

Metal catalyzed polycondensation reactions

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Abstract: Metal catalyzed polymerizations are chain reactions necessitating a constant valence of the metal. In contrast to that metal catalyzed polycondensations are step growth reactions involving a change of the valence of the metal. Tuning of the reaction by structural variations of the metal catalyst are demonstrated with the Pd-catalyzed vinyl polymerization of norbornene, the alternating copolymerization of ethylene with carbon monoxide and the Heck reaction as examples. One and two electron processes can be involved in metal catalyzed polycondensations. The oxidative polymerization of 2,6-dimethylphenol, the Heck reactions as well the Ni-catalyzed synthesis of polyphenylenes are discussed.

Introduction

Metal catalyzed reactions are of indispensable importance in the value adding chain of chemical technology. In the area of macromolecular chemistry metal catalyzed polymerizations are of basic importance to produce commodity polymers. The elaboration of metallocene catalysts is causing a strong push in the development (1). Metal catalysis is also of importance in the synthesis of monomers and in polycondensation as well as in polyaddition.

Metal catalyzed polymerization reactions are chain reactions and necessitate to keep the valence of the metal constant. According to this definition redox polymerizations are not included as metal catalyzed polymerizations; the metal is not participating in the chain growth reaction. Polycondensations and polyadditions feasible by metal catalysis are chain reactions involving a change of the valence of the metal.

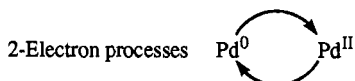
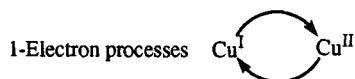
These reactions are predominantly two electron processes $\text{Pd}(0) \rightleftharpoons \text{Pd}(\text{II})$, $\text{Rh}(\text{I}) \rightleftharpoons \text{Rh}(\text{III})$, $\text{Ru}(0) \rightleftharpoons \text{Ru}(\text{II})$. One electron processes are prevailing in oxidation reactions: $\text{Cu}(\text{I}) \rightleftharpoons \text{Cu}(\text{II})$.

Metal-catalyzed Polymerizations

Chain reaction with constant valence of the metal

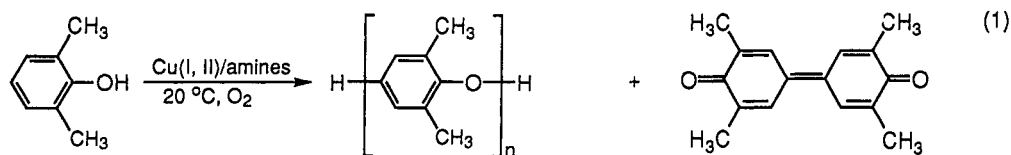
Metal-catalyzed Polycondensations

Step growth reaction with change of valence of the metal



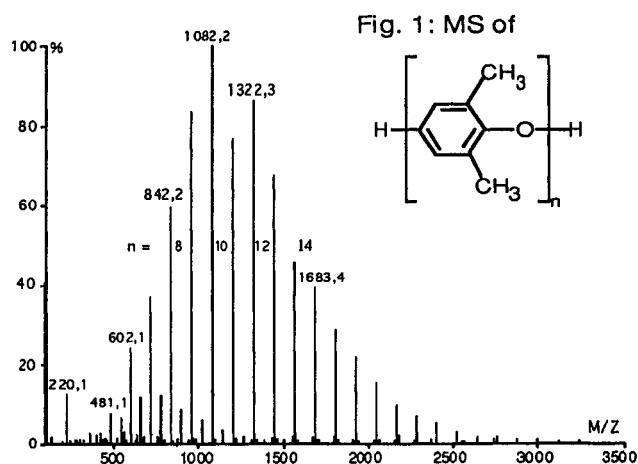
COPPER CATALYZED SYNTHESIS OF POLY(PHENYLENE OXIDE)

The copper catalyzed oxidative polymerization of 2,6-dimethylphenol to poly(oxy-1,6-dimethyl-1,4-phenylene) was described by Hay in 1959 (2).



Diphenoquinone is formed as a by-product of this synthesis. The amount of the diphenoquinone formed is dependent from the ligands of copper, the solvent and the substituents (3). The polyreaction is extremely selective and results in a product with one aromatic H and a phenolic hydroxy group as end group.

Products with low molecular weight can be isolated at short reaction times. The mass spectrum of this product is given in fig. 1. Doubly charged species are causing the smaller peak series in the range of lower masses.



The molecular weights obtained at the beginning of the reaction are relatively low in contrast to a polymerization (chain reaction). On the other hand they do not correspond to the values according to the classical theory of polycondensation.

At 50 % conversion a product is formed with a M_n of about 600. It is also confirmed by high resolution oligomer GPC that only one polymer homologous series is present (fig. 2).

The Flory distribution to be expected by classical polycondensation is given by

$$n_x = p^{x-1} (1-p) \quad (2)$$

n_x = mol fraction with the polymerization degree x , p = conversion

The ratio of two neighbouring polymer homologous is constant in polycondensation and corresponds to the conversion. This is not true in the synthesis of poly(phenylene oxide). At a conversion of 53 % a constant value of 0,7 is observed at ratios of polymerization degrees 3/2 and higher (4).

