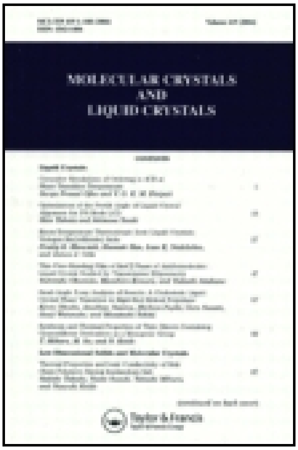

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Low Band-Gap Conjugated Polymers: Poly(Thienylene Vinylene) and Poly(Substituted Thienylene Vinylenes)

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LOW BAND-GAP CONJUGATED POLYMERS: POLY (THIENYLENE VINYLENE) AND POLY (SUBSTITUTED THIENYLENE VINYLENES)

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Abstract The electrochemical and optical properties of several heteroaromatic vinylene polymers including poly(2,5-thienylene vinylene) (PTV), and derivatives have been determined. These polymers possess the desired properties of processibility, environmental stability, and high conductivity in the doped form. Optical data and cyclic voltammetry show that by suitable substitution these conjugated polymers can have very low band-gaps and ionization potentials. The synthesis, characterization and properties of these polymers will be discussed.

I. INTRODUCTION

Convenient conducting polymer processibility has been achieved recently by the development of soluble precursor polymers for polyacetylene (PA)(1), polyphenylene (PPP)(2), and poly(p-phenylene vinylene) (PPV)(3). In each case, a two-stage process was used. First, a high molecular weight, soluble non-conjugated precursor polymer was prepared that could be easily solution cast into films. Then, thermal treatment converted the precursor polymer to the final conjugated polymer. However, neither doped PA, doped PPP, nor doped PPV has long term stability in ambient air, which severely limits their usefulness in wide scale electronic applications.

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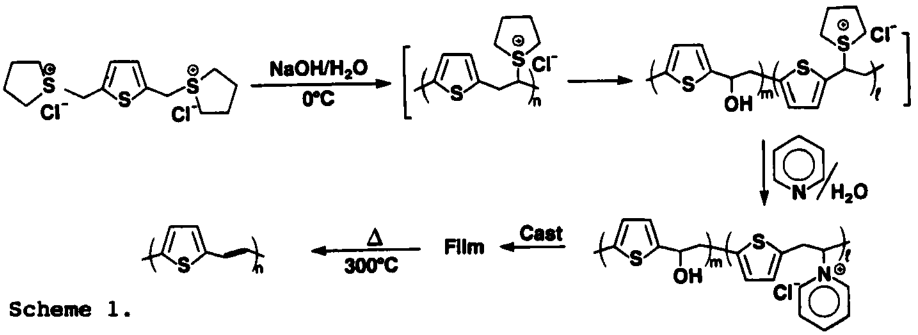

Scheme 1.

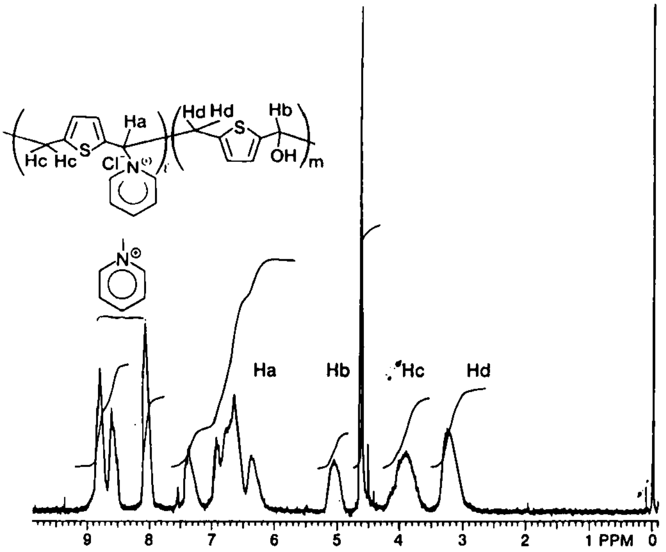

Figure 1. H^1 NMR of precursor polymer stablized by pyridine.

