully conjugated polymers, such as poly(acetylene) and poly(*p*-phenylenevinylene) (PPV), have often been chosen for third-order NLO studies, since they promise the greatest possible electron delocalization for organic materials.[1-3] However, the number of nuclei over which the $\pi$-orbital electrons are delocalized is limited in these materials due to bond-length alternation. Kuhn[4] showed spectroscopically that an equilibrium configuration in poly(acetylene) with all bond lengths equal at 1.389 Å was less stable than one in which bond lengths alternated between 1.346 and 1.463 Å. The presence of the longer "single" bonds disrupts bond conjugation. This makes such polymers poor vehicles for understanding the relationship of conjugation length to the magnitude of $\chi^{(3)}$, because a mixture of conjugation lengths is inherent to their structures.

Different conjugation lengths have inherently different hyperpolarizabilities. In addition, each conjugation length has a unique UV cutoff and is thus at a different proximity to resonance with input and output radiation.[5] For this study, therefore, polymers with well-defined conjugated segments of appreciable length were chosen as model chromophores to investigate the effect of appreciable length were chosen as model chromophores to investigate the effect of conjugation length on third-order NLO response. Distyrylbenzene, with its alternating phenylene and vinylene groups, is a three aromatic ring analogue of the frequently studied poly(phenylenevinylene). Bradley and Mori[6] provided further inspiration for the design of the present systems by following the changes in $\chi^{(3)}$ accompanying the curing of precursor-route PPV to the "all-conjugated" form, thus observing how $\chi^{(3)}$ accompanying the curing of precursor-route PPV to the "all-conjugated" form, thus observing how $\chi^{(3)}$ varies with average conjugation length.

In separate studies, an extensive series of main-chain poly(ethers) and poly(esters) combining diphenylbutadiene (DPB) and distyrylbenzene (DSB) groups with flexible alkyl spacer groups was synthesized, and most resulting polymers were found to be thermotropic liquid crystals.[7] Through NMR and IR analysis, the vinylene groups were found to be predominantly trans. An ethoxy substituted DSB polyester with heptane spacer (EtO7) and the DSB polyaramid (PA), both shown in Figure 1, were not liquid crystalline. In addition, the methyl-substituted DPB poly(ester) with pentane spacer (MBD-5) also shown in Figure 1 was liquid crystalline (LC), but a clear film could be produced by exposure to UV light with solvent present, due to cis–trans isomerization of the unsaturations, probably combined with slight degradation.[7] Since optical clarity is necessary for NLO measurements, the non-LC materials allowed $\chi^{(3)}$ values to be obtained for the unaligned situation using degenerate four wave mixing techniques. The resulting $\chi^{(3)}$ measurements of these new polymers are discussed here. The additional LC materials leave the possibility of future measurements on samples aligned into transparent monodomains.

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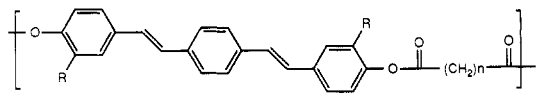
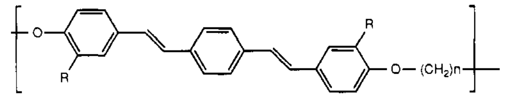
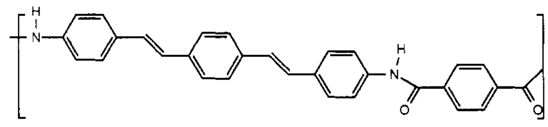
DSB Polyesters (EtO5, EtO6, EtO7, MeO8)



DSB Polyethers (MeO7/9)



DSB Polyaramid



DPB Polyester (MBD5)

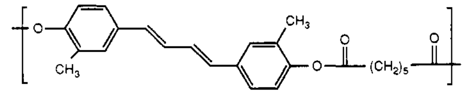


**Figure 1.** Structures of polymers examined in this study. R = ethoxy, methoxy; numbers in designation refer to spacer length(s).