Fig. 2: GPC of

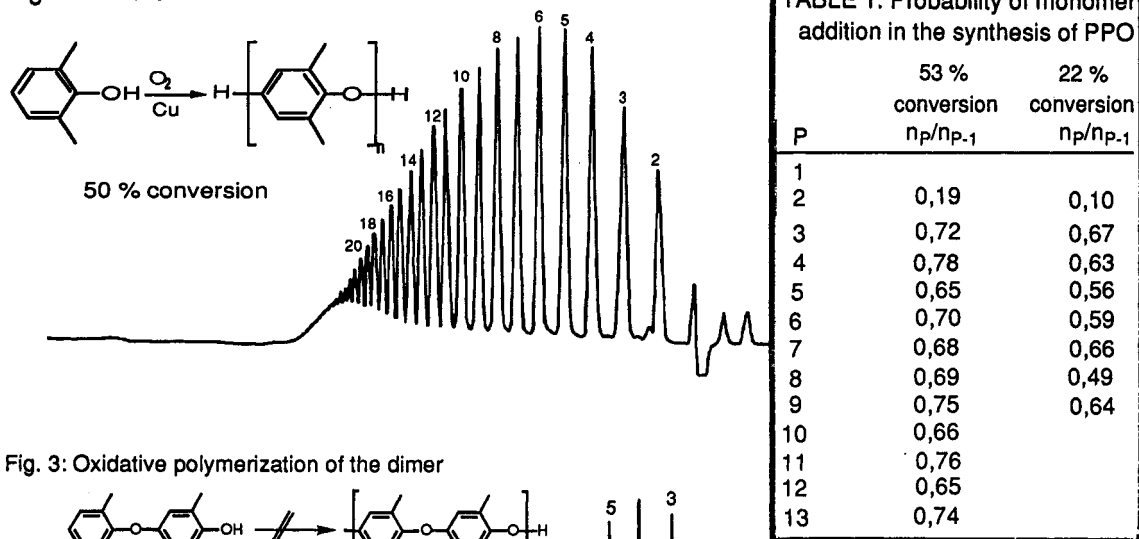
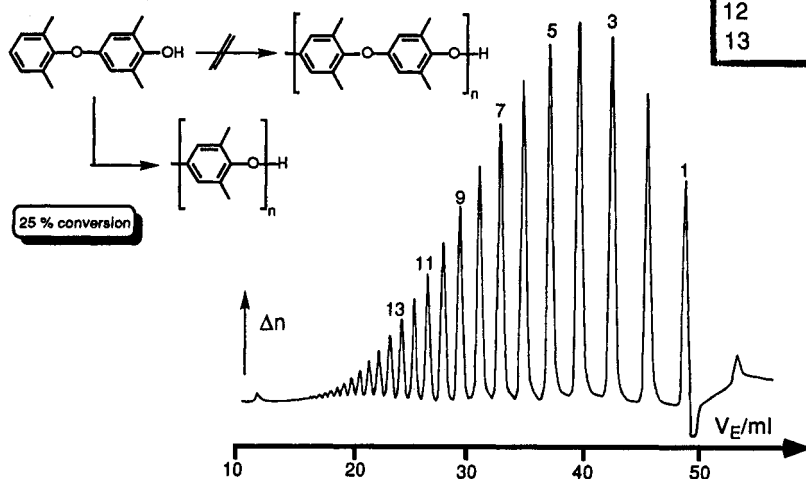


Fig. 3: Oxidative polymerization of the dimer



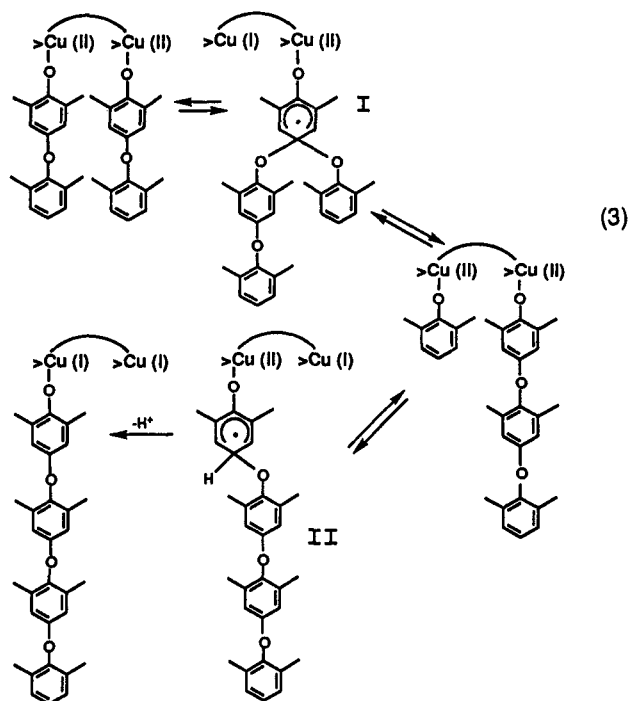
The ratio of n_2/n_1 is 0,19. Similar results are obtained at other conversions. This is caused by the apparently lower reactivity of the monomer. Using the dimer reveals another peculiarity in the oxidative polymerization.

