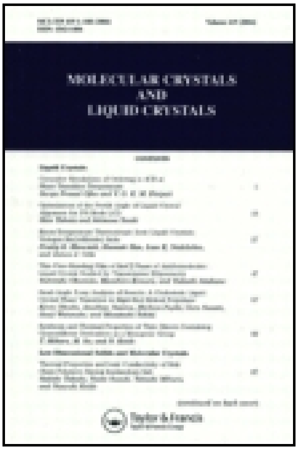

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Photoconductivity of Poly(Arylenevinylene)S and Poly(Hetarylenevinylene)S

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PHOTOCONDUCTIVITY OF POLY(ARYLENEVINYLENE)S AND POLY(HETARYLENEVINYLENE)S

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Abstract The intramolecular condensation of aromatic Schiff bases leads under strong alkaline conditions to the poly(arylenevinylene)s and poly(hetarylenevinylene)s A - H. Due to the extreme stereoselectivity the resulting products are rigid, (E)-configurated polymers. The broad band gap of the unsubstituted intrinsic insulators is decreased by alkoxy substituents. Investigations of the photoconductivity and the photoreactivity, as well as of the AC-conductivity of some undoped, doped and quaternized systems are performed.

Keywords: poly(arylene vinylene), poly(hetarylene vinylene), stereoselectivity, conductivity, photoconductivity, reactivity, prepolymers

INTRODUCTION

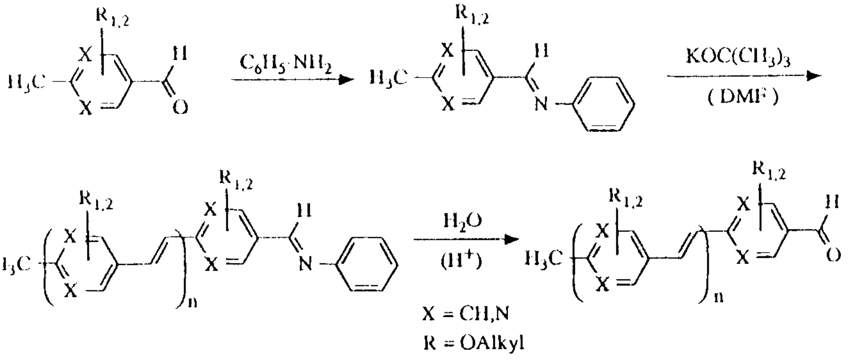
Poly(arylenevinylene)s [PAV] and poly(hetarylenevinylene)s [PHAV] attract as rigid, conjugated polymers an increasing interest in materials science.[1] Due to their favorable properties we are mainly investigating alkoxy substituted systems. These products are yellow to red colored insulators with a broad band gap. The value of 2.4 eV for the unsubstituted poly(phenylenevinylene) decreases to 2.1 eV by substitution with two electron releasing groups. Doped with electron acceptors these compounds show a considerable electrical conductivity. Prominent goals are macromolecular semiconductors in solar cells, photoconductors in electrophotographic devices and electrodes for polymer batteries.

SYNTHESIS

The overall (E)-configuration of the double bonds in the polymer backbone is a decisive precondition for the properties of the PAV and PHAV systems. A lot of synthetic routes, for example Wittig, McMurry and Heck reactions lead to (E/Z)-isomers - sometimes with small percentages of (Z)-configuration, but even these can lower the quality of the materials.

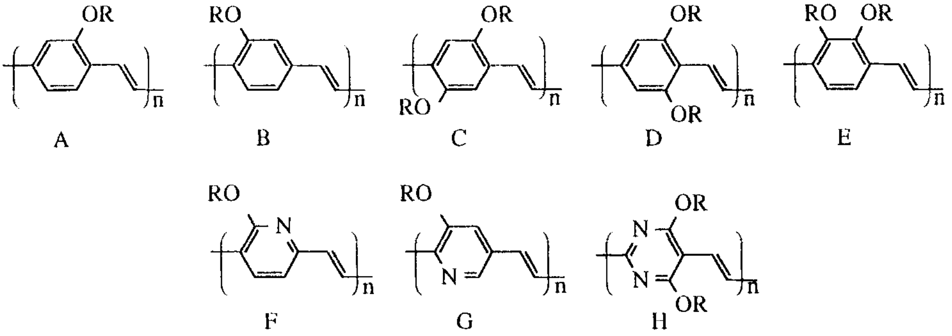
The often used precursor route via soluble prepolymers with saturated links between the aromatic building blocks has the additional disadvantage that uncomplete elimination processes lead to a main chain with an interrupted conjugation. In order to avoid these difficulties we developed a modification[2] of the so-called Siegrist reaction.[3]

The stepwise selfcondensation of aromatic Schiff bases containing methyl groups leads in a strongly alkaline medium in high yields to the polymers shown in SCHEME 1. Model compounds reveal for the generation of the double bonds a stereoselectivity of E:Z > 1000:1.[4]



SCHEME 1 Synthesis of mono- and dialkoxy substituted oligo- and poly(phenylenevinylene)s and their heteroaromatic analogues (7 < n < 40).

