Table II
Thermal Characteristics of Phenyl-Substituted Polyamides Determined by DSC[a]

	temp, °C			temp, °C	
code	T_M	PDT[b]	code	T_M	PDT[b]
PA-1	430	500	PA-3	475	510
PA-2	344, 497	520	PA-4	440, 500	530

[a] Heating rate 10 °C/min under nitrogen. [b] Polymer degradation temperature determined from DSC exotherm.

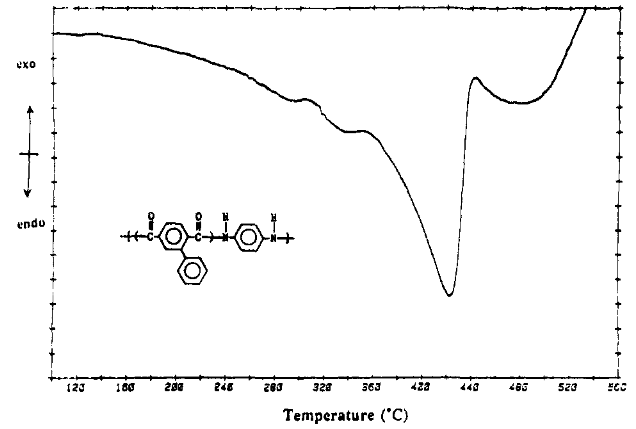

Figure 2. DSC heating curve (10 °C/min) for polyamide PA-1.

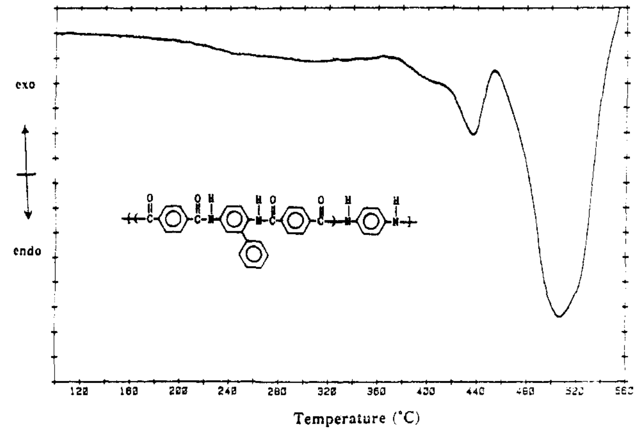

Figure 3. DSC heating curve for polyamide PA-4.

melting. Figure 2 illustrates the clear melting of polyamide PA-1. For the other three substituted polyamides, melting is followed by degradation. Polyamides PA-1 and PA-3 have a single melting transition, indicating only one crystalline form. Polyamides PA-2 and PA-4 exhibit two melting transitions, representing two crystalline polymorphs. A typical DSC thermogram for polyamide, PA-4 is given in Figure 3.

Full details of the monomer synthesis and polymerization procedures will be given in the next publication.

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Registry No. PA-1 (copolymer), 112196-94-8; PA-1 (SRU), 112269-88-2; PA-2 (copolymer), 112196-96-0; PA-2 (SRU), 112269-87-1; PA-3 (copolymer), 112196-98-2; PA-3 (SRU), 112269-89-3; PA-4 (copolymer), 112197-00-9; PA-4 (SRU), 112269-86-0.

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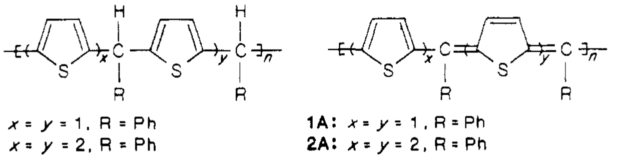
Bromine Treatment of Poly[α-(5,5'-bithiophenediyl)benzylidene] (PBTB) and Poly[α-(5,5'-bithiophenediyl)-*p*-acetoxybenzylidene] (PBTAB): A Complex Reaction

In a series of papers dealing with a clever way to implement current theoretical models for the design of degenerate ground-state conducting polymers, it was claimed that polymers 1–4 could be dehydrogenated by treatment with bromine vapor to low-gap polymeric semiconductors with E_g as low as 0.75 eV.[1-3] The bromination of thin films was followed by electronic and FTIR spectroscopy but no NMR experiments nor elemental analyses were mentioned.[2,3] It was also concluded that since there were no peaks due to C–Br stretching in the 500–650-cm^{-1} region, no electrophilic substitution had taken place. The products were postulated to have the general structures **1A**–**4A**[1] and more specifically structure **3A**[2,3] shown below.