The oxidative polymerization of the dimer is not resulting in the expected polymer homologous series with even degrees of polymerization.

Even at 25 % conversion the complete polymer homologous series of poly(phenylene oxide) is present (5). This shows that a fast equilibration reaction is dominating the oxidative polymerization. A proposal of the mechanism is given in equ. 3.

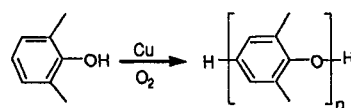
According to the literature neither Cu(0) nor Cu(III) species are involved in the oxidative polymerization (6). Since we start with a neutral monomer and end up with a neutral polymer two 1-electron processes have to occur during the reaction. The best catalytic activities are obtained with copper chloride and copper bromide. It is known that these copper compounds form binuclear complexes. A copper bound chinol radical is formed in an equilibrium reaction by a 1-electron transfer. In principal at this stage the second 1-electron process could occur to form the chinolether commonly cited in the literature (3). But we suppose that copper is participating in the reaction because all measures impeding the formation of phenolate result

in a larger formation of diphenoquinone. Cleavage of structure I can result in the starting phenolates of the polymerization degree 2 or the phenolates of the polymerization degree 1 and 3. By a repetition of this reaction sequence the product can be irreversibly formed by cleaving off a proton from II and a further 1-electron process.

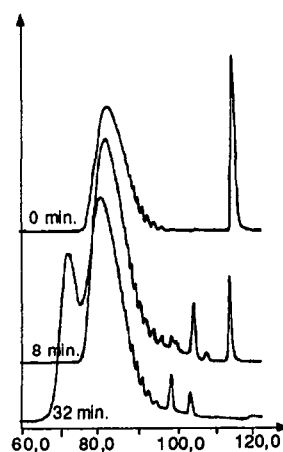
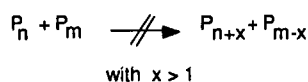
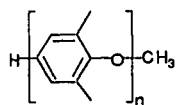


The proposal of the reaction sequence results in the intellectual difficulty that a molecular weight of about 2000 is present at a conversion of 90 % but 30000 to 50000 are obtained at the end of the reaction. Excluding a general equilibration between different degrees of polymerization would mean that after 90 % conversion more than 90 % of all molecules have to unzip to monomer in order to have a sufficient amount of monomer. The decisive experiment was done by Bartmann and Kowalszik 1988 (5). A poly(phenylene oxide) with molecular weight of 2000 is prepared and the phenolic hydroxy end group was quantitatively converted to the methyl ether. 2,6-Dimethylphenol was polymerized in presence of this product.

Fig. 4: Conversion of



in presence of



This result was confirmed in our group. The GPC of the starting mixture show the methylated poly(phenylene oxide) and the monomer. At a reaction time of 8 min. the molecular weight of the newly formed polymer is nearly identical with the methylated product. At a reaction time of 32 min. the new polymer has a much higher molecular weight and the methylated poly(phenylene oxide) is present with its original distribution. This results shows that a reaction is only possible with the free phenolic hydroxy end groups. A general equilibration between different degrees of polymerization can be excluded. The equilibration reaction allows only to change the degree of polymerization by ± 1 . This demonstrates also the ways to affect the course of the reaction. Only compounds with free phenolic hydroxy groups can participate in the reaction. By cocondensation with 2,6-dimethyl-4-*t*-butyl phenol the molecular weight can be adjusted. Monofunctional PPO blocks are accessible in preparative scale.

Fig. 5: GPC of the cooxidation

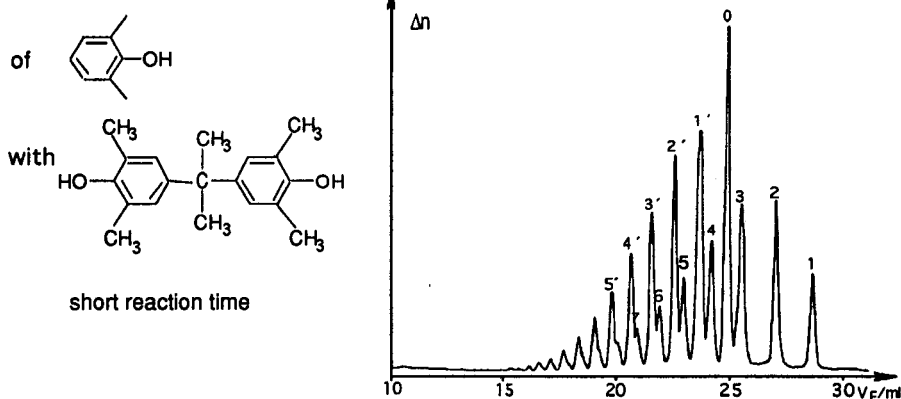
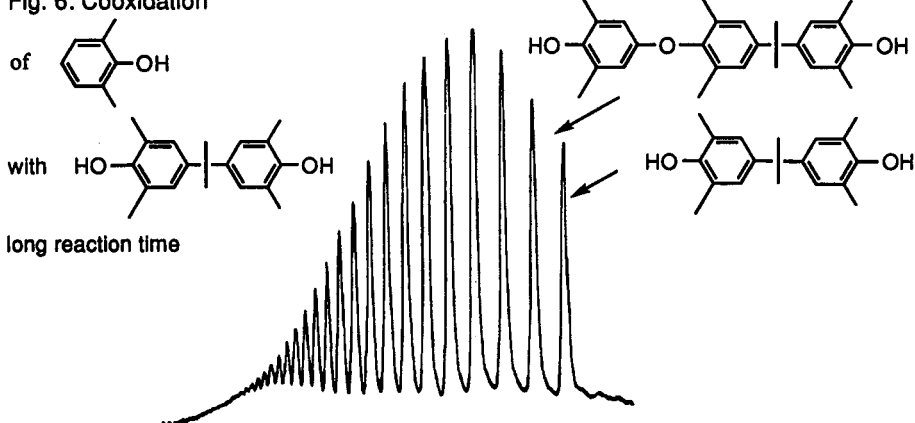


