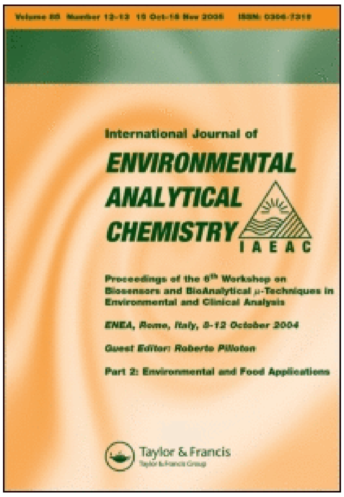

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Sensor System for Alcohol and Chlorinated Hydrocarbon Vapours on the Basis of Semiconducting Polymers

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To cite this Article Jahnke, S. -A. , Niemann, J. , Kautek, W. , Bischoff, R. , Pfeiffer, C. and Koßmehl, G.(1997) 'Sensor System for Alcohol and Chlorinated Hydrocarbon Vapours on the Basis of Semiconducting Polymers', International Journal of Environmental Analytical Chemistry, 67: 1, 223 — 236

To link to this Article: DOI: 10.1080/03067319708031406

URL: http://dx.doi.org/10.1080/03067319708031406

Intern. J. Environ. Anal. Chem., Vol. 67, pp. 223-236
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SENSOR SYSTEM FOR ALCOHOL AND CHLORINATED HYDROCARBON VAPOURS ON THE BASIS OF SEMICONDUCTING POLYMERS

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(Received 12 April 1996; In final form 25 October 1996)

A novel polymer-chemosensor microsystem which can be operated without additional energy consuming heating is presented. Production steps were reduced to metal coating of ceramic plates and structuring of an interdigital array by CAD-supported pulsed laser ablation (PLA) instead of conventional lithographic techniques which yield low production costs only for high production numbers. The active sensor film consists of a semiconducting polymer which can be deposited as a polymer precurser fluid onto the transducer, and can be tempered *in-situ* to yield the required polymeric species and chemical functionality. A precurser, poly-2,5-furylene-hydroxy-ethylene, is coated on the pulse-laser processed interdigital array structures on an Al_2O_3 substrate and converted to various poly-2,5-furylene-vinylene (PFV) derivatives by special heat treatments under inert atmosphere. Costly capacitive modulation and lock-in data acquisition techniques were replaced by simple direct current measurements. Certain sensor types exhibited remarkable sensitivity e.g. for 1,1,2-trichloroethylene and propanol, but moderate cross sensitivity for humidity. The response time is of the order of few minutes, and the current signal is linear in a wide analyte pressure range. Sensitivities for alcohols and chlorinated hydrocarbons are most probably related to hydrophobic van der Waals interactions whereas Brönstedt acidity or Lewis basicity seem to play minor roles. Electronic or van der Waals interaction leads to deviation of the idealy flat and rigid structure of the conjugated polymer thus allowing for more flexibility of the chains, more intimate inter-chain contacts and higher conductivity.

Keywords: Gas sensor; alcohol vapour sensor; chlorinated hydrocarbon vapour sensor; conducting polymer

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INTRODUCTION

Electronically (semi)conducting sensors can be manufactured with moderate costs. They function by charge transfer between the analyte molecules and the sensor film. Thus, mixed electronic and ionic sheet conductivity changes can be measured. Most conventional conductance sensors are based on inorganic semiconducting oxides with metal and/or oxide additives. The cross-sensitivity to humidity is normally reduced by increased operation temperatures. Typical polycrystalline ceramic SnO_2 sensors ("Tagushi sensors") for the detection of reducing gases have to run at elevated temperatures, e.g. around 350 °C, with internal heating wiring and typical power consumptions of up to 1 W [1,2]. Some reduction of the operation temperature (<150 °C) could be achieved by doping of oxides with metals (e.g. SnO_2 with Pd, Bi) [3,5], by blending oxides (e.g. SnO_2/CuO) [6], or by employing metal (e.g. Pb, Fe, Co, Cu, Ni, Zn) porphyrines [7].