Polymers with the DSB and DPB chromophores offered further opportunities for study. The electrical conductivity of doped fully conjugated systems has been extensively investigated,[8,9] and again evidence of limited delocalization of electrons has been observed. For example, Karasz and Obrzut[10] found that in the conductive regions in $LiAsF_6$-doped PPV p-type carriers were delocalized over regions 3–4 aromatic rings long. The DSB polymers (which are themselves phenylenevinylene analogues) have discrete conjugation lengths that enable the measurement of conductivity in which current must be largely carried between mesogenic groups. Several of the thermotropic polymers also have a smectic mesophase which is largely retained in the solid state. By doping such polymers, it was possible to restrict conduction to the plane of the mesogens. Results of our conductivity studies of these new polymers are reported and the effect on conjugation length and structure on these properties is discussed.

## Experimental Section

The synthesis and characterization of these polymers was described elsewhere[11,12] with the exception of the polyaramid, the synthesis of which is reported below. The naming and structure of these polymers are shown in Figure 1. The intrinsic viscosities of Et05 and MBD-5 were 0.33 and 0.36 dL/g respectively.

**Synthesis.** Reactions were run under prepurified nitrogen supplied by Pipe Welding Supply Co. Inc. Reagents were supplied by the Aldrich Chemical Co. and used without further purification except where noted. Reagent-grade solvents were supplied by Fisher Scientific and were used without purification except as follows: absolute ethanol (Quantum Chemical Corp., U.S.I. Division) was purified by distillation under nitrogen from 3-Å molecular sieves dried by evacuation at 150–160 °C; DMF was distilled from vacuum-dried BaO; carbon tetrachloride and 1,2-dichloroethane were distilled from $P_2O_5$; xylenes were distilled without a drying agent. Hexamethylphosphoramide (HMPA, 99%) and 1-methyl-2-pyrrolidinone (NMP, 99%) were vacuum-distilled through a 6-in. Vigreux column.

Melting points of monomers were determined on a Fisher-Johns melting point apparatus and are uncorrected. $^1$H NMR spectra were obtained on a Varian XL-200 spectrometer referenced to TMS at 0.00 ppm. Infrared spectroscopy (KBr) was made using 200 scans on an IBM Instruments IR/98 FTIR spectrometer. Elemental analysis was performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark. Intrinsic viscosity was measured with a Cannon-Ubbelohde 100 viscometer, using a Cannon Instruments Co. water bath and temperature controller at 35 °C.

*1,4-Bis[2-(4-nitrophenyl)ethenyl]benzene.* This synthesis was performed in the same manner used by Campbell and McDonald for similar compounds.[13] In a 2000-mL three-necked round-bottom flask equipped with an oil bubbler, a magnetic stirrer, and a condenser was prepared a solution of 25.0 g (164 mmol) of *p*-nitrobenzaldehyde and 56.3 g (71.0 mmol) of *p*-xylylenebis(triphenylphosphonium chloride) in absolute ethanol. To this was added 800 mL of 0.2 M lithium ethoxide (prepared from 99.8% lithium from Sargent Welch Co. and absolute ethanol) at room temperature under nitrogen. A yellow precipitate formed immediately, accompanied by a mild exotherm. Stirring was continued for 16 h, after which the precipitate was filtered and dried. The yellow solid (25.6 g) was dissolved in xylene, decolorized with charcoal, and refluxed for 4 h in the presence of a trace of iodine. From this solution precipitated 14.3 g (51.5%) of orange crystals: mp 285–287 °C (lit.[13] 285–288 °C; liquid-crystalline, as previously reported,[13] remaining birefringent from the melting point to above 300 °C); IR (KBr) 1590 s, 1509 s, 1334 vs, 1105 m, 959 m cm$^{-1}$. Anal. Calcd for $C_{22}H_{16}N_2O_4$: C, 70.96; H, 4.30; N, 7.53. Found: C, 70.92; H, 4.52; N, 7.24.