1: $x = y = 1$, R = Ph
2: $x = y = 2$, R = Ph
3: $x = y = 2$, R = p-$CH_3C(O)OC_6H_4$
4: $x = y = 3$, R = Ph

1A: $x = y = 1$, R = Ph
2A: $x = y = 2$, R = Ph
3A: $x = y = 2$, R = p-$CH_3C(O)OC_6H_4$
4A: $x = y = 3$, R = Ph

In this paper we report that the reaction of both PBTB (**2**) and PBTAB (**3**) with bromine vapor depends on the phase (solid–gas versus solution–gas), and the product of either reaction condition is not the simple dehydrogenated product reported before but a brominated material containing covalently bonded as well as ionic halogen. Once the bromination product of **2** is reduced with hydrazine to remove the dopant bromide, it exhibits a bandgap of 1.53 eV (presumably dehydrogenated, partially brominated material) and not 0.83 eV as claimed before.[1-3]

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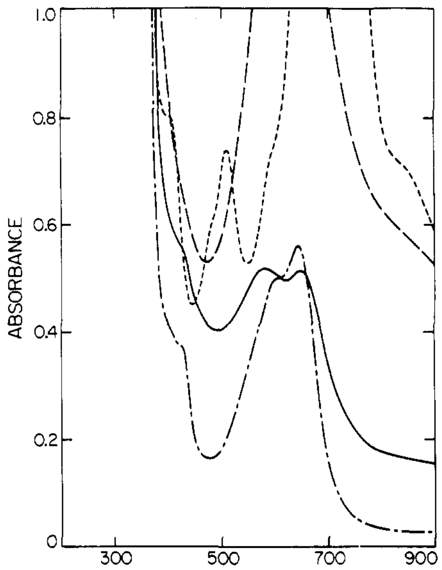


Figure 1. Ultraviolet–visible spectroscopic studies of solution-bromination of polymers **2** and **3**. The curves with lower absorptivity coefficients are due to the untreated polymers **2** (-•-) and **3** (—) in $CHCl_3$. (- - -) Spectrum due to the in situ bromination of the above solution of polymer **2**; (– – –) spectrum due to the in situ bromination of polymer **3**.

When the UV–vis spectrum of an impure sample[4] of the title compounds *in $CHCl_3$ solution* was recorded during in situ bromination, the impurity 680 and 810-nm bands increased in intensity as shown in Figure 1. This result, in the absence of other data, could easily lead one to believe that a dehydrogenation had taken place. However, when the ^1H NMR spectra of the title compounds were recorded during in situ treatment with bromine in homogeneous solution in $CDCl_3$ at ambient temperature, quite unexpectedly, the methine hydrogen resonance (singlet at δ 5.6 for **2** and broad singlet at δ 5.6–5.8 for **3**, relative to TMS) *remained unchanged* as a function of bromine treatment even after a large excess of the reagent had been added and the reaction was allowed to proceed for hours at room temperature. The only noticeable changes were in the aromatic region, particularly a decrease in the ratio of the bithiophene resonances relative to the phenyl resonances (δ 6.9–7.2, among the multiplet due to bithiophene).

When a thin film (~5–10 μm thickness) of polymer **2** or **3** was exposed to bromine vapor, the observed changes in the electronic spectrum were qualitatively the same as described above for homogeneous solution; however, dissolution of the brominated film in deuterio-THF, followed by ^1H NMR spectroscopy revealed that this time the methine hydrogen resonances had disappeared, indicating that dehydrogenation may indeed have taken place under these conditions, but the pattern of resonances in the aromatic region changed dramatically, analogous to the experiments described for solution bromination. Treatment of the solid, brominated film in situ with a mild reducing agent (hydrazine, $NaHSO_3$, etc.) resulted in the spectrum qualitatively similar to the dotted line spectrum shown in Figure 2. Treatment of a thiner film of **2** with bromine, making use of an extended-range spectrophotometer, gave the results depicted in Figure 2. On the basis of this figure alone, without consideration of the information given above or below, one could conclude that a semiconductor with a small bandgap (equal to or less than the record 1.0 eV of PITN[5]) had been produced.

