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A NEW SYNTHESIS OF SOLUBLE POLY(1,4-PHENYLENEVINYLENE)S AND POLY(2,5-PYRIMIDINYLENEVINYLENE)S

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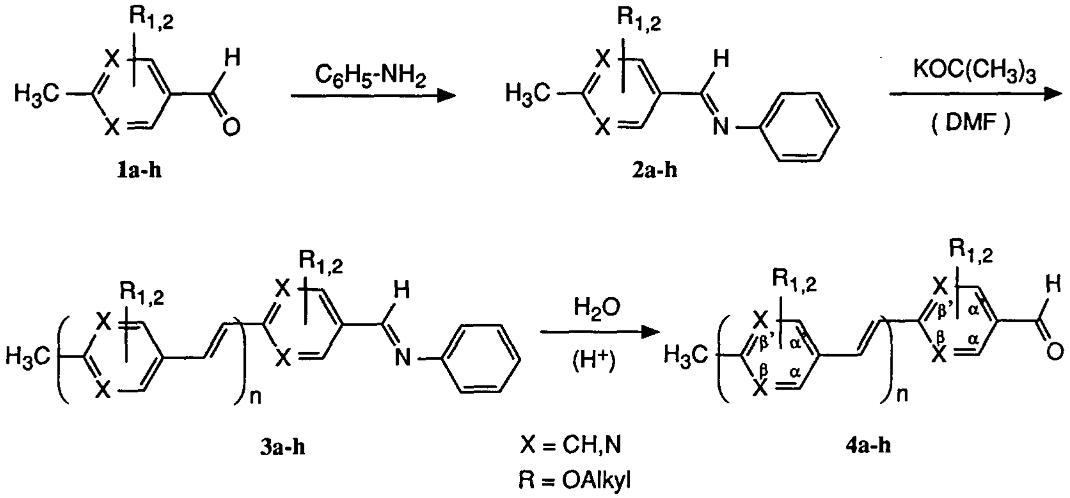
Abstract: Alkoxy-substituted 4-methylbenzylideneanilines **2a-f** and their pyrimidine analogues **2g,h** show an efficient selfcondensation in the alkaline medium $KOC(CH_3)_3$/DMF. The totally stereoselective reaction yields **3a-h** which are transformed by acidic work-up to **4a-h**. A narrow distribution of the molecular weight can be achieved.

Poly(phenylenevinylene)s and their heterocyclic derivatives deserve great interest because of their electrical and optical properties[1)]. In the last years soluble PPV systems have been obtained by different methods: McMurry reaction[2)], Hofmann elimination[3)], Wittig reaction[4)]. However, these syntheses lead always in longer chains to some failures like saturated carbon centres, (Z)-configurated double bonds, etc. Therefore we have tried to use the condensation of azomethines and aromatic methyl compounds for this purpose. In contrast to the known Siegrist reaction[5)] both reactive groups were incorporated into the same molecule, in order to provoke selfcondensation in an alkaline medium. The solubility in organic solvents like DMF has to be enhanced by flexible side chains as an "internal solvent"; otherwise the condensation reaction is immediately stopped by precipitation. A repetition of earlier attempts with (E)-N-(4-methylphenylmethylene)benzenamine[6)] showed us that the reaction is already terminated after three condensation steps (n=3). Less than 5% of the material possess a higher molecular weight (n=4,5...). Consequently, we have introduced alkoxy side chains in order to get real PPV systems. The method can also be applied on heteroaromatics like pyrimidine derivatives. Thus, we succeeded in the generation of poly(2,5-pyrimidinylenevinylene)s, the first PPV analogue materials with hetero atoms in every repetition unit. The incorporation of nitrogen atoms enhances additionally the solubility and hence the average chain length.

The 2-alkoxy-4-methylbenzaldehydes **1a,c** and the 3-alkoxy-4-methylbenzaldehyde **1b** were obtained in yields of 70-90% by the reaction of the corresponding hydroxy compounds[7,8)] with iodoalkanes in the presence of K_2CO_3 in acetone[9)]. The 2,5-dialkoxy-4-methylbenzaldehydes **1d,e** were prepared by a twofold alkylation of the potassium salt of 2-methylhydroquinone with bromoalkanes in the presence of Aliquat 336 (yield 30-99%)[10)] followed by a selective formylation[11)] with $Cl_2HC\text{-}OCH_3/SnCl_4$ in dichloromethane (yield 80-95%). 2,6-Dialkoxy-4-methylbenzaldehyde **1f** can be generated by an analogous alkylation of 5-methylresorcinol (orcinol) and treatment of the ether with $C_4H_9Li/C_6H_5N(CH_3)\text{-}CHO$ (yield 45-55%)[12)]. 4,6-Dialkoxy-2-methylpyrimidine-5-carbaldehydes **1g,h** can be obtained by nucleophilic substitutions[13)] of the chlorine atoms in 4,6-dichloro-5-(1,3-dioxolan-2-yl)-2-methylpyrimidine with sodium alkoxides and subsequent hydrolysis of the dioxolane (yield 80-90 %). All aldehydes **1a-h** react with one equivalent of aniline at 40-60°C forming the azomethines **2a-h** (yield 90-100 %). Polycondensation of **2a-h** can be per-