*1,4-Bis[2-(4-aminophenyl)ethenyl]benzene (DA-1).* The reaction was carried out in a manner analogous to the preparation of 4,4′-diaminostilbene by Huang-Minlon.[14] To a 300-mL three-necked round-bottom flask equipped with an oil bubbler, a magnetic stirrer, and a condenser were added 5.0 g (13.4 mmol) of 1,4-bis[2-(4-nitrophenyl)ethenyl]benzene, 150 mL of 2-hydroxyethyl ether (99%), 9.5 mL (192 mmol) of hydrazine hydrate, and 7.30 g (111 mmol) of KOH. The mixture was refluxed under nitrogen for 1 h, and the reflux condenser was replaced with a distillation head. Water was distilled from the dark brown mixture until the temperature of the reaction reached 200 °C. Refluxing was then resumed for 3 h, with little change in the appearance of the reaction mixture. The mixture was cooled to room temperature, allowed to stand overnight, then poured into water, filtered, and dried. The residue was recrystallized from DMF to yield 3.07 g (66.3%) of a light brown-orange solid: mp 300–303 °C (lit.[13] 303 °C); IR (KBr) 3387 m, 1604 s, 1519 s, 969 vs, 834 vs cm$^{-1}$; $^1$H NMR (DMSO) $\delta$ 5.37 (br s, 4 H, $-NH_2$), 6.55, 7.28 (doublets, 4 H arom), 6.86, 7.07 (doublets, 2 H, $=CH-$), 7.45 (s, 4 H, arom). Anal. Calcd for $C_{22}H_{20}N_2$: C, 84.62; H, 6.41; N, 8.99. Found: C, 83.27; H, 6.64; N, 8.71.

*Polyaramid Synthesis.* This polymerization was performed in the manner of Bair et al.[15] To a 300-mL three-necked round-bottom flask equipped with a magnetic stirrer, a septum, and an oil bubbler was added 1.00 g (3.21 mmol) of dried DA-1. Via double-ended needle, 25 mL of distilled HMPA and 10 mL of NMP were added under dry nitrogen. This mixture was stirred at 0 °C for 15 min, after which 0.651 g (3.21 mmol) of dry terephthaloyl chloride (99+%) was added. The orange-brown mixture was allowed to stir overnight, gradually warming to room

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temperature. The mixture was then poured into water and filtered. The residue was washed thoroughly with water and then extracted with acetone for 24 h. The residue was then dried to yield 0.406 g (28.7%) of a green-brown solid: infusible, began to decompose at approximately 350 °C; IR (KBr) 3367 br, w, 3025 w, 1719 m, 1518 vs, 962 m cm$^{-1}$. The intrinsic viscosity was 0.17 dL/g at 35 °C in NMP.

**Degenerate Four-Wave Mixing.** Measurements were made of both solutions containing 1 wt % polymer in NMP and of thin films cast from NMP solutions which had been filtered through 0.5-$\mu$m Millipore filters. The films were cast onto fused quartz disks and were all approximately 5 $\mu$m thick, thicknesses were measured using an Alpha Step profilometer.

The DFWM experiments were performed using a light source which was a mode-locked doubled Nd:YAG laser at 532 nm (Coherent) synchronously pumping at 598 nm (rhodamine 6G) with amplification provided by a Spectra-Physics pulsed dye amplifier system. The pulse duration was 5–6 ps, the spot size was 1.5 mm at the sample, and the forward beam carried approximately 30 $\mu$J/pulse. The values of $\chi^{(3)}$ were determined at 598 nm relative to carbon disulfide, CS$_2$, which has a $\chi^{(3)}$ of 6.8 × 10$^{-13}$ esu[16] (at 532 nm). The experimental (sample) intensities ($S_s$) were compared to the reference values for CS$_2$ ($S_r$) using the following expression:

$$\frac{\chi_s^{(3)}}{\chi_r^{(3)}} = \left[\frac{n_s}{n_r}\right]^2 \left[\frac{I_r}{I_s}\right]^{3/2} \left[\frac{L_r}{L_s}\right] \left[\frac{\alpha_s L_s}{(1 - e^{\alpha_s L_s}) e^{-\alpha_s L_s/2}}\right] \sqrt{\frac{10^{-\zeta} S_s}{S_r}} \quad (1)$$