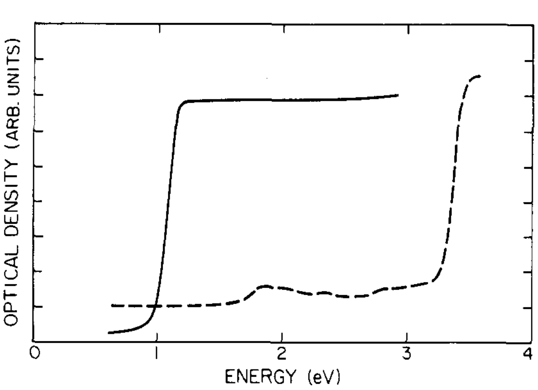


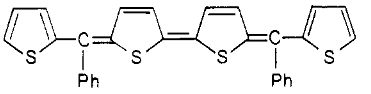
Figure 2. Electronic absorption spectrum of a very thin film of polymer **2** (– – –) on a quartz plate and in situ bromination (—) of the same film.

Elemental analyses of products of both types of experiments (solids evacuated for 24 h at 0.1 Torr prior to analysis) proved without doubt that a *large amount of bromine was incorporated.*[6] To determine the relative amounts of covalently bonded and ionic bromine incorporated during the gas–solid reactions, we "compensated" a brominated sample of **2** with hydrazine:

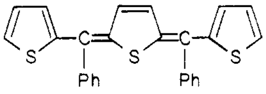
$$\mathbf{2} \xrightarrow{Br_2} \mathbf{2}\text{-}Br_{11.3} \xrightarrow{H_2NNH_2} \mathbf{2}\text{-}Br_{11.3-x} + (H_2NNH_2HBr)_x$$

Implicit in this scheme was the assumption that the hydrazine would act only as a reducing agent of the partially oxidized backbone. Elemental analyses[6] of the reduced compound revealed that ca. 1.5 mol % of hydrazine per tetramer was in fact incorporated ($C_{53}H_{40}Br_5N_3S_8$). If one considers that the entrained hydrazine exists as the hydrobromide,[6] then out of the 11.2 atom % of bromine, 7.8 atom % is ionic and the remaining 3.5 atom % is covalently bound.

Analogous experiments carried out on the model compounds **5**[7] and **6**[7] indicate that indeed bromination had taken place.[6] The bromination product of **5** had a composition corresponding to the empirical formula[8] $C_{30}H_{20}Br_{2.2}S_4(H_2O)_3$ (oxygen value by difference). Bromination of **6** afforded a simpler compound:[8] $C_{26}H_{18}Br_3S_3$.



5



6

The in situ spectroscopic studies of **5** are instructive. Its pristine spectrum is very similar to that of impure **2**, indicating that the latter may contain some dehydrogenated sequences in the backbone.[9,10] Bromination under the above gas–solid conditions appears to convert **2** to a "low-bandgap semiconductor" and quenching of the brominated product with hydrazine produces a material with absorption peaking at 600 nm, very similar to that of the pristine material (**5**).

We conclude from the above that the purported brominative dehydrogenation of methine-linked polythiophenes does not lead to simple products such as **2A** and **3A**[1-3] but is a complicated reaction, leading to products which are probably dehydrogenated[9] but which also contain bromine bonded covalently and ionically. Furthermore, since the in situ "dehydrogenation" products are actually *doped*, i.e., the spectrum shown in Figure 2 is that of a *doped sample*, the contention within ref 1–3 (which was based on a figure identical with Figure 2) that very low bandgap (as compared to polythiophene, E_g = 2 eV) semiconductor polymers were produced by this route is not valid.

Acknowledgment. We are indebted to the Office of Naval Research for support of this work.