Complete elimination of built-in heating for low-cost conductivity transducers is only possible when polymer sensor films, like e.g. polyacetylene [8] and polypyrrole [9,10] specimen are employed. Polysiloxanes [11] can function as a low-temperature dielectric sensor film for alkaline (NH_3) and acidic gases (SO_2, NO_x) only with a capacitive transducer. Chemisorption sensors may lead to selective chemisorption bonds and high specificity in contrast to physisorption sensors like e.g. humidity sensors. High specificity for organic solvents like alcohols and halogenated hydrocarbons exhibit synthetic macrocyclic receptor films with supramolecular recognition on the basis of cyclophanes, cyclodextrins, and triphenylsilanol with surface acoustic wave devices (SAW) or quartz microbalances (QMB) [12,13].

Ethanol and chlorinated hydrocarbons conductivity sensors were only reported with high temperature operation based on Sn [14], Zn [15], W [16] oxides, and Pb porphyrines [17]. At room temperature, methanol has been sensed with N-methylpyrrol [19]. Polymeric composites consisting e.g. of poly(o-phenylenediamine) and polyvinyl alcohol can simply function as humidity sensors in analogy to oxidic conductive type [18].

It is a special challenge to the organic chemist to taylor conducting polymers which show sufficient stability at air. This is achieved by the introduction of aromatic rings like e.g. heterocycles in the main polymeric chain [19,24] such as poly(2,5-thienylene-vinylene). Conducting polymers normally cannot be processed from melt. Composites of conducting and isolating polymers may solve this problem (e.g. poly-o-phenylenediamine with polyvinyl alcohol [18], tetrathiofulvalinium-tetracyanoquinodimethane, TTF-TCNQ with polyethylene [25]) but suffer from more or less ill-defined percolation thresholds of the conductive component and strong water sensitivity. Therefore, precurser processes have been developed [26,29]. We used organic semiconductors with oxygen-instead of sulfur-containing heterocycles, a poly(2,5-furylenevinylene) specimen, with high stability in the presence of air and water. It was synthesized via an aldol addition reaction of 5-methylfuran–2-carbaldehyde (MFC) to the precurser polymer poly(2,5-furylene-1-hydroxyethylene) (PFHE) which is well soluble in organic solvents like tetrahydrofuran [30,31]. It can be transformed to the conjugated poly(2,5-furylenevinylene) (PFV) and to a graphite-like planar structure by water elimination under heat treatment.

Micromachining has become an essential tool for fabrication of miniature sensors and actuators, and more generally, microsystems. Conventional lithographic techniques need involved wet chemical procedures which have to be adjusted to the materials employed, and need costly cleanroom facilities. They rely on high production numbers. We investigated a new type of a low-cost ohmic conductance sensor which does not need heating.

The conductivity changes upon loading of various alcohols and chlorinated hydrocarbons will be discussed in terms of either conductivity or conformational changes of the polymer chains induced by the formation of adducts, charge or hydrogen transfer.

EXPERIMENTAL

The transducers consisted in metallic interdigital electrode comb arrays on alumina plates (25 × 25 mm). They were manufactured by sputter-deposit a thin titanium layer (~0.1 μm) followed by either platinum, or evaporated gold about ≤4 μm thick. The interdigital arrays with by 20–40 μm separated ~120 μm wide electrodes exhibiting a total length of 1250 mm (Figure 1) were generated by local laser ablation of this thin metal film composit in a CAD/CAM set-up using a Nd-YAG pulse-laser (1064 nm, free running). Thus, cost-intensive lithographic techniques can be avoided and custom-made interdigitated resistor (IDR) transducers of flexible design and low number could be provided at low cost.

The synthesis of the processable precurser polymer poly(2,5-furylenehydroxyethylene) (PFHE) for the semiconducting sensor film was done via an aldol addition reaction of 5-methylfuran–2-carbaldehyde with a basic catalyst [31,32]: the aldehyde (5.00 g; 0.045 mol) was stirred with KOH (20.0 g; 0.36 mol) in 50 ml H_2O at ambient temperature for 70 h. The reaction mixture was neutralized using hydrochloric acid under cooling with ice. After filtration and washing with water, the reaction product poly(2,5-furylenehydroxyethylene) was finally dried by P_4O_{10} under vacuum. The resulting material was a dark brown powder. The

