Aspects of synthesis, analysis and application of aromatic conjugated polymers

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A wide variety of soluble and fusible derivatives of poly(1,4-phenylenevinylene) were prepared by the Pd-catalysed arylation of ethylene with dihalogenoarenes. Although thermogravimetry indicates good thermal stability of most of the fusible derivatives of poly(1,4-phenylenevinylene), irreversible changes combined with a loss of anisotropy, solidification and insolubility occurred in the molten state on annealing. Soluble and fusible poly(phenyl-1,4-phenylene) was prepared by a Ni-catalysed Grignard reaction and by a precursor route.

(Keywords: synthesis; analysis; aromatic polymers; conjugated polymers)

INTRODUCTION

Aromatic conjugated polymers such as poly(1,4-phenylene) (PP) and poly(1,4-phenylenevinylene) (PPV) are insoluble and infusible below their decomposition temperatures. Therefore classical stepwise polymerization results only in low-molecular-weight products with limited options for applications.

High-molecular-weight samples of PPV were obtained by thermal elimination of dialkyl sulphide from poly(*p*-xylylenebis(dialkylsulphonium salts)) as a soluble precursor polymer[1] but little is known about structural defects of the PPV obtained by this route. Derivatives of PPV were obtained by structural variations of monomers such as lateral substitution in 2,5-positions on the phenylene unit by dialkoxy groups[2] or substitution of the protons on the vinylene unit by phenyl groups[3]. Far less is known about soluble derivatives of PP. Soluble derivatives were obtained by lateral substitution in the 2,5-positions on the phenylene unit[4].

The polymer backbones of PP and PPV are rigid-rod-like and contain conjugated sequences. Therefore soluble and fusible derivatives of both polymers are of interest for high-strength fibres and for electro-optical applications as long as structural variations do not affect the rigid-rod-like character.

The purpose of our work is to investigate structure–property relationships of derivatives of PP and PPV.

EXPERIMENTAL

Measurements

Molecular weights were determined by g.p.c. on four Hibar 250-7 columns filled with Merckogel *versus* polystyrene standards. Thermogravimetric investigations were performed on a Mettler TG-50 (heating rate 20°C min^{-1}). D.s.c. measurements were done on a Mettler DSC 20 (heating rate 20°C min^{-1}). Softening points and phase behaviour of the polymers were observed by shearing the samples between slide and coverslide on a Leitz Orthoplan polarizing microscope combined with a Mettler FP 80 (heating rate 10°C min^{-1}). X-ray investigations (Cu K$_\alpha$) were carried out using a Kissig camera.

Synthesis

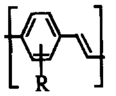
Synthesis of the derivatives of PPV was performed as described previously[5] as well as the synthesis of phenyl-substituted PP[6].

RESULTS AND DISCUSSION

Derivatives of poly(1,4-phenylenevinylene)

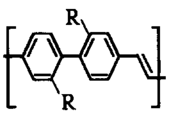
The main objective of our work was to synthesize soluble and fusible rod-like derivatives of PPV. In order to reduce the interchain interactions, the structural regularity was reduced in the following ways.

(1) Lateral substituents on the phenylene segments:



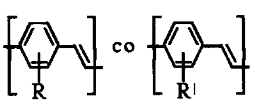
R = H, F, NO_2, CF_3, CH_3, C_6H_5
(cf. *Table 1*)

(2) Twisted biphenylene units in the main chain:



R = H, CH_3
(cf. *Table 2*)

(3) Copolymerization of monomers with different lateral substituents:



R/R' = C_6H_5/H, C_6H_5/CH_3, C_6H_5/NO_2
(cf. *Table 3*)

