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(8) Present address: Department of Mechanics and Materials Science, Rutgers University, Piscataway, NJ 08854.
(9) Permanent address: Department of Applied Physics, University of Tokyo, Tokyo, Japan.

Y. Takase,[8] Hajime Tanaka,[9] T. T. Wang,* R. E Cais, and J. M. Kometani

AT&T Bell Laboratories, Murray Hill, New Jersey 07974

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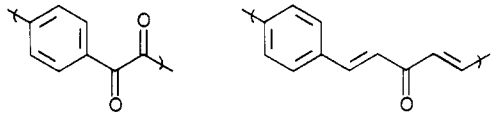
Synthesis of Conductive Polymers. Lewis Acid Doping of Terephthalaldehyde Polymers

With the exception of polyaniline, which must be doped with aqueous acid,[1] all the conducting polymers reported to date have required doping with redox agents, e.g., I_2 and AsF_5 (p-type dopants) or sodium naphthalide (n-type dopant), to achieve semiconductivity.

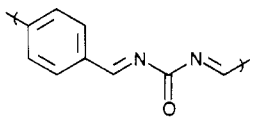
We now report three polymers that show enhancements in conductivity on treatment with BF_3 etherate and H_2SO_4, both Lewis acids, as well as with AsF_5.

The three polymers that we report are prepared by the condensation of terephthalaldehyde with itself (I), acetone (II), and urea (III). Although polymers I and II are



I

II



III

known,[2,3] their data have not been reported. We have synthesized these polymers in an effort to explore new conductive polymer systems. We had hoped that the higher oxidation states of these polymers might impart intrinsic conduction to them or, at least, that they might be convertible into conductors by the application of acidic reagents. Chien and Babu[4] have reported copolymers of acetylene and carbon monoxide which conduct at high levels on p-type doping. They protonated their polymer with methanolic HCl but did not report the conductivity of the resulting adduct.

Polymerization. We have polymerized terephthalaldehyde (Aldrich) to the yellow polybenzoin by a benzoin-type condensation, T_m 200–220 °C (lit. 170–200 °C[2]); IR (KBr pellet cm^{-1}) 3500 (br, OH str), 1700 (s, singlet, C=O str).

We could not oxidize the polybenzoin to I according to the published procedure.[2] Even $CuSO_4$/pyridine/air oxidation proved ineffective. We oxidized the polymer in 90% yield by refluxing it with a large excess of HNO_3/H_2O (1/4 mixture) for 72 h when we observed the disappearance of hydroxyl group absorption in the IR spectrum: IR (KBr pellet cm^{-1}) 1650 (s, sharp, C=O str), 1180 (s, singlet, C=O bend). This polymer is insoluble in practically all common organic solvents.

We prepared polymer II, a yellow powder, in 55% conversion by known methods[3,5] using acetone distilled over K_2CO_3; IR (KBr pellet cm^{-1}) 3500 (br, OH str), 1653 (s, singlet, C=O str), 1600 (s, singlet, C=C Ar str). We ascribe the OH band to the hydroxyl group of the simple aldol adduct, even though the fully conjugated system was reported[3] as the product of this reaction. The occurrence of a doublet at δ 4.75 and a triplet at δ 5.5 in the ^1H NMR spectrum (DMSO-d_6) further supports the presence of some initial aldol polymer.

Attempts to dehydrate this polymer with P_2O_5/H_2SO_4 failed; however, BF_3 etherate caused rapid dehydration as shown by loss of the OH band and the change in color to brown. This polymer is insoluble in all solvents.