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(4) In ref 2 and 3 it is claimed that polymer **3** is blue with a λ_{max} of 692 nm and a bandgap of 810 nm (1.53 eV). The pure polymer is actually off white with λ_{max} of 332 nm (ϵ = 23 400) and a hint of absorption in the 700–800-nm region of (ϵ = 31.4, cf. Figure 2), indicating a small degree of unsaturation. *However, both pure and impure polymers show qualitatively the same electornic spectroscopy behavior when brominated (the former less dramatically so than the latter).*

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(6) Anal. Calcd. for $C_{53}H_{36}S_8$ (**2**, *n* = 3.5) [$H(C_4H_2S)(C_4H_2S)-(CHC_6H_5)-(C_4H_2S)(C_4H_2S)-(CHC_6H_5)-(C_4H_2S)(C_4H_2S)-(CHC_6H_5)-(C_4H_2S)(C_4H_2S)H$]: C, 68.50; H, 3.90; S, 27.60. Found: C, 68.45; H, 3.78; S, 27.31. Anal. Calcd. for $C_{53}H_{36}Br_{11.3}S_8$ (**2**, gas–solid reaction): C, 34.73; H, 2.02; Br, 49.29; S, 14.01. Found: C, 34.94; H, 2.40; Br, 48.80; S, 9.77. Anal. Calcd. for $C_{49}H_{30}Br_3O_3S_7$ (**2A**, *n* = 2.5, gas–solution reaction): C, 52.05; H, 2.65; Br, 21.24; S, 19.82. Found: C, 51.83; H, 2.63; Br, 21.42; S, 19.79. Anal. Calcd. for $C_{53}H_{40}Br_5N_3S_8$ (**2A**, *n* = 2.5, gas–solid followed by evacuation, followed by gaseous hydrazine): C, 46.28; H, 2.91; Br, 29.11; N, 3.05; S, 19.79. Found: C, 46.64; H, 2.74; Br, 29.26; N, 2.84; S, 18.52. Anal. Calcd. for $C_{26}H_{18}Br_3S_3$: C, 46.93; H, 2.69; Br, 36.00; S, 14.39. Found: C, 46.38; H, 2.45; Br, 36.30; S, 14.09. Anal. Calcd. for $C_{30}H_{26}Br_{2.2}S_4$: C, 48.65; H, 3.52; Br, 24.32; S, 17.29. Found: C, 48.48; H, 3.06; Br, 23.74; S, 15.70 (residue, 9%).

(7) Patil, A. O., unpublished results.

(8) A referee requested we propose structures for the bromination products of **5** and **6**. Based on the elemental analysis, the structure of bromine-treated **6** is very likely just [$\mathbf{6}^{\bullet+}$][Br_3^-]. In the absence of more studies, we do not want to speculate about possible structures of [**5**][$Br_{2.2}$][H_2O].

(9) Kertesz and Lee (Kertesz, M.; Lee, Y. S. *J. Phys. Chem.* **1987**, *91*, 2690) have calculated a bandgap of 1.13 eV for polymer **2A**.

(10) Buchwalter and Viehbeck (Buchwalter, S. L.; Viehbeck, A. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1987**, *28*, 211; Buchwalter, S. L. *J. Polym. Sci., Polym. Chem. Ed.* **1985**, *23*, 2897) have suggested that long-wavelength absorptions in similarly prepared furan analogue polymers are due to partial dehydrogenation of the backbone.

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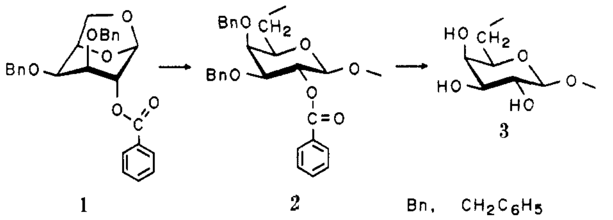
Sterically Controlled Ring-Opening Polymerization of a 1,6-Anhydro-β-D-galactopyranose Derivative by Neighboring Group Participation. (1→6)-β-D-Galactopyranan