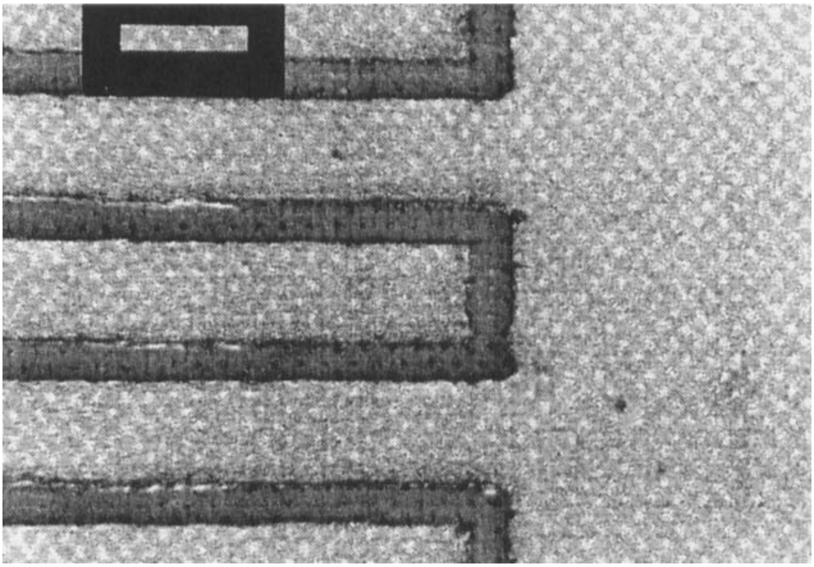

FIGURE 1 Detoil of interdigitated electrode array generated by CAD/CAM controlled pulse-laser ablation (black bar ≈ 250 μm)

yield was 3.95 g (79%). This could be easily dissolved in 5-methylfuran–2-carbaldehyde or N,N-dimethylformamide to form a solution which could be applied to the transducer by spin-coating or painting. Heat treatment under vacuum up to 400°C led to various semiconducting and conducting sensor types designated according to their annealing temperature (e.g. PFV400). This was performed in a quartz tube oven evacuated by a two-step oil pump allowing for base pressures of less than 0.001 hPa.

Separate from this, the measuring tube could be evacuated by the same pump (Figure 2). However, a zeolithe filter and a liquid nitrogen cooled trap avoided contamination of the sensor test chamber. The analyte gases were fed into this by three dosage valves driven by a gas dosage controller (MKS Instruments). Gas pressures were monitored by a Pirani sensor (Thermovac Leybold) for 10^{-3}-1.0 hPa, or an Baratron type instrument (MKS Instruments) for 0.1-25 hPa. The temperature at measuring conditions was 22°C. As analytes served methanol, ethanol, propanol, isopropanol, water, and five halogenated hydrocarbons, methylene chloride (dichloromethane), chloroform (trichloromethane), tetrachloromethane, 1,1,1-trichloroethane, and 1,1,2-trichloroethylene. Their vapours were sucked into the evacuated analysis chamber to reach controlled pressures.

Instead of using capacitive bridge or high-cost lock-in techniques the resistance of the IDR sensors was measured simply by applying a dc voltage of

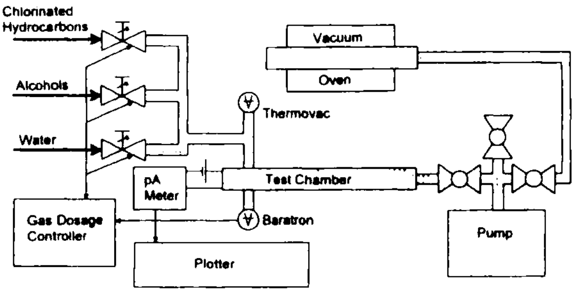

FIGURE 2 Sensor testing and annealing apparatus

$U_B = 18$ V from a battery and recording the dc current I in the range of 40 and 800 pA with a nanoamperemeter (Rohde & Schwarz). The conductivity ($\Delta\sigma$) and resistance change of the sensor film, ΔR_{sen}, could be determined directly by the measured current change ΔI:

$$\Delta R_{sen} = \frac{1}{\Delta\sigma} \approx \frac{U_B}{\Delta I} \tag{1}$$

because the parallel capacitance, C_p, was negligibly small due to the relatively large IDR structures. Moreover, series resistances as e.g. contact resistances stayed constant. The sensitivity limit was found near 10 Pa (comparable to 100 ppm, since oxygen has no effect on the polymer) in respect to atmospheric pressure: a 10 Pa analyte pressure change resulted in a change of a couple of pA's. The noise amounted to about 0,1 bis 0,5 pA.