We prepared polymer III by refluxing equimolar quantities (0.025 mol) of urea (Aldrich) and terephthalaldehyde in 25 mL of DMF (Aldrich, dried over molecular sieve). The solution turned yellow after 10 min. After 1 h of reflux we poured the solution into 100 mL of methanol. The precipitated polymer was redissolved in 20 mL DMF and reprecipitated by methanol. The DSC scan shows no transitions up to 450 °C. After the second precipitation, the polymer dissolves in DMF with great difficulty, owing either to a change in the morphology of the polymer or to an increase in the molecular weight during workup. IR (KBr pellet cm^{-1}) 1656 (s, singlet, C=O str), 1625 (s, singlet, CH=N); ^1H NMR (DMSO-d_6) δ 10.38 (CH=N) and 8.28 (C_6H_4). We have not been able to determine the molecular weight of these polymers by conventional methods owing to their insolubility in all common organic solvents. However, we are pursuing other means to determine molecular weights.

Table I
Conductivities of Polymers with Various Types of Dopants

	conductivity, S/cm					
polymer	undoped	AsF_5[a]	AsF_3/AsF_5[b]	BF_3 etherate[c]	BF_3 etherate[d]	H_2SO_4
I	10^{-13}	10^{-13}	10^{-6}	10^{-8}	10^{-8}	10^{-13}
II	10^{-13}[e]	10^{-7}	10^{-8}	10^{-6}	10^{-8}	10^{-6}
III	10^{-13}	10^{-8}	10^{-7}	10^{-6}	10^{-8}	10^{-7}
$-(CH_2CH_2)-$	10^{-13}	10^{-13}	10^{-13}	10^{-13}	10^{-13}	10^{-13}

[a] 400 Torr. [b] 400 Torr AsF_5, equilibrium vapor pressure of AsF_3 at 25 °C. [c] Ca. 2 Torr, equilibrium vapor pressure at 25 °C. [d] Equilibrium vapor pressure of BF_3 etherate at −196 °C (ca. 0 Torr). [e] This value was obtained on the undehydrated precursor to II.

Electrical Conductivity. We measured electrical conductivity by using the standard two-probe method with a Keithley bridge and exposing the pressed pellets to AsF_5, BF_3 etherate, H_2SO_4, and AsF_3/AsF_5. The apparatus has been described elsewhere.[8] Conductivity data are summarized in Table I.

BF_3 Doping. We measured the conductivity of these polymers exposed to BF_3 etherate in the following manner: BF_3 etherate was transferred to the doping chamber under Ar, and the chamber was cooled to liquid nitrogen temperature. The pellet mounted on the probes was inserted in a current of Ar. The chamber was evacuated for 15 min while cooling with liquid nitrogen. BF_3 etherate was allowed to warm to room temperature by removing the liquid N_2 bath. As soon as BF_3 etherate reached room temperature the conductivity increased. Polymer I exhibited a smaller conductivity enhancement than II and III.

We could not make a pellet of dehydrated brown polymer II, so we exposed the pressed pellet of yellow polymer (the undehydrated precursor to II) to BF_3 etherate vapor. As soon as the pellet came in contact with the vapor its color changed from yellow to brown, and its conductivity increased from 10^{-11} to 10^{-8} S/cm and finally to a maximum value of 10^{-6} S/cm. After 30 min we cooled the

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doping chamber in liquid nitrogen and evacuated the system, whereupon the conductivity dropped to 10^{-8} S/cm. On removing the cooling bath and allowing the system to rise to room temperature, the conductivity reached its maximum value of 10^{-6} S/cm. We observed the same values when the above process was repeated twice. In order to test whether the conductivity increases by BF_3 doping or because of surface effects, we conducted the same experiment with a pressed pellet of powdered polyethylene. In this case we did not observe any conductivity difference with or without any of the doping reagents.

The decrease in conductivity on removing BF_3 etherate vapor from the system may also be attributed to a decrease in the temperature of the sample during the freezing out procedure.

To explore the nature of the binding of BF_3 to polymers I, II, and III, we examined the IR and ^1H NMR spectra of these polymers before, during, and after exposure to BF_3 etherate. The presence of BF_3 binding was signaled by a strong IR band near 1100 cm^{-1}. BF_3 etherate exhibits this absorption at 1200 cm^{-1},[6,7] but the band is shifted to 1100 cm^{-1} when the BF_3 is bound to our polymers. As a further confirmation we also obtained spectra of dibenzalacetone in ether solution with and without added BF_3 etherate. This compound also shows the strong band at 1100 cm^{-1}, indicating bonding to the BF_3.