Recently we reported the facile preparation and electrochemical behavior of high molecular weight, environmentally stable poly(2,5-thienylene vinylene) (PTV)(4) and poly(2,5-furylene vinylene) (PFV)(5) via a sulfonium salt precursor polymer. Later, Murase(6) and Saito(7) et al. also reported the synthesis of PTV via a low temperature process which produces a methoxy-substituted neutral precursor polymer. PTV prepared by these methods appear to be extensively conjugated and have good mechanical properties. Furthermore the chemical potential of heavily doped PTV is 0.2V lower than heavily doped polythiophene, which improved the environmental stability of the highly conductive form.

However, the high reactivity of the intermediate polyelectrolyte of PTV, which starts to eliminate sulfide and hydrochloric acid even at room temperature in aqueous solution, that causes the precipitation of the polymer by partial elimination or further acid catalyzed cross-linking reactions. This prevents the long term storage and the ease of processing for the precursor polymer. Although Murase and Saito's method obtained more stable neutral precursor polymer, they had to employ the low temperature, mixed solvent process which caused the inconvenience and higher cost.

In this paper, we report the novel synthesis of high molecular weight, free-standing films of PTV derived from a pyridine-stabilized new precursor polymer, and the detailed studies of structure/property relationships for a variety of poly(heteroaromatic vinylenes).

II. RESULTS AND DISCUSSIONS

PTV was prepared according to a modified Kanbe(8) and Wessling(9) procedure as shown in Scheme 1. To a degassed, stirred solution of 2,5-bis(tetrahydrothiophenonium methyl)

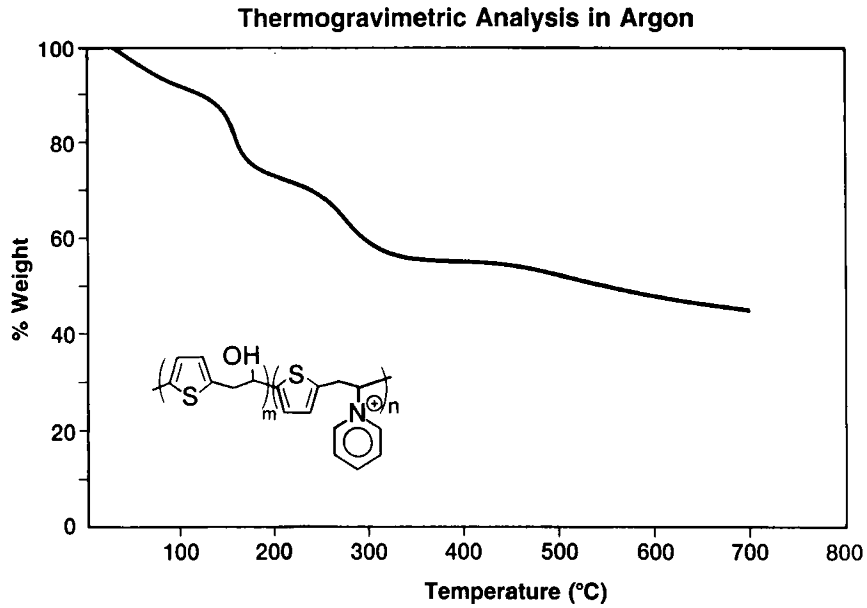

Figure 2.