RESULTS

The precursor polymer dissolved in the monomer 5-methylfuran–2-carbaldehyde (or in N,N-dimethylformamide) was applied on the transducer substrates and heat treated under vacuum for 24 h. Thus the solvents were evaporated. The resulting polymer films were characterized by IR diffuse reflection spectroscopy (Table I). Heating at 56°C mainly led to drying of the precurser PFHE. This sample was called PFV56 in this context. Annealing to 175°C (PFV175) showed no major changes. One has to assume, however, that heating produced the conjugated semiconducting polymer poly(2,5-furylenevinylene) by dehydration (trans-elimination). This spectroscopic finding is supported by the electronic properties (Table II). The uncoated IDR exhibited extremely high resistances $\gg 10^{13}\,\Omega$ corresponding to $\sigma \ll 3 \times 10^{-14}\,\Omega^{-1}\mathrm{cm}^{-1}$ representing a negligible shunt

TABLE I Relative changes of diffuse reflection FT-IR intensity ($\Delta I_\delta = I_\delta - I_{56°C}$) with thermal treatment of precurser polymer poly(2,5-furylene-l-hydroxyethylene) (PFHE). ↑: increase; ↓: decrease; ↓ ↓: strong decrease

Chemical Function	*Wavenumber [cm^{-1}]*	$\Delta I_{175°C}$ *(PFV175)*	$\Delta I_{240°C}$ *(PFV240)*	$\Delta I_{400°C}$ *(PFV400)*
Furan	795	–	↓	↓↓
Furan	1025	↑	↓	↓↓
Furan	3125	–	↓	↓
Vinylene	970	–	–	(↓)
Carbonyl	1675	–	↓	↓
Aromatic	3000–3080	0	(↑)	↑

TABLE II Conductivity after thermal treatment of precurser polymer poly(2,5-furylene-l-hydroxyethylene) (PFHE)

Temperature [°C] (24h)	*Resistance [Ω]*	*σ [Ω^{-1}cm^{-1}]*
uncoated IDR	$\gg 10^{13}$	$\ll 10^{-14}$
56°C	2×10^{10}	5×10^{-11}
175°C	2×10^{10}	5×10^{-11}
245°C	1×10^{10}	3×10^{-11}
300°C	2×10^{7}	5×10^{-8}
400°C	2×10^{5}	5×10^{-6}
600°C	1×10^{2}	3×10^{-3}

to the sensor films. Interestingly, both PFV56 and PFV175, like in IR, gave comparable results of the order of $10^{12}\,\Omega$ corresponding to $\sigma \ll 3 \times 10^{-13}\,\Omega^{-1}\text{cm}^{-1}$. Obviously, minor conjugation at 56°C already suffices to sustain conductivities also achieved in the mainly conjugated PFV175. Annealing at 240°C led to reduction of the furan function and some occurance of additional aromatic signals indicating the formation of graphitic domaines with minimum polarity and highest hydrophobicity (PFV240). Above this, this graphitization reaction commenced (e.g. PFV400). Also resistances started dropping for several orders of magnitude in this temperature domain. Simple measurements of dc changes, therefore, became difficult.

Uncoated transducers show comparatively high sensitivities (current change per pressure change, pA/hPa) for all investigated analytes. However, humidity would mask any signals from the other chemicals because its sensitivity is about two orders of magnitude higher (700 pA/hPa; Table III). This is the typical behaviour of oxide gas sensors which require transducer heating. Besides water, 1,1,1-trichloroethane and propanol showed the highest sensitivities.

TABLE III High water sensitivity (>10^2 × greater than all other analytes) of uncoated transducer (18V applied)

Analyte	*Sensitivity [pA/hPa]*
Water	700
Methanol	1.1
Ethanol	1.3
Propanol	2.9
Isopropanol	0.7
Tetrachloromethane	2.0
Dichloromethane	0.5
1,1,1-Trichloroethane	7.0
Trichloromethane	0.4
1,1,2-Trichloroethylene	0.9

Application of the semiconducting sensor films PFV56/175/240 allowed to reduce the cross-sensitivity for water by screening the oxide substrate (Table IV and V). PFV175 represents the best film in this respect. The smallest current changes exhibited the partially graphitized specimen PFV245. The correlation between pressure and current signal was practically linear up to more than 10 hPa analyte pressure, i.e. from the sensitivity limit near 10 Pa to more than 10 hPa (Figure 3). The time response and reversibility is shown in Figure 4 for a representative case PFV56 with analyte isopropanol. Pressure decrease steps resulted in current answers of the order of 1 min. The signal returned reversibly to practically zero after an excursion to more than e.g. 400 Pa.