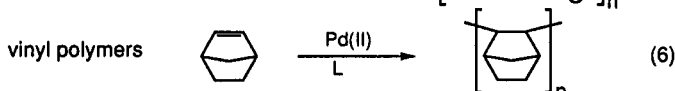
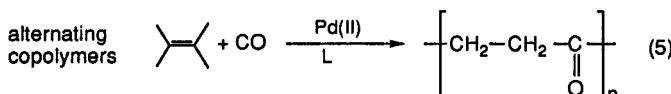
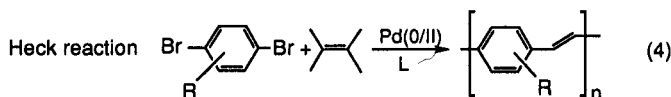
Fig. 6: Cooxidation



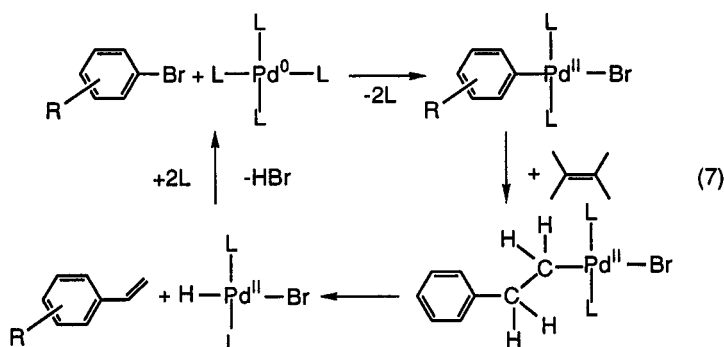
Bifunctional poly(phenylene oxide) is obtained by cocondensation with bisphenol A. The GPC of products obtained after short reaction times show two polymer homologous series, one being the monofunctional one. At long reaction times only one peak series is observed. The bifunctionality is confirmed analytically.

POLYCONDENSATIONS BY TWO ELECTRON PROCESSES

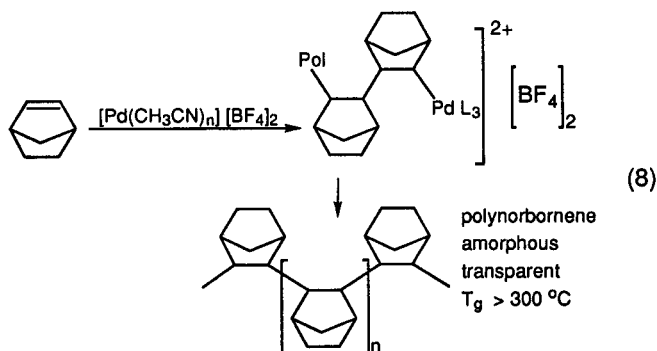
Metal catalyzed polycondensations are investigated with special intensity using palladium as example. With palladium the necessary differences can be demonstrated very well between polymerization and polycondensation.



Derivatives of polyphenylene vinylene are formed in the Pd-catalyzed reaction of ethylene with substituted dihalogeno arenes. This requires a change of the valence of the metal. In contrast to this the alternating copolymerization of olefins with carbon monoxide and the vinylic polymerization of norbornene is successful only if the two valent state of Pd is maintained. The mechanism of the Heck reaction (7) (equ. 7) shows the limiting requirements to tune the reaction in one or the other way.

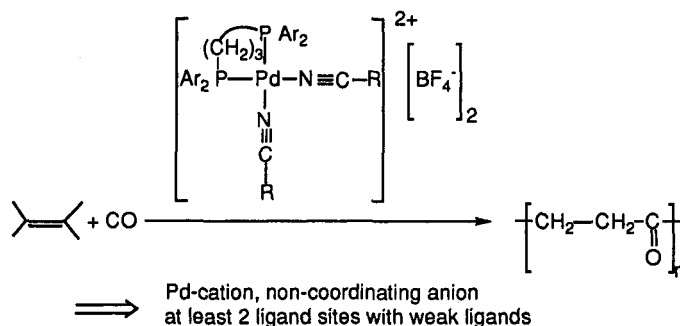


The halogen compound reacts with the Pd(O) species by oxidative addition to form a Pd(II) complex. After insertion of the olefin in the aryl-Pd-bond the target molecule is formed by β -H-elimination. At this stage palladium is still in the two valent state. Separation of HBr in presence of the bases leads back to the Pd(O) complex. The application of the Pd chemistry in polymerization reactions requires that the β -H-elimination can be neglected.