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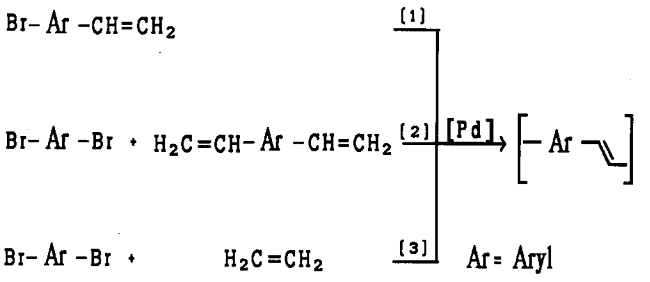
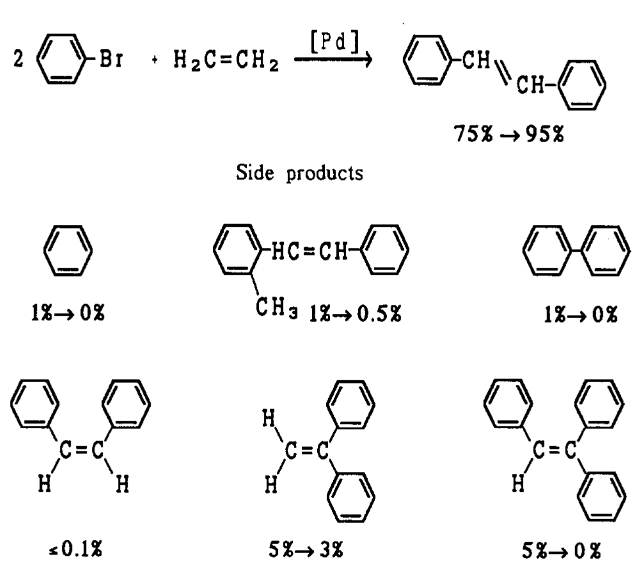
In order to realize these structures, a synthetic route was needed that tolerates a wide variety of different substituted monomers and results in a high yield of *trans* isomers. Stimulated by the investigations of Heck[7] on the palladium-catalysed arylation of olefins by halogeno compounds, we tested this reaction for the synthesis of PPV and its derivatives. Three monomer combinations are possible for the synthesis of PPV and its derivatives:



All routes were successfully applied for the synthesis of PPV[8–10]. We used for our investigations the most economical route (3).

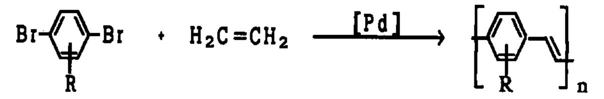
In order to estimate structural defects caused by side-reactions and to optimize the synthesis we investigated the model reaction of bromobenzene and ethylene to *trans*-stilbene. Benzene, 2-methylstilbene, biphenyl, *cis*-stilbene, 1,1-diphenylethene and triphenylstilbene were detected as side-products. The formation of these side-products can be limited by lower reaction temperatures and lower amounts of catalyst as indicated in *Scheme 1*. Details of this study are given elsewhere[11]. The polymer reaction was optimized based on the results of the model reaction.

The polymerization of ethylene and 1,4-dibromobenzenes substituted by lateral substituents resulted in infusible low-molecular-weight products with R = H, F and NO_2 (*Table 1*). Fusible products with higher molecular weights were obtained with trifluoromethyl- and methyl-substituted 1,4-dibromobenzenes. The best solubility was obtained with phenyl-substituted 1,4-dibromobenzene. This polymer was also readily soluble in chloroform and tetrahydrofuran. All fusible products formed partially or totally birefringent melts, which indicates thermotropicity. The formation of partially birefringent melts can be due to a large fraction of low-molecular-weight material in the sample or due to a fraction with structural defects causing the formation of isotropic domains.



Scheme 1 Formation of side-products in the model reaction of bromobenzene and ethylene to *trans*-stilbene (yields are related to the conversion of bromobenzene)

Table 1 Polymerization of monosubstituted 1,4-dibromobenzenes and ethylene



R	M_w[a]	Solubility[b]	Thermal behaviour T_s[c] (°C)	Thermal behaviour Birefringence[d]
H, F, NO_2	>500	–	infusible	–
CF_3	3500	+	175	+ +
CH_3	9300	+	180	+
C_6H_5	7100	+ +	155	+

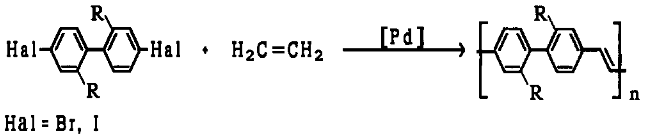
[a] Molecular weights were obtained by g.p.c. calibrated by polystyrene standards