TABLE IV Sensitivities of the PFV sensors for alcohol vapours and humidity (18V applied)

Analyte	*PFV56*	*Sensitivity [pA/hPa] PFV175*	*PFV245*	*Order of sensitivity*	*Order of Hydrophobicity*
Water	1.2	0.25	0.5	–	–
Methanol	0.22	0.1	0.05	1	1
Ethanol	0.4	0.19	0.12	2	2
Isopropanol	0.5	0.32	0.1	3	4
Propanol	1.5	1.4	0.4	4	3

The sensitivity increased systematically from primary to secondary alkane groups neighboring the alcohol oxygen atom: $-CH_3 < -CH_2-CH_3 < -CH-(CH_3)_2$ (Table IV). Propanol, however, represents an extreme outranging all other alcohol analogs. The sensitivity of the sensors for the chlorinated hydrocarbons does not correlate with the dipole moments of these analytes but increases with the Brönstedt acidity (Table V), i.e. in the order tetrachloromethane ≈ dichloromethane < 1,1,1-trichloroethane < trichloromethane ≪ 1,1,2-trichloroethylene.

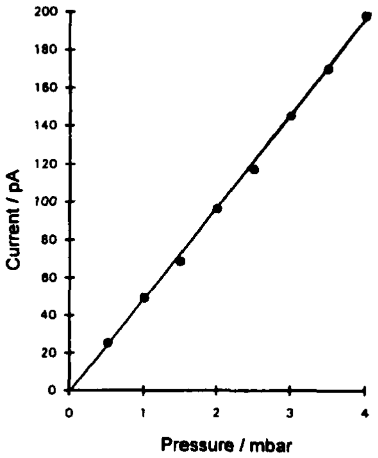

FIGURE 3 Linearity of a PFV56 sensor for isopropanol

TABLE V Sensitivities of the PFV sensors for chlorinated hydrocarbon vapours (18V applied)

Analyte	*Dipole moment [D]*[39]	*Order of Brönsted acidity*	*Sensitivity [pA/hPa]*		
			PFV56	*PFV175*	*PFV245*
Tetrachloromethane	0	0	0.14	0.05	0.05
Dichloromethane	1.60	1	0.1	0.05	0.05
1,1,1-Trichloroethane	1.78	2	0.12	0.09	0.05
Trichloromethane	1.01	3	0.2	0.16	0.05
1,1,2-Trichloroethylene	0.90	4	0.7	0.86	0.1

DISCUSSION

Two properties of the sensor material are generally considered to determine its specificity. One is the functionality in terms of electron-rich and -deficient centres. Analytes with different charge distributions and dipolar groups can be discriminated by the sensor functionality due to donor-acceptor interactions. Parallel to this, host-guest inclusion or steric hindrance (e.g. molecular cavities) can modify the binding scenario (propanol and isopropanol). Heat treatment of the precurser of more than 200°C leads to partial graphitization (Table I) and dramatic conductance increase (Table II) so that large direct currents made sensitive

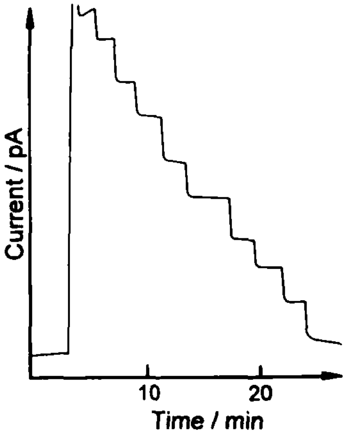

FIGURE 4 Time response of a PFV56 sensor for isopropanol. Pressure decreases from 400 to 0 Pa

current change measurements practically impossible. Therefore, such specimen (e.g. PFV245, PFV400) where the discrete polymeric chain character is partially replaced by graphitic domains were not further investigated as sensor layers.

Assuming only surface adsorption and employing electronic semiconductor theory, the conductivity σ should depend exponentially on the gas analyte pressure p [32,34] :

$$\sigma \approx \sigma_0 e^{\alpha p} \tag{2}$$

where σ_0 and α are the unloaded polymer conductivity and a constant with the dimension [Pa^{-1}]. Our results (e.g. Figure 3), however, indicate a practically linear dependence:

$$\sigma = \sigma_0(1 + \beta p) \tag{3}$$

with the proportionality constant β [Pa^{-1}]. This indicates that simple charge transfer to semiconducting matrix volumes or chains seems not to determine the conductivity changes.