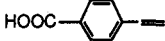
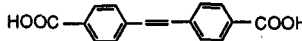
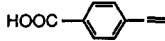
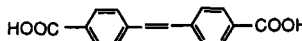

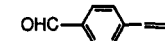

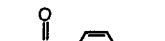

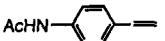

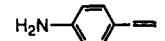

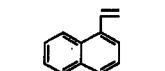
The β -H-elimination is impeded in the norbornene polymerization by the reformation of a highly strained ring system. The catalysts required for this reaction have a non-co-ordinating

anion and weak nitril ligands as a characteristic. Such a palladium complex was described 1981 by Senn (8). The modification of this catalyst by Risse et al resulted in a homogeneous reaction in the polymerization of norbornene (9). Vinyl polymerized norbornene is an example of conformationally restricted polymers having typically very high transition temperatures.



Pd-complexes described for the alternating copolymerization of olefins with carbon monoxide shows similar characteristics: non- or low coordinating anions as well as two ligand sites occupied by nitril. The β -H-elimination is a relatively fast reaction but compared to the insertion of carbon monoxide it is slow. This reduces the β -H-elimination. The Heck reaction opens the possibility to obtain substituted styrenes and stilbenes in a one step reaction.

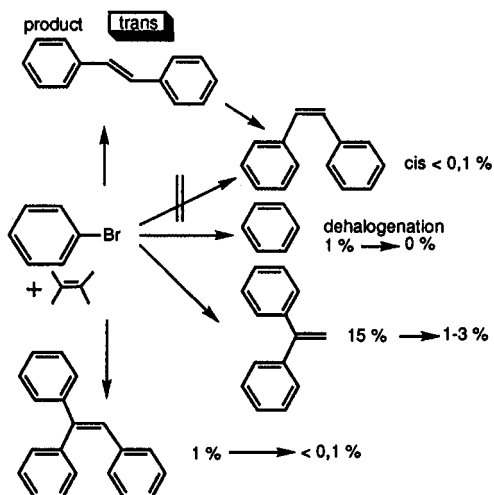
TABLE 2. Synthesis of styrene and stilbene derivatives by the Heck reaction (10)

starting material	press /bar	product	yield /%
HOOC- 	40	HOOC- 	80
		HOOC- 	8
	1	HOOC- 	< 10
		HOOC- 	83
OHC- 	50	OHC- 	62
H ₂ NC(=O)- 	55	H ₂ NC(=O)- 	78
AcHN- 	30	AcHN- 	72
H ₂ N- 	50	H ₂ N- 	99(GC)
	50		50

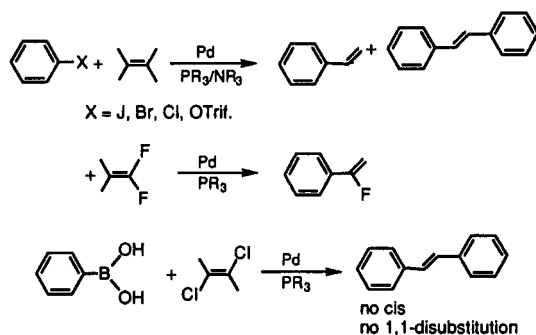
Pd-catalyzed reactions tolerate a great variety of functional groups. Vinyl benzamide or vinyl anilin are examples obtained in good yields and at polymerization-grade purity. By substitution of ethylene with acrylic acid derivatives products with cinamic acid structures are obtained (11).

The warranted structure of a polymer obtained by the Heck reaction can be investigated by model reactions (12).

In the reaction of bromo benzene with ethylene trans-stilbene is formed as the target product. The formation of cis stilbene is not found within the detection limit of gas chromatography. The limitation of the molecular weight in the polyreaction is mainly caused by the dehalogenation of bromo benzene. By optimization of the reaction conditions (low reaction temperature, low catalyst concentration) the dehalogenation is pushed back below the detection limits of gas chromatography. The main defect structures in the polymer are caused by 1,1-disubstitution. This reaction can not be suppressed even by optimal reaction conditions. Therefore polyphenylene vinylene obtained by the Heck reaction has statistically a fold in the



macromolecule after 30 - 100 monomer units. Metal catalyzed reactions can be tuned by the metal ligand or the educt besides the usual change of reaction conditions.