[b] In *N*-methylpyrrolidone (NMP) at 150°C: (–) insoluble; (+) >0.1 wt%; (+ +) >1 wt%

[c] T_s = softening point determined by polarization microscope (heating rate 10°C min^{-1})

[d] As determined by polarizing microscopy: (–) not birefringent; (+) partially birefringent; (+ +) totally birefringent

Table 2 Polymerization of 4,4′-dibromobiphenylenes and ethylene



R	M_w[a]	Solubility[b]	Thermal behaviour T_s[c] (°C)	Thermal behaviour Birefringence[d]
H	>500	–	infusible	–
CH_3	10 700	+	158	+

[a] Molecular weights were obtained by g.p.c. calibrated by polystyrene standards

[b] In NMP at 150°C: (–) insoluble; (+) >0.1 wt%

[c] T_s = softening point determined by polarization microscope (heating rate 10°C min^{-1})

[d] As determined by polarizing microscopy: (–) not birefringent; (+) partially birefringent

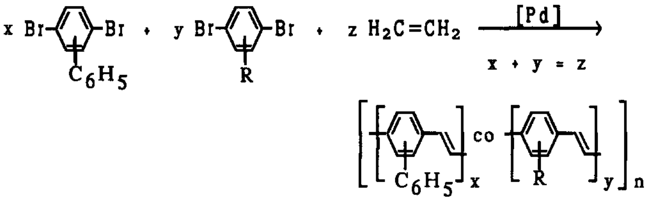
The polymerization of ethylene and 4,4′-dibromobiphenylenes resulted in insoluble and infusible products if the substituent in the 2,2′-positions is hydrogen. Soluble and fusible products were obtained with methyl groups in the 2,2′-positions (*Table 2*).

A wide variety of soluble and fusible products were obtained by the copolymerization of ethylene and 1,4-dibromobenzenes with different lateral substituents. Some examples are given in *Table 3*. The polymerization of 1,4-dibromobenzene or 2,5-dibromonitrobenzene and ethylene results in insoluble and infusible products. Soluble and fusible products with these monomers were obtained by copolymerization with phenyl-substituted dibromobenzene.

Thermal stability of fusible derivatives of PPV

The phenyl-substituted PPV was the polymer with the

Table 3 Copolymerization of ethylene and 1,4-dibromobenzenes with different lateral substituents



R	y (mol% z)	M_w[a]	Solubility[b]	Thermal behaviour T_s[c] (°C)	 Birefringence[d]
CH_3	50	4100	+ +	154	+ +
NO_2	5	6300	+	175	+ +
NO_2	10	8000	+	162	+ +
NO_2	20	8600	+	152	+

[a] Molecular weights were obtained by g.p.c. calibrated by polystyrene standards

[b] In NMP at 150°C: (+) >0.1 wt%: (+ +) >1 wt%

[c] T_s = softening point determined by polarization microscope (heating rate 10°C min^{-1})

[d] As determined by polarizing microscopy: (+) partially birefringent; (+ +) totally birefringent

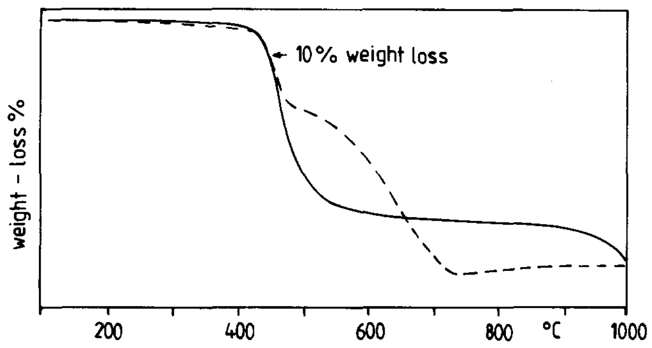


Figure 1 T.g.a. of phenyl-substituted PPV in N_2 (——) and in air (- - -); heating rate 20°C min^{-1}

best thermal stability according to the results of the thermogravimetric analysis under a nitrogen atmosphere. A 10% weight loss was detected at 420°C (*Figure 1*). A much lower thermal stability was detected by polarizing microscopy for the phenyl-substituted PPV as well as for all other fusible derivatives of PPV. An irreversible change combined with a loss of anisotropy, solidification and insolubility occurred in the molten state on annealing 20–50°C above the softening point. This irreversible change was detected for the phenyl-substituted PPV on annealing at 220°C. A strong exotherm in the same temperature range was observed by d.s.c. for the phenyl-substituted PPV (*Figure 2*).