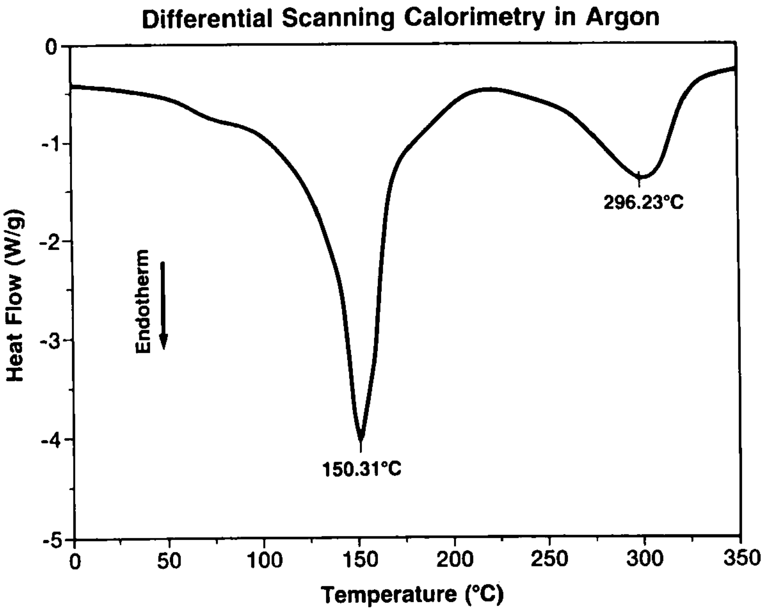

Figure 3. DSC of precursor polymer

thiophene chloride (1) (3.57g, 10 m mole) in distilled water (15ml) at 0°C was added a cooled (0°C) degassed solution of sodium hydroxide (0.4 g, 10 m mole) in distilled water (10 ml). A light orange color developed immediately and the solution became viscous. After stirring at 0°C for 1 hour, one equivalent of pyridine was added and the mixture was dialyzed against water (1.5L) for one week to afford a light brown solution. A tough, flexible cast film was obtained by evaporating the water at room temperature. The resulting film is very stable at room temperature and can be stored in a desicator for a long period of time. The structure of precursor polymer (3) was determined by NMR spectra of this polymer dissolved in D_2O (Fig. 1). It clearly indicated that (3) is a copolymer of pyridinium salt polyelectrolyte and hydroxy group substituted neutral polymer. The ratio (1/m=52/48) was determined by the integration of the benzylic proton (Ha,Hb). Thermal characterization (TGA & DSC) of polymer (3) showed a continuous weight loss from room temperature to 400°C (Fig.2). About 45% of the weight was lost in at least two steps due to the thermal elimination of pyridine, HCL and water. Careful GC/Mass studies of the volatile components confirmed this composition. DSC showed two endothermic peaks at 150°C and 296°C (Fig. 3). The sample was quenched from temperature above each peak, and the peaks did not reappear upon reheat. Therefore, they are related to the weight loss steps shown in TGA. The same film was preheated to 375° under argon to form conjugated PTV (4). Then, the cooled sample was reheated and showed no additional weight loss up to 350°C, followed by the weight loss degradation (Fig. 4). The resulting polymer has a golden lustrous color. X-ray and SEM data showed the final polymer (4) was more crystalline and highly space-filled compared to the polymer obtained by the thermal treatment of the sulfonium salt precursor polymer (4). PTV obtained from this procedure was slowly doped with iodine and ferric chloride to reach a conductivity of 315 S/cm and 110 S/cm for an unstretched film. These values are higher than the conductivity of PTV prepared via the neutral precursor polymer route or sulfonium salt precursor polymer route. Using pyridine as and acid scavenger for the precursor polymer (2) possibly prevents initiation of the acid catalyzed cross-linking reaction. Furthermore, it formed the more stable pyridinium salt and hydroxy substituted copolymer via nucleophilic displacement of sulfide. The cast film is also very stable at room temperature for long period of time. This greatly improves the ease of processing and storage of PTV compared to the previous methods.

To study what effect substituents would have on the properties of PTV, a series of oligomers and low molecular weight substituted thienylene vinylene polymers were prepared and characterized. Initial attempts to prepare high molecular weight substituted thienylene vinylene polymers by the quinodimethane route were unsuccessful due to the high reactivity of the bischloromethyl derivatives of substituted thiophenes. Thus, for initial screening purposes we chose to prepare these polymers by coupling the 5,5' -dilithio derivatives of 3,3' -disubstituted dithienoethylene with 1,2-dichloroethylene. Average degrees of polymerization were on the order of 20 which is sufficiently high to assess a polymer's electronic properties.

A methyl substituent on the thiophene rings in PTV causes little change in polymer properties. But alkyl substituents the size of propyl or greater result in polymers with much increased solubility in organic solvents at room temperature. In fact, even the doped form of PTV bearing butyl groups appears to be soluble. The presence of the alkyl groups has little effect on the conductive properties of the polymers; methyl, ethyl, and butyl substituted thienylene vinylene polymers all reached conductivities around 1-5 S/cm for doped pressed powder pellets.