Aromatic iodo, bromo, fluoro and triflic compounds can be used for educt tuning in the Heck reaction. Using iodo arenes the reaction runs without problems and the use of phosphine ligands can be avoided. With bromo arenes the use of phosphine ligands is obligatory. Phosphines are oxidized in presence of catalyst metals to phosphine oxides very easily. This can happen by small contaminations with oxygen in the reaction mixture. In preparative scale work a higher amount of phosphine can be of advantage. With chloro arenes higher reaction temperatures are necessary (13). No quantitative conversions are obtained. Aryl triflates result in a lower regio selectivity. Much higher proportions of 1,1-disubstitution products are formed (14). Vinylidene fluoride as olefin results in a charge controlled insertion in the aryl-Pd-bond and the product is formed by β -F-Elimination. This reaction is a simple one-step approach to

obtain substituted α -fluoro styrenes (15,16). By reaction of phenyl boronic acid with trans-dichloro ethylene trans-stilbene is selectively obtained. This reaction shows no cis-addition and no 1,1-disubstitution. The molecular limiting step is the deboronation. The reaction temperature is reduced to room temperature using Ag_2O as the base (17).

Substituted polyphenylene vinylenes can be obtained by the Heck reaction.

TABLE 3.

Pd-catalyzed synthesis of poly(phenylene vinylenes)

polymer	M_w	therm. properties T_g	therm. properties melt	solubility
	—	—	—	—
	12000	180	aniso.	NMP, 180 °C
	3500	120	aniso.	NMP, 180 °C
	2600	—	—	NMP, 180 °C
	8000	145	aniso.	CHCl_3 , room temp. 55 % soluble
	11000	130	aniso.	CHCl_3 , room temp. quant. soluble

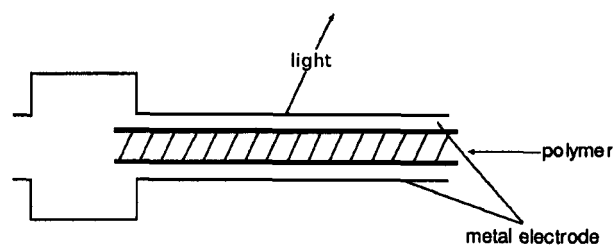
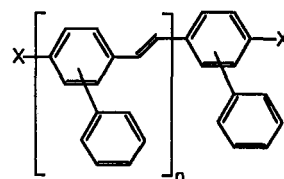


Fig. 8: Schematic design of an electro luminescence experiment

Unsubstituted dibromo benzene and centro symmetrically substituted 2,5-dimethyl-1,4-dibromo benzene result in materials with low molecular weight. Amorphous substituted polyphenylene vinylenes show an anisotropic melt above the glass transition temperature. At about 200 °C this melt solidifies losing the anisotropy. Insoluble products are formed in an irreversible reaction (18).

The optical properties of polymer conjugated hydrocarbons are of increasing importance due to the possibility to induce an electrically stimulated luminescence. Because the fluorescence is depended from the conjugation chain length the information of absorption dependence from the chain length is necessary.



X = Br, vinyl

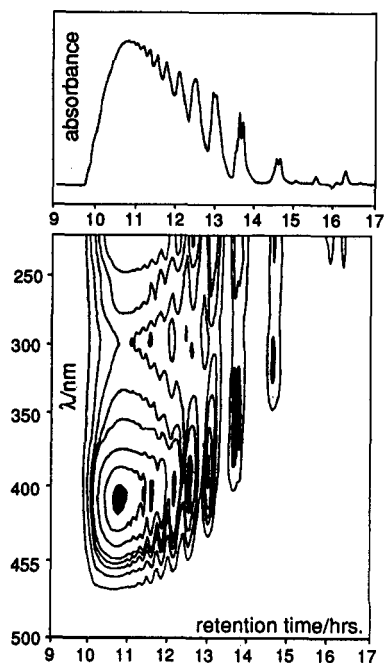
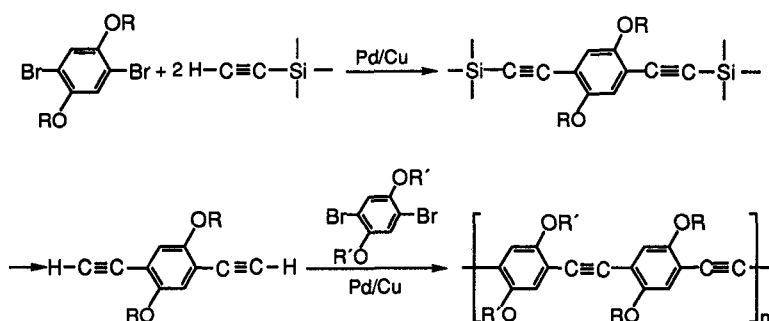


Fig. 7: Oligomer GPC of poly(phenylene vinylene) with chain length dependent UV/VIS spectra

This information is obtained from a single sample by high resolution oligomer GPC coupled with a diode array detector. As shown in the figure the absorption maximum of phenyl substituted polyphenylene vinylene is approached at a polymerization degree 7-8.

Electroluminescence is observed with very different polymer systems. Polyphenylenes, Polyphenylene ethynylenes or polyhetero cycles can be used besides polyphenylenevinylenes. The application of blends results in an increase of the relative quantum efficiency by a factor of 100.

The synthesis of polyphenylene ethynylene by a Pd/Cu catalyzed reaction was described by Marvel et al (19). The solubility problems of the para structure were reduced by the synthesis of the meta products. Soluble para connected polyphenylene ethynylene were synthesized by Schulz and Giesa in 1990 (20). Trimethylsilylacetylene have been used to avoid the preparative problems of stoichiometric use of acetylene.