The repetition units were varied widely in order to optimize the photoconductivity of the materials. SCHEME 2 summarizes the repetition units which differ in the number, the position and the length of the side chains:



A $R = CH_3, C_2H_5, C_3H_7, C_4H_9, C_6H_{13}, C_8H_{17}, C_{12}H_{25}, C_2H_4OC_2H_5, (C_2H_4O)_3H$
B $R = CH_3, C_2H_5, C_6H_{13}, C_{12}H_{25}, C_{16}H_{33}$
C $R = CH_3, C_2H_5, C_3H_7, C_4H_9$, iso-$C_4H_9$, neo-$C_5H_{11}$, $C_6H_{13}, C_8H_{17}, C_{16}H_{33}, C_2H_4OC_2H_5$
D $R = C_8H_{17}, C_2H_4OC_2H_5$
E $R = C_6H_{13}$
F $R = CH_3, C_2H_5, C_6H_{13}, C_{12}H_{25}$
G $R = CH_3, C_2H_5, C_3H_7, C_4H_9, C_6H_{13}, C_8H_{17}, C_{12}H_{25}, C_{16}H_{33}$
H $R = C_2H_5\ C_4H_9, C_6H_{13}, C_8H_{17}, C_2H_4OC_2H_5$

SCHEME 2 Repetition units of the investigated poly(phenylenevinylene)s and poly(hetarylenevinylene)s.

GENERAL PROPERTIES

Differential scanning calorimetry reveals that the yellow to dark red powders often begin to decompose above 140 °C. The solubility of the compounds depends strongly on the lengths of the main chain and the side chains. Contrary to longer rigid backbones, longer side chains enhance the solubility. The degree of the oligomerization can be estimated by GPC, FD-MS measurements and end group determinations in the ^{1}H nmr spectroscopy. FIGURE 1 shows an FD-MS spectrum of a sample with a relatively low molecular weight.

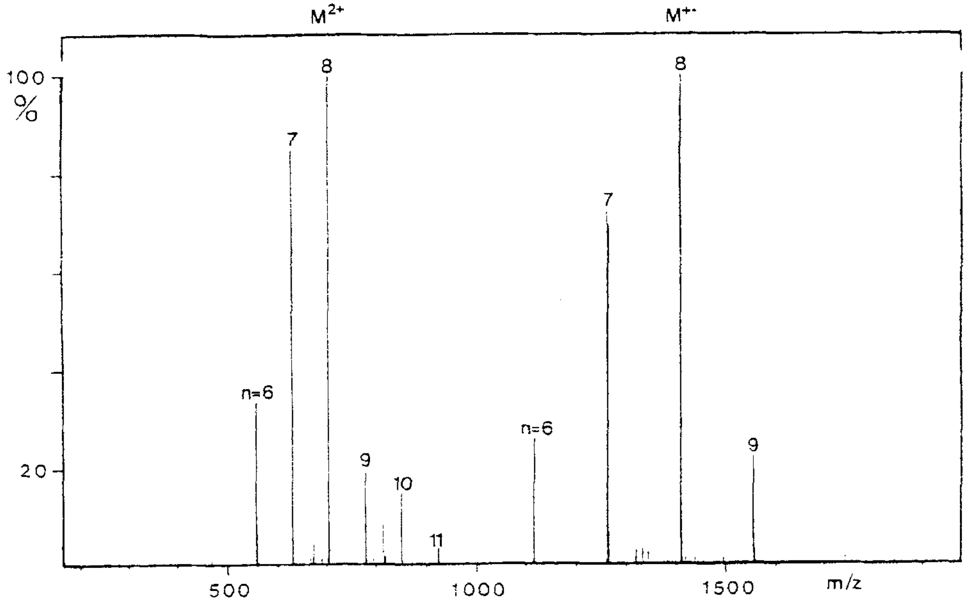


FIGURE 1 Field desorption mass spectrum of oligo(ethoxyphenylenevinylene) with methyl and phenylimino end groups: single and twofold charged molecular ions.[5]

All compounds possess an intense absorption in the visible region between 440 and 500 nm. The absorption maxima depend solely on the substitution pattern - provided that the maximum conjugation length of n ≈ 9 is reached.