No significant difference was found in the i.r. and X-ray patterns of the unannealed and annealed phenyl-substituted PPV (*Figures 3* and *4*). Therefore the formation of a new crystalline phase from the molten state can be excluded.

The synthesis of PPV and its derivatives by the reaction of dibromoarenes and ethylene results in macromolecules with vinyl and/or bromine end-groups. Heat treatment of vinyl-terminated macromolecules may result in a thermally induced crosslinking reaction by the vinyl end-groups. Annealing experiments resulted in irreversible changes in the molten state with phenyl-substituted PPV with exclusively vinyl end-groups as well as with phenyl-substituted PPV with exclusively bromine end-groups. Therefore, thermally induced crosslinking by vinyl end-groups is an insufficient explanation for the irreversible changes in the molten state.

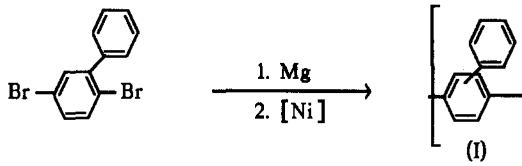
A crosslinking reaction may also be induced by palladium catalyst not completely removed. Indeed, a content of 0.5% was estimated by atomic absorption spectroscopy in a sample of the phenyl-substituted PPV. The palladium residues were completely removed by chromatography with triphenylphosphine-substituted polystyrene gels as stationary phase[12]. Still, the same irreversible change in the molten state was observed with the palladium-free phenyl-substituted PPV. Therefore crosslinking induced by Pd residues is also an insufficient explanation for the observed irreversible changes in the molten state.

We conclude from our studies on the thermal stability of fusible derivatives of PPV that the irreversible changes in the molten state combined with a loss of anisotropy, solidification and insolubility are an inherent property of this class of polymers. Further examinations on low-molecular-weight model compounds are in progress in order to understand the mechanism of the irreversible changes in the molten state.

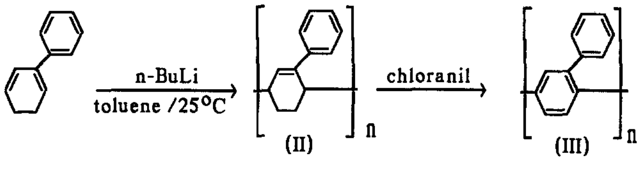
Poly(phenyl-1,4-phenylene)

Poly(1,4-phenylene)s are expected to have excellent thermal stability. Synthesis, analysis and application of this class of polymers is limited due to insolubility and infusibility. Phenyl-substituted monomers were used in order to synthesize soluble and fusible derivatives of PP with a rigid-rod-like polymer backbone and a high thermal stability.

Phenyl-substituted PP (I) was synthesized by a nickel-catalysed Grignard reaction[13] of 2,5-dibromobiphenyl. The product is soluble in boiling diphenyl ether. A glass transition was detected at 180°C and a melting point at 280°C (by d.s.c.). The melt of the product is thermotropic. The product seems to be of low molecular weight since it precipitated during the reaction.



Phenyl-substituted PP was also synthesized by a precursor route in order to have better control over molecular weight.



The anionic polymerization of phenyl-1,3-cyclohexadiene with butyllithium in toluene at 25°C resulted in poly(3-phenylcyclohexa-1,3-diene) (II) with exclusively 1,4-connection[6]. A typical reaction resulted in a product with a molecular weight of 45000 (determined by gel permeation chromatography and calibration with polystyrene standards) and a glass transition at 210°C