Using the same synthetic approach a wide variety of structures in this class of polymers were obtained. The soluble polymers were mainly investigated with respect to their NLO properties (21). The exponent of 1,92 obtained in the viscosity molecular weight relationship confirms the rod like structure of these polymers.

The model reaction between bromo benzene and phenylacetylene gives information about the chain limiting reactions and defect structures in the polymer (22). The dehalogenation can be neglected in contrast to the Heck reaction. Diin and enin formation as well as trimerization are demonstrated in the model reaction. The trimerization and the formation of enin can be suppressed quantitatively.

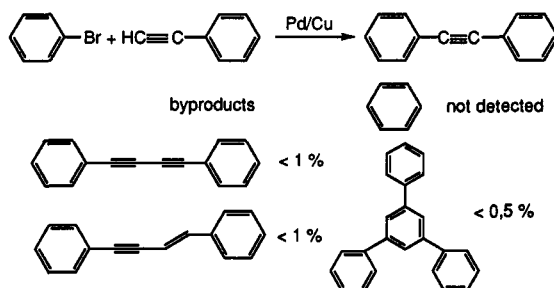
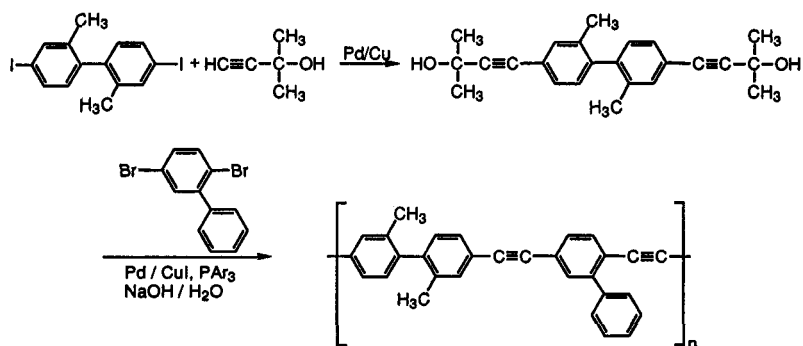
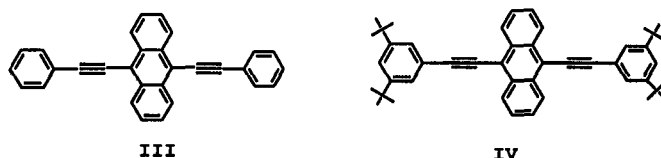


Fig. 9: Model reaction of the synthesis of polyphenylene ethynylene

The formation of diin occurs in the range < 0,5 %. It is not clear if the diin is formed during the reaction or on working up.



The educt of acetylene with acetone allows a simple synthesis of polyphenylene ethynylene (23). The absorption of these polymers is in the same range as polyphenylene vinylene. This absorption is reached at a polymerization degree 7 - 8 also in this case. Oligomers can be used as active components in LED films. The flexibility of catalytic reactions makes a wide variety of derivatives available.



The anthracene derivative III is sparingly soluble and shows a quantum yield of 1 in the fluorescence and no O₂-quenching. The substitution of benzene unit by *t*-butyl groups results in an oligomer (IV) with a high solubility, an absorption maximum at 454 nm and a fluorescence maximum of 580 nm.

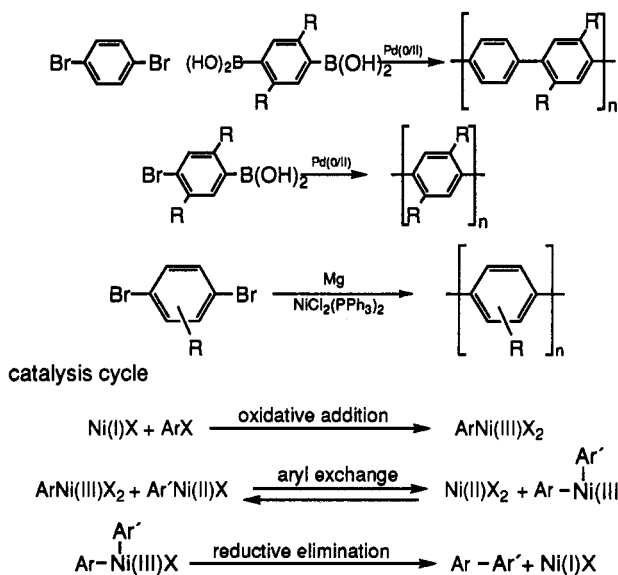
Unsubstituted oligo- and polyphenylenes show the same problem as with the earlier described classes of polymers with stiff chain structure: they are insoluble and non-meltable. Even with methyl substitution the solubility can be drastically improved and the melting points are decreased. Oligo- and polyphenylenes form anisotropic melts (24).

The Ullmann reaction (25) and the metal mediated oxidative polymerization (26) were used for the synthesis. These methods are replaced by metal catalyzed reactions nowadays. Schlüter and Wegner (27) used in 1989 the coupling of boronic acids described by Susuki (28) to synthesize soluble polyphenylenes. The Pd catalyzed reaction tolerates a large number of



Fig. 10:
Polarisation microscopy of the anisotropic melt of octamethyloctiphenylene

functional groups. The diaryl coupling of Kumada can be used as well to synthesize polyphenylenes (29,30).