Here, $n$ = refractive index, $L$ = sample length (film thickness), $\alpha$ = absorption coefficient, $I$ = intensity of the beam used for sample measurement, and $\zeta$ = 1.488, the ratio of the intensity of the input beam used for the reference measurement to the intensity used for the sample measurement. Absorption coefficients were measured on a Perkin-Elmer Lambda 9 UV-vis spectrophotometer. The refractive index of one of the polymers, EtO5, was determined at 600 and 595 nm to be 1.5924, and 1.5934, respectively using laser interferometry.[17] A value of 1.6 was used for the other two films, and $n_r$ of 1.628 was used for CS$_2$.

**Conductivity Measurements.** Films were cast from NMP solution and filtered through Millipore 0.5-$\mu$m filters. The films to be doped were dried overnight in vacuum at 60 °C, and then their thicknesses were measured using an Alpha Step profilometer. The films were all approximately 10 $\mu$m thick, and conductivity was measured across a 5-mm width. Voltage was supplied by a TCR voltage supply (Electronic Measurement Inc., Neptune, NJ). Voltage was measured with a Fluke 87 True RMS multimeter, and current was measured with a Fluke 77 multimeter (Fluke International Corp., Everett, WA).

Iodine and H$_2$SO$_4$ doping were carried out in the controlled-atmosphere apparatus used to measure conductivity. Electrical connection to the films was made with Electrodag carbon paint. Current was measured at 80, 160, 240, 350, and 440 VDC. Two films were routinely doped and measured together to check repeatability.

In the case of iodine, the apparatus was sealed with atmospheric air for 24 h, and then it was opened, the crystals were removed, and the apparatus was resealed and exposed to room temperature dynamic vacuum for 24 h. In the case of H$_2$SO$_4$, the samples and dopant were simply exposed to room temperature dynamic vacuum for 72 h. Conductivity measurements were made without the removal of residual acid. All measurements were made with the apparatus sealed under static vacuum.

## Results and Discussion

**Degenerate Four-Wave Mixing.** Table I provides a comparison between the measured $\chi^{(3)}$ values of the polymers in this study and those previously reported for poly($p$-phenylenevinylene) (PPV), by DFWM. Values from third harmonic generation (THG) are shown for reference. Control specimens consisting of the quartz plates without polymer films always gave null values of $\chi^{(3)}$ relative to CS$_2$.

**Table I. $\chi^{(3)}$ Values and Comparison to PPV**

| material | $\chi^{(3)}$ (10$^{-12}$ esu) | method | wavelength,[a] nm |
|---|---|---|---|
| MBD5 | 2.2 ± 0.1 | DFWM | 598 |
| EtO7 | 2.6 ± 0.4 | DFWM | 598 |
| polyaramid (PA) | 3.1 ± 0.5 | DFWM | 598 |
| PPV[22] | 75 | THG | 355 |
| PPV[24] | 7.8 | THG | 602 |
| PPV[24] | 5.0 | THG | 702 |
| PPV[23] | 20 | DFWM | 650 |
| PPV[23] | 120 | THG | 355 |
| PPV[27] | 400[b] | DFWM | 580 |

[a] Wavelength values in THG studies refer to the third harmonic. [b] Parallel to oriented chains (perpendicular value is 37 times smaller).

The $\chi^{(3)}$ values obtained with these polymers in NMP solution exhibited the same trend among the three materials as did the thin films which had values of ~2 × 10$^{-12}$ esu (Table I). The solution values were uniformly ~2 orders of magnitude smaller than the film values because the solutions contained approximately 1% as great a volume concentration of NLO chromophore as the films. Major sources of error were laser shot to shot instabilities and film thickness variations.