The experiment for determining the IR spectra of BF_3 adducts of polymers I, II, and III consisted of allowing a mixture of the solid sample in BF_3 etherate to stand for several hours. The liquid was filtered, the slurry was dried as rapidly as possible at room temperature and pressure, a KBr pellet was pressed, and the IR spectrum was determined. Another portion of the same sample was dried at 120 °C under vacuum for several hours and the IR spectrum similarly determined. We obtained the following results: Polymer I showed the broad band at 1100 cm^{-1}, but it was absent in the vacuum-dried sample. With polymers II and III, the band at 1100 cm^{-1} persisted even in the vacuum-dried samples. Corresponding bathochromic shifts in the carbonyl region were also observed with all samples including dibenzalacetone.

The IR evidence suggests that BF_3 forms a stable addition compound with polymers II and III. The corresponding addition compound with polymer I appears to be less stable.

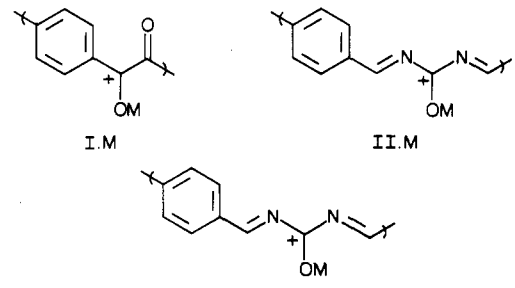
Sulfuric Acid Doping. Sulfuric acid doping was accomplished by mixing a sample of 0.001 mol of each polymer with 5 mL of 96% H_2SO_4 and allowing the mixture to stand for 2 h. At that time the sample was washed several times with ethyl ether and dried overnight at 50–60 °C and 10 Torr. The dried samples were pressed into pellets for conductivity measurements. Exposure to sulfuric acid caused II to turn dark violet and III to turn orange; I did not change color on exposure to sulfuric acid.

The infrared spectra of polymers II and III show several pronounced changes, whereas that of polymer I shows no change in the IR spectrum on exposure to sulfuric acid. Polymer II, on doping with sulfuric acid, contains new bands at 1288 (OH bending), 1070, 887, 847, 614, and 581 cm^{-1}, as well as broad absorption in the 3600–3200-cm^{-1} region; bands at 1653 (C=O str), 1100, and 825 cm^{-1} disappear. With polymer III, doping with sulfuric acid produces new IR bands at 1300 (OH bend), 1237, 1172, 887, 612, and 576 cm^{-1}, as well as broad absorption in the 3600–2400-cm^{-1} region; bands at 1656 (C=O stretch), 1511, and 980 cm^{-1} disappear.

To determine whether sulfuric acid treatment causes a permanent change in the polymer, we triturated doped II and III with aqueous NH_3 and allowed the mixtures to stand for 2 h followed by filtration and washing with water and ethanol. The IR spectra of these samples were identical with those of the pristine polymers.

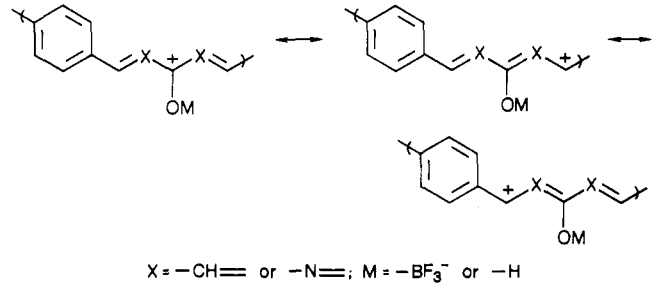
Interpretation. From the data it is clear that the conductivity of I does not increase significantly on exposing the polymer to AsF_5 vapors; however, there is a considerable increase in the conductivity especially in I when AsF_3 is introduced into the doping chamber along with AsF_5. This phenomenon has been previously observed[8,9] and is probably due to changes in morphology brought about by the solvent action of AsF_3. Because of their high oxidation states these polymers should be susceptible to n-type doping, and we are pursuing this avenue. Polymers II and III exhibit conductivity enhancements with AsF_5 both with and without AsF_3.