Ni(II) compounds are used usually in this Ni catalyzed reaction. Kochi disproved already in 1979 (31) the obvious assumption that the catalytic cycle is dominated by a change of Ni(0)/Ni(II). The shortened reaction scheme shows that the oxidative addition involves Ni(I)/Ni(III). In the reductive elimination the product fragments are involved. The halogen is eliminated from the reaction cycle as a Ni(II) compound. Methyl substituted polyphenylenes can be obtained according to this reaction scheme. The GPC of the THF soluble part is shown in fig. 11. In this GPC the peaks of bi-, quarter-, sexi- and octiphenylene derivatives are included.

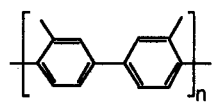
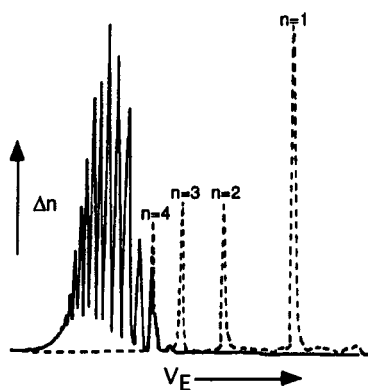
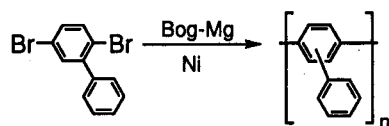


Fig. 11:
GPC of the THF soluble fraction of poly(1²,2³-dimethylbiphenyl) and of model oligomers

Oligophenylenes containing up to 30 p-linked benzene units are visible in the chromatogram.



Methyl substituted polyphenylene has a limited thermal stability. The phenyl substituted polyphenylene is soluble in chloroform, anisole and toluene (32). DSC shows a step at 180 °C.

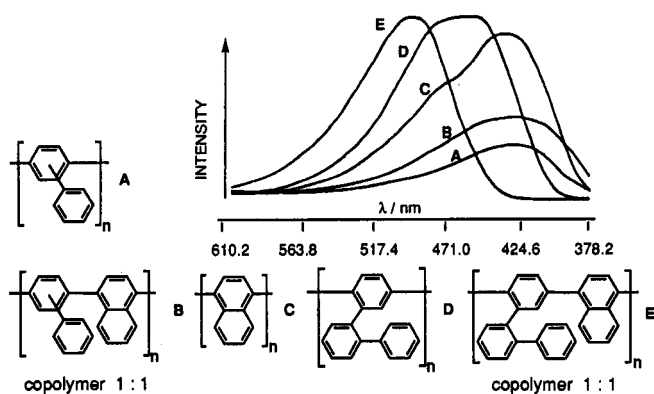
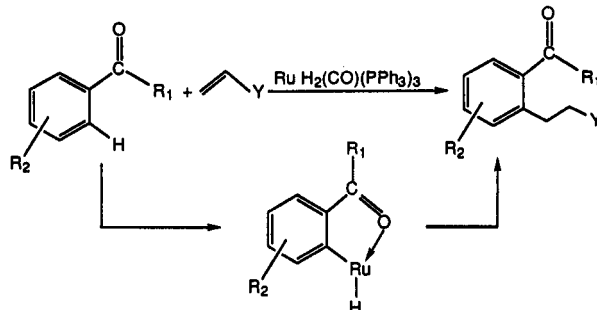


Fig. 12: Fluorescence spectra of polyphenylene derivatives

The melting point of 280 °C is observable only during the first heating. The material solidifies to an anisotropic glass from anisotropic melt.

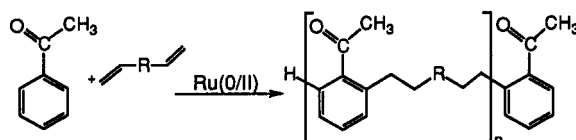
By variation of the pattern of substitution the site of the fluorescence maximum of polyphenylenes can be influenced (33). Specially by use of copolymers the width of the range of emission can be changed.

In the Heck reaction the educt participates in the oxidative addition. The reductive elimination occurs without the target molecule. In the Ni catalyzed polyphenylene synthesis the target molecule participates also in the reductive elimination and halogen is removed in another reaction step. Fundamentally different classes of products can be expected if oxidative addition and reductive elimination involves fragments of the product and no halogen participate in the reaction. This can be expected with ArH activated reactions. The



regioselectivity of activation of hydrogen must be guaranteed by the structure of the aromatic units. The selective activation of hydrogen in o-position to carbonyl respectively azomethin groups is known for many years in stoichiometric reactions (34). By ruthenium complexes a catalytic reaction is possible (35).

Murai describes this reaction with acetophenone as an example. The insertion of the olefin in the o-ArH-bond is observed with a high selectivity. In this reaction the change Ru(O)/Ru(II) is involved. Both ortho positions are accessible to the reaction. There is a strong difference in the reactivity between mono- and disubstitution.



At longer reaction times oligomers were formed in this reaction using divinyl compounds.

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