An alternative to a solid state related mechanism consists in an ionic conductivity (σ_{ion}) of a fluid phase existing within the voids between the polymer chains filling more or less the hopping distances. Here, a conversion between electronic and ionic conduction in analogy to heterogeneous electrochemical processes could take place. In the case that not only the hopping cannot contribute to conductivity (σ_{hop} low), but also the chains show a too high resistance (σ_{ch} low), the condensed hydrous or analyte phase could support conductance (σ_{ion}). The highest conductivity will be generated by the highest proton concentration, i.e. the strongest Brönsted acid, which would be water. The replacement of water by sufficient alcohol or chlorinated hydrocarbons should result in lower conductivity. This is in clear contradiction to our finding that water and strongest Brönsted acids give lowest conductivity. The ionic conductivity mechanism, therefore, can be practically excluded.

The electrical sensor response of the conductance sensor is based on changes of the polymeric chain conductivity σ_{ch}, the hopping conductivity σ_{hop}, or the ionic conductivity between the chains σ_{ion}, assumed in series in a first order approximation:

$$\sigma = (\sigma_{\mathrm{ch}}^{-1} + \sigma_{\mathrm{hop}}^{-1} + \sigma_{\mathrm{ion}}^{-1})^{-1}. \tag{4}$$

σ_{ion} is not only influenced by ion migration in the humidity or analyte condensation film but also by proton tunneling when hydrogen bonds can be established. The overall intra-chain conductivity (of all chains in the film volume) σ_{ch} is itself affected by the concentration of mobile charges n and the average charge mobility in the conjugated units in the polymeric chains $\bar{\mu}$:

$$\sigma_{\mathrm{ch}} \propto \bar{\mu} n. \tag{5}$$

It has been shown that such conjugated units can normally show various lengths, not longer than seven units [30], and are separated by hydroxyethylene moieties. The electron intra-chain concentration n can be affected by charge transfer complexes of the analyte molecule with the polymer backbone either at the film surface or in the bulk (when bulk diffusion occurs). Electron injection by e.g. Lewis bases would increase n, but would decrease the conjugated character of the poly(furylenevinylene) chain, thus lowering the mobility $\bar{\mu}$. The netto change of σ_{ch}, therefore, depends on the influences of n and $\bar{\mu}$ (Eq. 5). An increase of n not necessarily leads to higher conductivity. Actually, provision of excess electrons to the π-electron system can impair the conjugated character, and therefore decrease the intramolecular mobility $\bar{\mu}$. Protonation, on the other hand, leads to a bathochromic shift of the UV-VIS absorbtivity [35], and partial positively charged polymer regions with planar sp^2-hybride character. This means that the conjugation and $\bar{\mu}$ should increase.

Changes of conjugation are always accompanied by structural reorganizations: when electrons are withdrawn, the furan ring systems in the polymeric chains tend to stabilize by assuming the utmost conjugation, sp^2-hybride character, and flatness. I.e. the conjugated chains units will assume the maximum length and rigidity. In crystalline polymers [36,37,38], interchain gaps between the ends of neighbouring chains would minimize, and electronic hopping should reach maximum values (higher σ_{hop}). With electron excess, on the other hand, the chains would shrink, the hopping distance would increase, and σ_{hop} would decrease.

In the present case, of widely amorphous isotropic entangled polymer chains with trans-bends, hopping most probably takes place at crossing contact points of the single chains, between the electronic π systems. Flexible molecules with moderate conjugation and a high freedom to twist and fold will achieve a maximum number of crossing contacts with minimum hopping distance (high σ_{hop}). Highly conjugated stiff polymer chains, on the other hand, would give up most of the inter-chain contacts retaining less of them. This means that electron donors (Lewis bases) could lead to higher *n* with either a σ_{ch} increase or a decrease of conductivity due to conjugation reduction (lower $\bar{\mu}$), and an inter-chain hopping contact increase (higher σ_{hop}). Electron acceptors (Lewis acids) adsorption or protonation (Brönsted acids), however, should cause the opposite: conjugation enhancement (higher σ_{ch}), inter-chain hopping contact decrease (smaller σ_{hop}), and an overall decrease of conductivity σ so that Eq. 4, therefore, simplifies to

$$\sigma \approx \sigma_{hop}. \tag{6}$$

Alcohols are very weak Brönsted acids. Methanol is the strongest acid. The acidity should decrease (pK_a value increases) with increasing (+I)-effect, i.e. from primary to secondary alkyl groups neighbouring the oxygen atom: $-CH_3 < -CH_2-CH_3 < -CH-(CH_3)_2$. On the other hand, the (+I)-effect of the various alkyl groups enhances the electron density at the oxygen bridge atom between the alkyl group and the hydrogen thus increasing the Lewis base strength and nucleophilicity.