The polyaramid had the highest volume concentration of chromophore of the three and also had the highest $\chi^{(3)}$ value. It was expected that MBD5 would have the lowest $\chi^{(3)}$ value, since its chromophore contained fewer double bonds than the other two materials and the preparation process may have reduced the concentration of conjugated segments. However, all three samples prepared for this study were very close in terms of their $\chi^{(3)}$ response, and the results cannot be used to support a power-law dependence of $\chi^{(3)}$ on conjugation length.

Typical values for the UV–vis absorption edge and peak maximum of PPV are 520 and 430 nm, respectively.[18,19] Therefore, any values reported at 355 nm represent resonant values. The spectral cutoffs for MBD-5, EtO5, and PA are 392, 406, and 470 nm, respectively. Their respective absorption maxima are 346, 357, and 386 nm. One value from an aligned material is included in Table I in order to demonstrate the importance of alignment; the largest $\chi^{(3)}$ value was measured in the direction parallel to the delocalization, or chain direction.

It can be seen that the values obtained in the DSB and DPB systems are within an order of magnitude of the DFWM result for unaligned PPV. (Given the mild dispersion in the 600–700-nm range shown by the values from ref 24, one would expect the increase in $\chi^{(3)}$ from 598 to 650 nm to be small.)

**Electrical Conductivity.** The electrical conductivity results of the doping experiments are shown in Table II along with conductivity values for undoped films and literature values for conductivity of PPV and graphite. The new materials shown are either polyethers or polyesters containing the distyrylbenzene group; "MeO" and "EtO" designations refer to methoxy and ethoxy substituents respectively (see Figure 1) and numerals indicate the number of carbons ($n$) in the alkyl spacer. The iodine-doped films were nearly black and the H$_2$SO$_4$-doped films

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**Table II. Conductivities in the Present and Other Organic Systems**

| polymer | treatment | conductivity, S/cm |
|---|---|---|
| EtO6 (ester) | none | $1.9 \times 10^{-8}$ |
| EtO5 (ester) | none | $3.8 \times 10^{-10}$ |
| MeO8 (ester) | none | $1.8 \times 10^{-10}$ |
| MeO7/9 (ether) | none | $1.9 \times 10^{-10}$ |
| MeO7/9 | $I_2$ | $4.0 \times 10^{-5}$ |
| MeO8 | $I_2$ | $7.2 \times 10^{-5}$ |
| MeO7/9 | $H_2SO_4$ | $1.6 \times 10^{-5}$ |
| MeO8 | $H_2SO_4$ | $3.9 \times 10^{-5}$ |
| PPV[11] | none | $\sim 1 \times 10^{-13}$[a] |
| PPV[11] | $H_2SO_4$ | 100 |
| PPV[14] | $I_2$ | $2.5 \times 10^{-3}$ |
| PPV[12] | $AsF_5$ | 10 |
| graphite (parallel)[28] | none | $2 \times 10^{4}$ |

[a] Reported values vary widely.

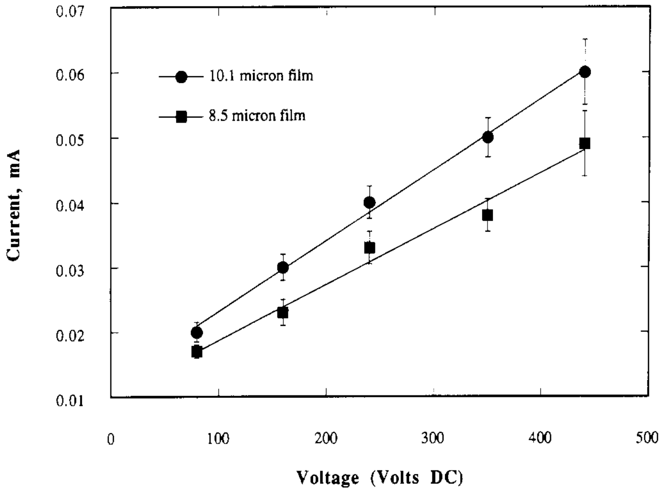

**Figure 2.** Current versus dc voltage plot of polyether, MeO7/9, doped with iodine. The two films were doped and measured simultaneously.

were dark brown. All of the values in Table II pertain to unaligned materials.