We attribute the BF_3-enhanced and the H_2SO_4-enhanced conductivity of II and III to the formation of resonance-stabilized carbocations which can act as charge carriers:



Structure I.M is higher in energy than II.M and III.M because it is destabilized by an adjacent carbonyl group.

We postulate that reaction of the carbonyl oxygens of II and III with Lewis acids results in a conjugated system with delocalization of the positive charge along the chain:



Such delocalized positive charges can act as charge carriers. This interpretation is consistent with the loss of the carbonyl band (1653 and 1656 cm^{-1} for II and III, respectively). The presence of bisulfate ion is evidenced by the appearance of bands near 1100, 880, and 600 cm^{-1}. The lower conductivity of III may be explained by protonation of the nitrogen atoms which limits the delocalization of charge. The regeneration of the original polymers after washing the acid-doped polymers with NH_3 demonstrates that acid doping is a reversible process.

The fact that both BF_3 and H_2SO_4 doping give the same conductivity suggests that the ionic mobility of HSO_4^- contributes negligibly to the overall conductivity because the BF_3 adduct has no mobile counteranion.

We also attempted to dope these polymers with HCl. Both II and III showed color changes when they were exposed to concentrated HCl or to HCl fumes; however, when these samples were dried or removed from the HCl fumes, they reverted to their original colors within a few seconds.

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Surandar Nath Kaul and Jack E. Fernandez*
Chemistry Department and Center for Materials Development
University of South Florida, Tampa, Florida 33620

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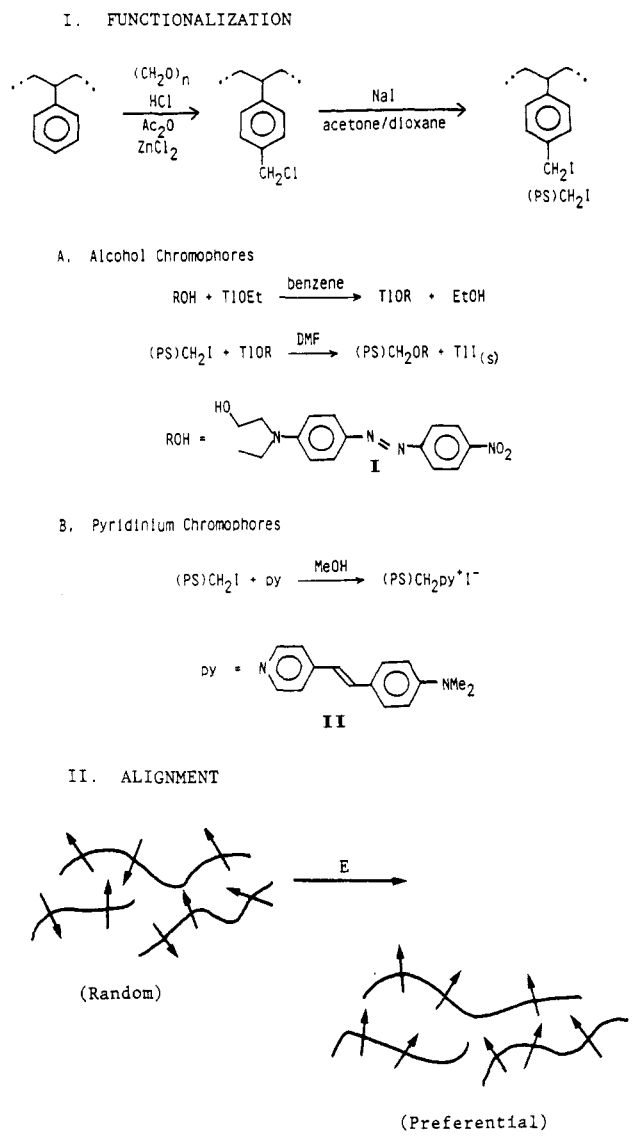
Synthesis of Molecular Arrays with Nonlinear Optical Properties. Second-Harmonic Generation by Covalently Functionalized Glassy Polymers