PHOTOCONDUCTIVITY

The photoconductivity measurements of the compounds were performed either in dispersion layers or in thin films. The formation of pure films is possible for the compounds with long alkoxy side chains. All systems were compared with the commercial standard perinone in equivalent dispersions and with dye sensitized films of carbazole, respectively.

FIGURE 2 shows the measurement of the photoconductivity of poly(methoxyphenylenevinylene).[4] The curves for the decay of the voltage U(t) in the dark and in the light match exactly the curves of the perinone standard.

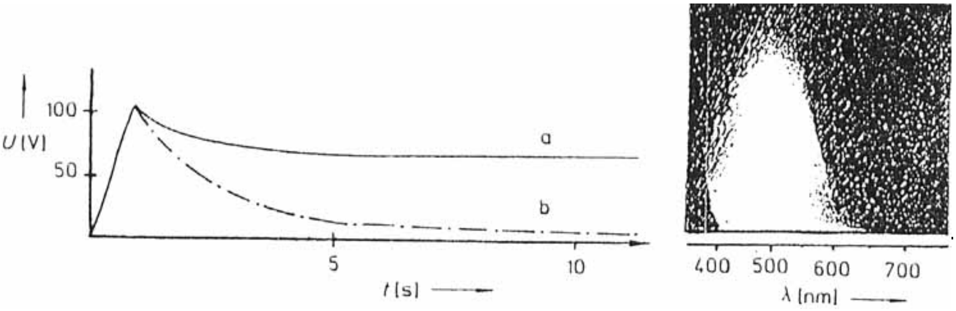
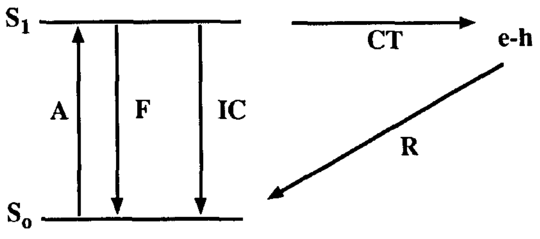


FIGURE 2 Discharge of a dispersion layer of poly(methoxyphenyleneviny lene) in the dark and on irradiation with visible light in the range of 400 to 600 nm. The right part shows the wavelength dependence of the photosensitivity, which reaches a maximum for about 500 nm.[4]

The absorption (A) of visible light leads to the first excited single state S_1 which is partly deactivated by fluorescence (F) and by a radiationless internal conversion (IC). However, some of the electronically excited species give a charge transfer (CT) generating radical cations and radical anions (polarons). According to the theory of effectively conjugated chain segments conceived by Hörhold[1], this disproportionation process is responsible for the formation of charge carriers. Additional processes should occur at the electrodes. Since we have electron rich donor systems, the electron transfer at the anode should provoke a mechanism for a hole transport. Actually, not all electron-hole (e-h) pairs can contribute to the charge transport. Direct and indirect electron-hole recombinations (R) have to be taken into account.[6]



SCHEME 3 Light-induced generation of electron-hole pairs.

The efficiency of a photoconductor can be characterized by the time $t_{1/2}$ which is needed for the discharge of 50 % of the initial voltage gained after the charging process. Our measurements revealed that a prolongation of the alkoxy side chains leads to lower values $t_{1/2}$ till a minimum is reached for the propyloxy group (FIGURE 3). Longer side chains enhance the ability of forming films but decrease the photoconductivity. The substitution pattern plays also a decisive role. The 2,5-dialkoxy substituted systems are better photoconductors than the monosubstituted compounds. 2,3-Disubstitution is also less favorable. Obviously there is an almost activationless transport of the charge in the fully conjugated polymer chain; the crucial point is the electron hopping process from chain to chain. Longer side chains can deteriorate this process because of longer average distances of the backbones and coiling effects. The number of alkoxy substituents changes the band gap; the position of the substituents may have some influence on the average conjugation length.