Neighboring group participation serves to control the stereochemistry of glycosidation reactions.[1] Glycopyranosyl halides with an acetyl or benzoyl group at position 2 are efficient glycosyl donors in the synthesis of β-linked oligosaccharides of the gluco and galacto series. In this paper, polymerization of 1,6-anhydro-2-*O*-benzoyl-3,4-di-*O*-benzyl-β-D-galactopyranose (**1**)[2] followed by deprotection was carried out according to Scheme I and a β-(1→6)-linked D-galactopyranan **3** of $\overline{DP}_n$ = 7 was obtained. The structure determination of **3** was made in comparison with model (1→6)-β-D-galactooligosaccharides[2-6] which were prepared via stepwise and blockwise glycosidation methods to study the interaction with homogeneous myeloma monoclonal antibodies.[7]

Scheme I
Synthesis of β-(1→6)-Linked Galactopyranan Oligosaccharide 3



A variety of linear stereoregular polysaccharides have been synthesized via ring-opening polymerization of anhydro sugar derivatives of different configuration, ring size, and substituent.[8] Polymerization of 1,6-anhydro sugar derivatives proceeds with inversion presumably via a trialkyloxonium ion intermediate.[9] Only one anhydro sugar, 1,6-anhydro-2,3-di-*O*-benzyl-4-deoxy-β-L-*ribo*-hexopyranose, has polymerized with retention of configuration.[10,11] A more general method for the polymerization of anhydro sugars with retention of configuration could lead to the chemical synthesis of biologically relevant polysaccharides that are not presently accessible. The present method using neighboring group participation is suggested for that purpose. Previously, an increase of the β-form content in the polymerization of a bicyclic acetal (4-bromo-6,8-dioxabicyclo[3.2.1]octane) was explained in terms of bromonium ion participation.[12] Exclusive cis-opening polymerization has been attained in the present investigation by means of neighboring benzoyl group participation.

The polymerization of **1** was carried out at 0 °C using 10 mol % of phosphorus pentafluoride in dichloromethane ([**1**] = 1.5 mol/L) for 48 h and a white powdery polymer was isolated in a 66% yield by reprecipitation and chromatography. The number-average molecular weight estimated by GPC was 2.6×10^3 ($\overline{DP}_n$ = 6); $[\alpha]_D^{25}$, +26.8° (*c* 1.0, chloroform); lit.[3] $[\alpha]_D^{25}$, +25.8° for allyl β-glycoside of a tetrameric galactopyranose derivative. The polymerization of **1** was much more sluggish than that of the corresponding tribenzylated analogue (1,6-anhydro-2,3,4-tri-*O*-benzyl-β-D-galactopyranose)[13,14] and required a higher polymerization temperature and a larger amount of initiator. The molecular weight of the polymer was lower than those of the polymers obtained from the tribenzyl analogue.

Both debenzylation and debenzoylation of the polymer **2** were simultaneously performed with sodium in liquid ammonia and a free polysaccharide **3** was obtained quantitatively as a hygroscopic powder. It was soluble in water, partially soluble in dimethyl sulfoxide, and insoluble in other common organic solvents.

The optical rotation and ^{13}C NMR data of **3** were consistent with β-(1→6)-linked galactopyranan structure in comparison with those of the model oligosaccharides; $[\alpha]_D^{25}$, +26.9° (*c* 1.0, water); lit.[4] $[\alpha]_D^{20}$, +20° (*c* 1.2, water) for (1→6)-β-D-galactotriose. The six major peaks in the ^{13}C NMR spectrum (D_2O, 5%; internal reference, methanol, 49.0 ppm; 50 MHz) were assigned to the central β-D-galactopyranosyl units: C-1, δ 103.38; C-2, 70.80; C-3, 72.69; C-4, 68.69; C-5, 73.78, C-6, 69.29. These chemical shifts were in agreement with the reported data of methyl (1→6)-β-galactohexaose (C-1, δ 103.46; C-2, 70.77; C-3, 72.66; C-4, 68.70; C-5, 73.79; C-6, 69.23).[6] Corroborating evidence of β-linkage was the coupling constant, $J_{C\text{-}1,H\text{-}1}$ = 162.6 Hz, which was assigned to the coupling between the anomeric carbon and axial hydrogen.[10,11,15] There were several smaller resonances assignable to the terminal units. However, no signal whose chemical shift was close to that