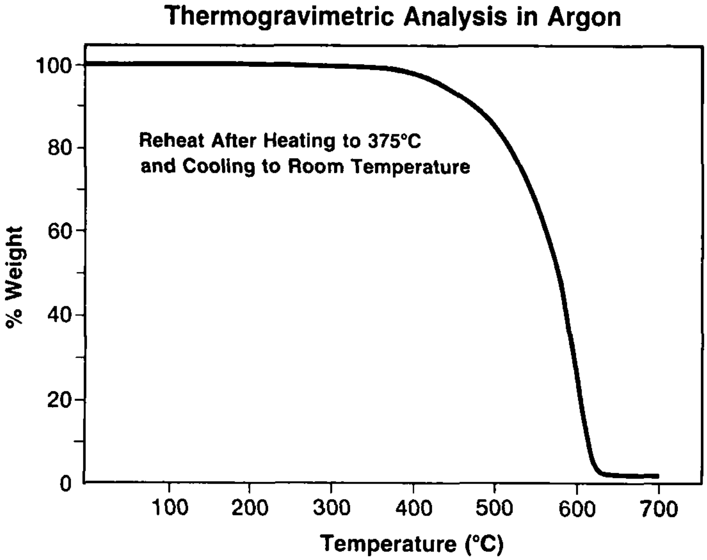

Figure 4. TGA of precursor polymer

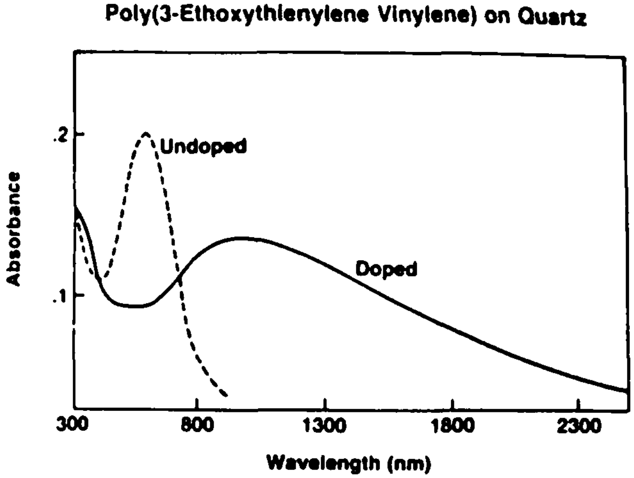

FIGURE 5 Electronic Spectra of cast oligomers of PExTV. Dashed curve, undoped polymer; solid curve, doped ($FeCl_3$) polymer.

From model studies on small molecules, the presence of strongly electron donating alkoxy substituents was found to reduce the pi to pi* transition by 0.3 eV. Such a large effect on a small molecule warranted the investigation of such substitution on the electronic properties of the high polymer. Poly (3-ethoxythienylene vinylene)(10) (PEOXTV) was prepared. The optical spectrum of a cast thin film of extracted oligomers revealed an absorption edge for the pi to pi* transition at 800 nm, which is at significantly longer wavelength that observed for PTV and indicates that the alkoxy substituent caused a significant decrease in band gap.

On doping the cast oligomers of PEOXTV with acceptor dopants such as ferric chloride or nitrosonium salts, a strong absorption appears in the near IR at the expense of the absorption in the visible (Fig. 5). When fully doped, the absorption in the visible has significantly decreased such that thin films on glass substates appear much less colored (faint blue gray). Reduced color (absorption in the visible) for doped polymers appears to arise when the band gap of the polymer is sufficiently small (i.e., less than about 1.5eV) so that the absorption band (π - π*) for the undoped polymer lies closer to the near IR and the corresponding band for the doped polymer lies closer to the IR with reduced tailing into the visible. Such optical behavior has been observed for polyisothianaphthene (band gap ~ 1 eV).(11)

The electrochemical characteristics of (PEOXTV) (insoluble polymer fraction) in an electrolyte of 1M $NaPF_6$ in dimethoxyethane were determined using a potential step voltammetry technique.(12) Powdered polymer mixed with carbon black (25 w/o) and Teflon (5 w/o) was pressed onto a platinum gauze and used as the working electrode. Sodium metal foil was used as both the counter and reference electrodes. Clean oxidation and reduction waves of PEOXTV were observed in this electrolyte for both p-type doping and