Current interest in organic (π-electron) nonlinear optical (NLO) materials derives from the attraction of large nonresonant susceptibilities, ultrafast response times, low dielectric constants, high damage thresholds, and the intrinsic tailorability of organic structures.[1] For second-harmonic generation (SHG), a major synthetic challenge is to construct *necessarily noncentrosymmetric* molecular assemblies having high structural integrity and suitable processability. We report here an approach[2] in which nonlinear chromophores are covalently linked to a glassy, film-forming macromolecule to produce, after alignment in an electric field, a new class of single-component polymeric frequency-doubling materials.[3-5]

Polystyrene was chosen as backbone because of its excellent transparency,[6,7] low dielectric constant,[7] relatively high T_g (*to help stabilize chromophore alignment*),[7] and amenability to varying kinds/levels of functionalization and processing. Polystyrene ($\bar{M}_w \approx 22\,000$) was chloromethylated,[8] followed by conversion to the more reactive iodomethyl derivative,[9] as shown in Scheme I. These and subsequent steps are conveniently monitored by 400-MHz ^{1}H NMR.[10] Introduction of high-β chromophores I and II[11,12] was effected by thallium-mediated etherification[13] or quaternization,[14] respectively. The new polymers were characterized by standard spectroscopic/analytical techniques and by DSC.[15] Most experiments have been carried out with polymers having 4.5–12.5% (by elemental analysis and NMR) of the benzene rings functionalized.

Solutions of (PS)CH_2-I (12.5% functionalization, in dioxane) and (PS)CH_2-II (4.5% functionalization, in $ClCH_2CH_2Cl$) were multiply suction filtered through a 5-μm frit and were spin coated[16] onto pieces of ITO-coated conductive glass in a class 100 laminar-flow clean hood (to minimize contamination by dust). After they were dried under vacuum, the 0.3–7.0-μm thick[17] films were covered with a second ITO electrode and were then poled in an

Scheme I



electric field[18] (0.040–0.500 MV cm^{-1}) for 20 min at 115 °C. The films were then cooled in the presence of the electric field.

Second harmonic coefficients of the poled films were measured in the p-polarized geometry at 1.064 μm by using the Q-switched Nd:YAG laser-based instrumentation described previously.[19] Verification of the second-harmonic character was provided by measurement of the spectral purity with a 0.5-m monochromator and by the quadratic dependence of the intensity on the fundamental beam intensity (Figure 1). In Figure 2, the dependence of the second harmonic intensity on the incident angle of the fundamental beam is shown for a typical film. This angular dependence can be analyzed by using the theoretical expression of Jerphagnon and Kurtz[20] for uniaxial materials and by assuming that the five nonzero second-harmonic coefficients are interrelated by $d_{31} = d_{21} = d_{24} = d_{15} = {}^1/_3 d_{33}$,[3a,21] where 3 refers to the unique axis of the uniaxial material. By calibrating against d_{11} of quartz, the d_{33} of (PS)CH_2-I is determined to be 2.7 (3) $\times 10^{-9}$ esu at a poling field of 0.300 MV cm^{-1}. This value exceeds the analogous parameter for KDP where $d_{36} = 1.1 \times 10^{-9}$ esu and is comparable to the d_{33} of PMMA films doped with similar concentrations of I and poled at comparable fields.[3a,b] For the (PS)CH_2-I films, the magnitude of d_{33} is found to be linearly proportional to the strength of the

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