At PFV56 and PFV175, we observed increasing conductivity with increasing (+I)-effect in the alcohol molecules with the alkyl groups $-CH_3 < -CH_2-CH_3 < -CH-(CH_3)_2$. This analogous behaviour agrees well with the IR and resistance measurements indicating partial or almost complete conjugation in these PFV types. This means that either the Brönsted acidity or the Lewis basicity could be responsible for the increase of σ_{hop}. The secondary alcohol isopropanol (stronger +I) should give a higher conductivity than the primary alcohol propanol. Actually the opposite is true (Table IV). This indicates that another mechanism like steric or hydrophobicity effects may play a role.

Chlorine atoms cause (-I)-effects. An increasing number of chlorine atoms neighbouring a C-H bond therefore should increase the Brönsted acidity in the order dichloromethane < trichloromethane. A neighbouring double bond stabilizes the formation of the anion radical so that, in our case, 1,1,2-trichloroethylene becomes the strongest proton donor. We, however, found a conductivity increase at both PFV56 and PFV175 with increasing acidity (Table V):

dichloromethane < 1,1,1-trichloroethane < trichloromethane
< 1,1,2-trichloroethylene.

Tetrachloromethane is no proton donor and exhibits the lowest conductivity comparable to the weakest Brönsted acid dichloromethane. These results are in clear contradiction to the above model basing on the conjugation enhancement by protonation followed by a polymer chain rigidity increase and the interchain contact conductivity (σ_{hop}) decrease. Further, there is no correlation between sensitivity and dipole moment (Table V).

One has to assume at that stage of research that van der Waals interactions between aliphatic C-H or C-Cl bonds influence the energetic status of the conjugated chains so that they loose their rigidity and straightness and lead to higher hopping conductivity. Hydrophobicity may play an important role. The longest aliphatic chains in an alcohol (propanol) causes the highest sensor effect. In the case of chlorinated hydrocarbons, most tested compounds exhibited more or less equally low sensitivity in contrast to the only system with a π-electron system, i.e. 1,1,2-trichloroethylene. This molecule obviously can strongly interact with its delocalized electrons with those of the polymer chain thus affecting its conformation. Further experimental and theoretical studies are necessary to clarify these questions.

CONCLUSIONS

The production steps of the interdigital array resistor transducer were reduced to metal coating of alumina plates and structuring of the interdigital array by CAD-supported pulsed laser ablation (PLA) instead of conventional lithographic techniques. This development targets low customer-determined unit numbers and customized design specialities.

Sensors on the basis of the semiconducting species poly(2,5-furylenevinylene) (PFV) with various hydroxylation and conjugation degrees (copolymers with 1-hydroxyethylene and vinylene units) can mask the cross-sensitivity of the alumina substrate at room temperature without internal transducer heating. Specimen with partial graphitization generated at temperatures above 200°C (e.g. PFV245) exhibit relatively low sensitivities because of high conductivities and direct currents. Highest sensitivities are provided by the sensor types PFV56 and PFV175 for propanol and isopropanol, chloroform (trichloromethane) and 1,1,2-trichloroethylene.

Sensitivities for alcohols and chlorinated hydrocarbons are most probably related to hydrophobic van der Waals interactions whereas Brönstedt acidity or Lewis basicity seem to play minor roles. Stronger electronic or van der Waals interaction leads to deviation of the idealy flat and rigid structure of the conjugated polymer thus allowing for more flexibility of the chains, more intimate inter-chain contacts and higher conductivity.

Acknowledgements

This work has been supported by the German Federal Ministry for Research and Technology (Project 13 AS 110–1970/34). Valuable technical assistance by A. Conradi, M. Männ, and U. Beck, all the Federal Institute for Materials Research and Testing (BAM), has to be acknowledged.

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