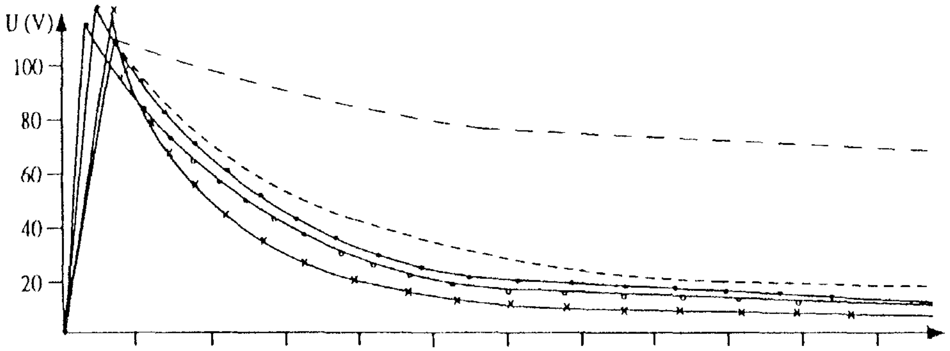


FIGURE 3 Discharge U(t) of poly(2,5-dimethoxy-1,4-phenylenevinylene) (•••), poly(2,5-diethoxy-1,4-phenylenevinylene)(-●-) and poly(2,5-dipropyloxy-1,4-phenylenevinylene)(-×-×-) by irradiation with visible light. The dotted lines represent the discharge of the standard perinone in the dark and in the light.

The poly(hetarylenevinylene)s [PHAV] possess a much lower photoconductivity in comparison to the corresponding carbocyclic materials. An explanation for this result is not obvious. Quaternized PHAV is currently investigated.

PHOTOSTABILITY

All synthesized oligomers and polymers are completely photostable in the solid state. Moreover, a chemical transformation of the compounds in solution cannot be observed by irradiation in the visible region. On the contrary a relatively fast degradation occurs at 254 nm. The formation of CC single bonds leads to a crosslinked polymer. The material looses totally its fluorescence and its photoconductivity. The UV spectrum reveals that all stilbene units have disappeared. Additional photoreactions leading to a cleavage of the polymer backbone can be observed for illuminations in the presence of oxygen.

AC-CONDUCTIVITY

The conductivity measurements of the undoped materials were performed by casting 50 µm thick films.

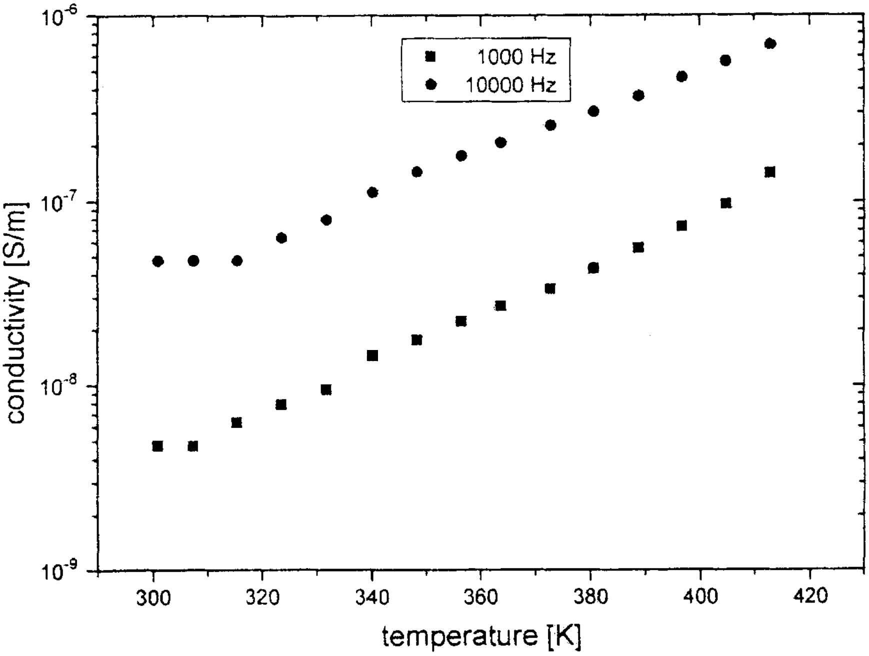


FIGURE 4 AC-Conductivity of poly(3-octyloxy-2,5-pyridinylenevinylene)

Exposing of the probes in a saturated iodine atmosphere leads to doped systems with a probably higher conductivity ($\sigma = 10^{-2} - 10^{-7}$ S cm^{-1}). The quaternized systems should show an even higher conductivity.

ACKNOWLEDGEMENTS

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