X = CH,N
R = OAlkyl

Compound 4	R	X	Yield %	Melting range [°C]	Average chain length n_{NMR}	 n_{GPC}	 n_{MS}
a	α-OC_6H_{13}	CH	96	190...:280	9	8	9
b	β-OC_6H_{13}	CH	60	195.....280	9	9	-
c	α-$OC_{12}H_{25}$	CH	94	210.....280	13	12	(9)
d	α,β'-OC_8H_{17}	CH	97	190.....235	12	9	(8)
e	α,β'-$O(CH_2)_2OC_2H_5$	CH	84	265.....320(Z)	27		
f	α,α'-OC_8H_{17}	CH	89	190.....280	27		(8)
g	α,α'-OC_6H_{13}	N	38	>250 (Z)	>30		
h	α,α'-OC_8H_{17}	N	93	>250 (Z)	>30		

formed at 90°C in dry DMF with two equivalents of potassium tert-butoxide[14]. Work-up with hydrochloric acid leads to the hydrolysis **3a-h** → **4a-h**. The polycondensation reactions are in all cases **a-h** highly stereoselective. There are no hints for a (Z)-configuration at all. The investigated products correspond to a reaction time of approximately 1 hour and are insoluble in acetone but soluble in chloroform[15]. The singlet signals of the terminal groups CH_3 and CHO in the ^{1}H-NMR spectra allow a reliable determination of the average molecular weight. In some cases a GPC analysis was made for comparison; however, the calibration by polymer standards like polystyrene turned out to be complicated for n>10. Similarly, field desorption mass spectrometry gives only good results for n<10.

Normally, the yields of a Siegrist reaction[5] are much lower. However, an intramolecular activation is important in our systems **2a-h**. The imino group enhances by its electronic effect the reactivity of the methyl group. Consequently, this activation is decreased by an increasing chain length. Finally, the reactivity approaches to the behavior of a non-activated methylarene like toluene. Due to this effect, it is possible to generate products with a relatively narrow distribution of the molecular weight[16)]. We obtained for example **4a** as a solid, in THF soluble product which consists mainly of the decamer (n=9). The GPC diagram (figure 1) shows some nonamer (n=8) and a trace of undecamer (n=10).

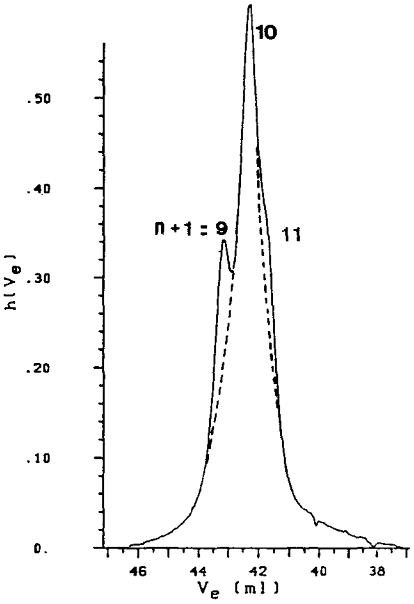


Figure 1, GPC diagram of **4a** (THF, 22°C, standard: polystyrene, UV detection)

The products **4a-h** were well defined by elementary analysis, UV-IR-, ^{1}H-NMR and ^{13}C-NMR spectra. The following chemical shift values δ in $CDCl_3$ are characteristic for the PPV systems **4a-f**:

4a-f		^{1}H-NMR	^{13}C-NMR
end groups	CH_3	2.25 - 2.35	16 - 22
	CHO	9.9 - 10.4	189 - 192
PPV - chain	CH (arom.,olef.)	7.0 - 7.7	109 - 140
	C_qO	-	157 - 158
side chains	O - CH_2	4.0 - 4.2	68 - 70
	CH_2	1.2 - 1.95	24 - 33
	CH_3	0.85 - 0.95	13 - 16

Naturally, the N atoms in the pyrimidine systems **4g,h** change the resonance signals, especially for the main chain. The characteristic ^{13}C-shift ranges for the pyrimidine segments are $\delta = 99\text{-}100$ (C-5), 162-164 (C-2), 167-169 (C-4,6), and for the carbon atoms in the double bonds $\delta = 126\text{-}132$. The olefinic protons lead to an AB spin pattern at $\delta = 7.3\text{-}8.4$. The coupling constant $^3J = 16$ Hz as well as the IR band at 970-990 cm^{-1} confirm the (E)-configuration.

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14)The reactivity of the methyl group is in the pyrimidine systems **g,h** much higher than in the benzene systems **a-f**; even in the absence of catalysts **1g,h** show some selfcondensation on storage at room temperature.

15)The amount of product soluble in acetone as well as the amount of product insoluble in chloroform are very small under these conditions. However, a much shorter reaction time increases the first one, whereas a reaction time of 24 hours or more enhances the portion of totally insoluble product.

16)Usually an average rate constant is assumed in such polycondensation processes1). However, in our case we have a much faster reaction at the beginning than towards the end. Hence, the curve for the average molecular mass versus the reaction time should cross the "normal" curve. One can assume in the region of the crossover a plateau which might be responsible for the high uniformity of the oligomer.

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