Figure 2 shows an example of the current versus voltage plots for two simultaneously doped films of poly(ether) MeO7/9 (ether), from which the conductivity values were calculated. The error bars as drawn do not pertain to the current and voltage measurements alone but include the error in measuring the sample width, thickness, and length. Approximately 90% of the error displayed was attributable to the dimensional measurements. The values reported in Table II were all averages of two films.

In addition to the two common dopants such as $I_2$ and $LiAsF_6$, fully conjugated polymers have been successfully doped to high conductivities with other substances. PPV have been doped to 100 S/cm with $H_2SO_4$ vapor (as above),[20] and up to 500–3000 S/cm parallel to aligned chains, using $AsF_5$.[21–24] Amorphous samples of poly(phenylene sulfide) have been doped with $NOPF_6$ to give conductivities of 1 S/cm.[25] Attempts were made to dope the polymer by immersion in a methylene chloride/nitromethane solution of $NOPF_6$, but this destroyed the films.

All of the dopants presented in Table II are therefore "p-type" dopants. Some ionic conductivity due to the presence of unreacted acid is possible in the $H_2SO_4$-doped specimens. The iodine values are considered to be reliable since residual iodine should have been removed by the 24-h vacuum treatment. The maximum error in the conductivities is less than ±10% and is mainly due to thickness variations in the films.

As can be seen in Table II, values for the undoped DSB polymers ranged from $2 \times 10^{-10}$ to $2 \times 10^{-8}$ S/cm. Values for doped samples were $\sim 2 \times 10^{-5}$ S/cm independent of whether the sample used $I_2$ or $H_2SO_4$ dopant. Iodine-doped samples were 2 orders of magnitude lower than those reported for PPV, whereas values for PPV doped with $H_2SO_4$ with $H_2SO_4$ were 5 orders higher.

**Comparison of Optical and Electrical Results.** It was shown that the polymers in this study have $\chi^{(3)}$ values within an order of magnitude of the nonresonant value observed previously by Murase et al.[22] for unaligned PPV, but that the doped conductivities of the present materials are far lower than those of PPV.

The optical nonlinearities result from the strong polarization of electron charge clouds and not the movement of electrons or holes across the entire length of a specimen. Therefore one would expect a reduction in $\chi^{(3)}$ in EtO7 on the order of 50% compared to PPV, commensurate with the fraction of the volume taken up by the spacers, which have a negligible $\chi^{(3)}$. In the case of conductivity however one can expect a dramatic increase in the energy required for charge transport in the present materials. The presence of the saturated spacer groups greatly increased the average distance carriers must "hop" between conductive regions.

Lenz et al.[26] found that while PPV cannot be doped to a very high conductivity with iodine (see Table II), alkoxy-substituted PPV can. This difference was thought to be due either to the lower ionization potential of the substituted materials or to their greater permeability to iodine.[26] All the doped materials presented here were alkoxy-substituted and so the lower conductivity cannot be attributed to the poor doping properties of $I_2$. The lower conductivity is instead due to the presence of a domain structure caused by the alternating spacer and conducting chromophore. In these domains, the chromophores will lie parallel to one another and enable conduction perpendicular to a common orientation. On passing from one domain to another, planes of conducting chromophore will encounter regions of nonconducting spacer and thereby reduce the net conductivity of the sample.

## Conclusions

Degenerate four-wave mixing experiments have shown that polymers featuring the distyrylbenzene and diphenylbutadiene mesogens have third-order optical nonlinearities within an order of magnitude of unaligned PPV. Such relatively high values in structures with such short

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conjugation lengths highlight the difficulties of producing fully-conjugated polymers with large $\chi^{(3)}$ values.

Despite this fact, the electrical conductivities of polymer samples doped with $H_2SO_4$, and $I_2$ were found to be several orders of magnitude lower than those of comparably treated PPV. This difference is believed to be due to a larger energy requirement for charge transport in the DSB polymers because of the greater distance between these regions than is found in "all-conjugated" materials.

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