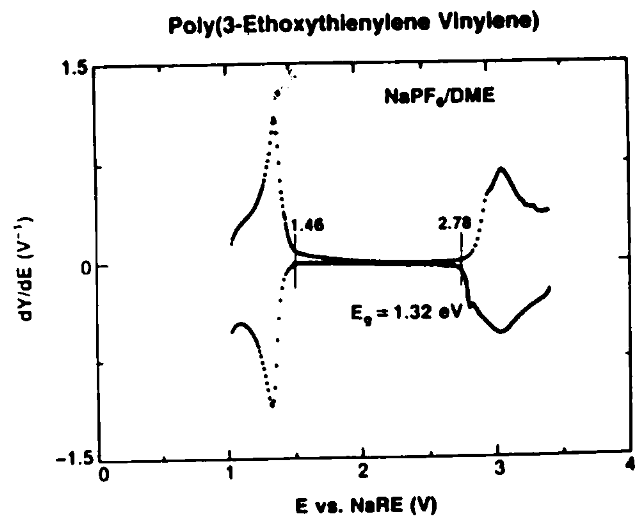

FIGURE 6 Electrochemical characteristics of *n*-type and *p*-type doped PExTV *Ib*. Upper curve represents current/potential characteristics during doping; the lower curve is for undoping. Potentials are referenced *vs*. Na/Na$^+$ using 1M NaPF$_6$ in dimethoxyethane. (E_{Li} = E_{Na} + 0.065 V, as determined experimentally).

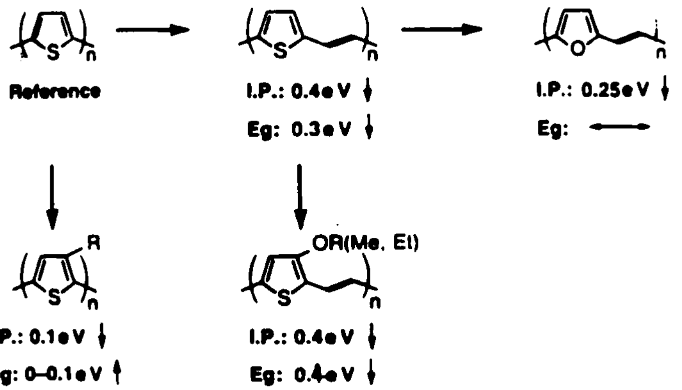

FIGURE 7 Substituent effects on the band gaps and ionization potentials for substituted polythiophenes and poly(heteroaromatic vinylenes).

n-type doping (Fig.6). The oxidation peak potential for p-type doping occurred at 3.05 V vs. Na/Na$^+$ (3.12 V vs. Li/Li$^+$) and the reduction peak for n-type doping occurred at 1.35 V vs. Na/Na$^+$ (1.42 V vs. Li/Li$^+$).

Substitution with an alkoxy substituent has a dramatic influence on the ionization potential of the parent polymer as exemplified by the observed large difference in oxidation potential between the substituted and unsubstituted PTV polymers (Table 1). The electrochemical half-wave potentials for p-type doping of (PEOXTV) (3.11 V vs.Li/Li$^+$,respectively) are 0.25 to 0.43 V less than that for unsubstituted PTV (where,depending on solvent,we observe 3.36 to 3.54 V vs. Li$^+$). Alkoxy substitution dramatically lowers the ionization potential and the band gap. From the onset electrochemical potential for oxidation (p-doping, 2.78 V vs. Na/Na$^+$, 2.85 V vs. Li/Li$^+$) and for reduction (n-doping, 1.46 V vs. Na/Na$^+$, 1.53 V vs. Li/Li$^+$), the onset band gap of (PEOXTV) was determined to be about 1.32 V, which is comparable to the measured on trans-polyacetylene (1.3 eV) by a similar technique, (12) and nearly 0.4 eV less than the parent polymer PTV. After the initial "break-in" oxidation and reduction cycle, subsequent cycles occurred with over 98% coulombic efficiency up to a doping level of 26 mole % (moles of dopant-ion per thienylene vinylene unit x 100%) for p-type doping and 25 mole % doping level for n-type doping was observed only at potentials above 1.0 V vs. Na/Na$^+$; below 1.0 V coulombic efficiency decreased substantially presumably because of electrochemical degradation of the polymer backbone. From extensive spectroscopic and electrochemical characterization of a variety of substituted poly(heteroaromatic vinylenes) a detailed description of structure/property relationships within these classes of polymers has emerged. A summary of substituents and their influence on the electronic properties of the parent polymer is given in (Fig. 7).

Using polythiophene as a reference point, we have found that alkyl substitution at the 3 position of thiophene causes a slight decrease in ionization potential (inductive effect) and a slight increase in band gap (increased steric effect). A vinyl unit incorporated between each heterocyclic ring causes a 0.4 eV reduction in ionization potential and a 0.3 eV reduction in band gap compared to polythiophene. A further reduction in oxidation potential by 0.25 eV arises from exchange of sulfur with oxygen in the heterocyclic ring (PTV to PFV). An alkoxy substituent has about the same effect on electronic properties as a vinylene unit; 0.4 eV reduction in both oxidation potential and band gap. One sees these substituent effects are additive. By the addition of a vinylene unit and an alkoxy substituent (PT to PTV), both the oxidation potential and the band gap are reduced by a total of 0.8 and 0.7 eV, respectively. Through judicious choice of substituents, one can now fine-tune the electronic properties of heterocyclic polymers in a predictable way.

Table 1. Summary of electrochemical spectroscopic data for p-type doping of thiophene containing conducting polymers.

Polymer[a]	Oxidation onset potential[b], V vs. Li/Li$^+$	$E_{1/2}$[c], V vs. Li/Li$^+$	E_{d}[d], V vs. Li/Li$^+$
PBMT	3.43	3.77	3.99
PTV	3.28	3.54	3.72
PMeTV	3.16	3.41	3.60
PMxTV (**1a**)	2.88	3.23	3.45
PExTV (**1b**)	2.85	3.11	3.39

[a] PBMT = poly(3-butylthiophene-co-3-methylthiophene) (50:50); PTV = poly(thienylene vinylene); PMeTV = poly(3-methylthienylene vinylene); PMxTV = poly(3-methoxythienylene vinylene); PExTV = poly(3-ethoxythienylene vinylene). [b] Potential where polymer begins to electrochemically p-type dope. [c] Half-wave potential. [d] Potential of highly conductive doped polymer at the completion of the first stage of doping.

III. REFERENCES

1. Edward, J. H. and Feast, W. J., Polym, Commun.,21, 595 (1980).
2. Ballard, D.G.H., Courtis, A., Shirley, I.M. and Taylor, S.C., J. Chem. Soc. Chem. Commun., 954 (1983).
3. Karasz, F. E., Capistran, J.D., Gagnon, D. R., and Lenz, R. W., Mol. Cryst. Liq. Cryst., 118, 327 (1985).
4. Jen, K.Y., Maxfield, M., Shacklette, L.W. and Elsenbaumer, R.L., J. Chem. Soc. Chem. Commun., 309 (1987).
5. Jen, K.Y., Jow, T.R. and Elsenbaumer, R.L., J. Chem. Soc. Chem. Commun., 1113 (1987).
6. Murase, I., Ohnishi, T., Noquchi, T. and Hirooka, M., Polymer Commun. 8, (1987).
7. Yamada, S., Tokito, S., Tsustui, T. and Saito, S., J. Chem. Soc. Chem. Commun., 1448 (1987).
8. Kanbe, M. and Okawara, M.,J. Polym. Sci., Part A-1, 6, 1058 (1968).
9. Wessling, R.A. and Zimmerman, R.G., U.S. Pat. #3,401,152 and U.S. Pat. #3,706,677.
10. Jen, K.Y., Eckhardt, H., Jow, T.R., Shacklette, L.W. and Elsenbaumer, R.L., J. Chem. Soc. Chem. Commun., 215 (1988).
11. Kobayaski, M. Colaneril, N., Boysed, M., Wudl, F. and Heeger, A.J., J. Chem. Phys., 82, 5717 (1985).
12. Kaufman, J.H., Chung, T.C. and Heeger, A.J., Solid State Commun., 47, 585 (1983).
13. Shacklette, L.W., Toth, J.E., Murthy, N.S., Baughman, R.H., J. Electrochem. Soc., 132, 1529 (1985). Thompson, A.H., Rev. Sci. Instrum., 54 229 (1983).