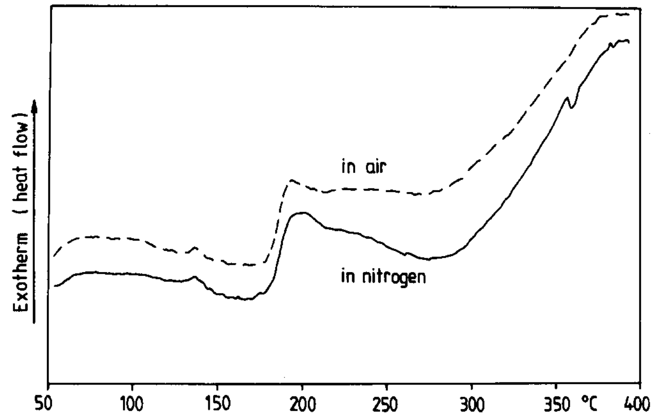


Figure 2 D.s.c. of phenyl-substituted PPV in N_2 (——) and in air (---); heating rate 20°C min^{-1}

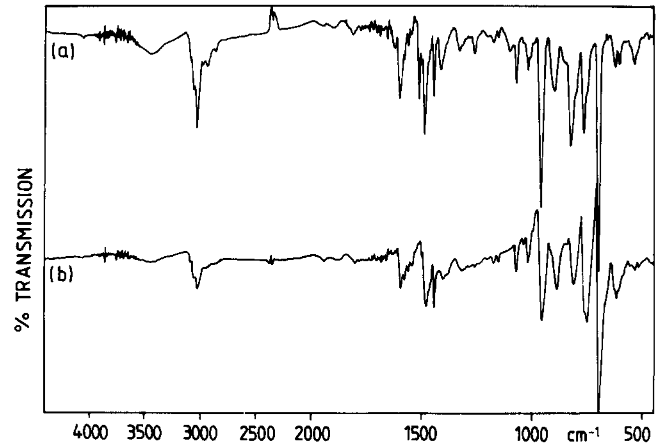


Figure 3 I.r. spectra of phenyl-substituted PPV (a) unannealed and (b) annealed at 220°C for 5 h

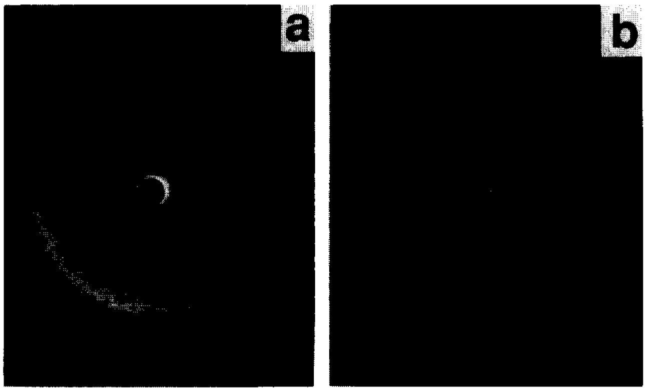


Figure 4 X-ray spectra of phenyl-substituted PPV (a) unannealed and (b) annealed at 220°C for 5 h

(determined by d.s.c.). II is soluble in common organic solvents. The aromatization of II with chloranil resulted in poly(phenyl-1,4-phenylene) (III). This product has a glass transition at 180°C as well as I. It also forms an anisotropic melt and is soluble in boiling diphenyl ether. No significant difference was found by i.r. between products I and III. The thermal stabilities of I, II and III were compared in order to get more information about the degree of conversion from II to III. A 10% weight loss of I was detected at 600°C (*Figure 5*). A 10% weight loss of the precursor II was detected at 300°C (*Figure 6*).

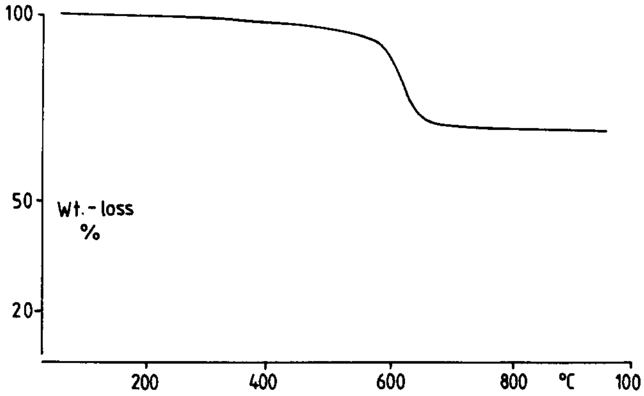


Figure 5 Thermogravimetry of I in N_2; heating rate 20°C min^{-1}

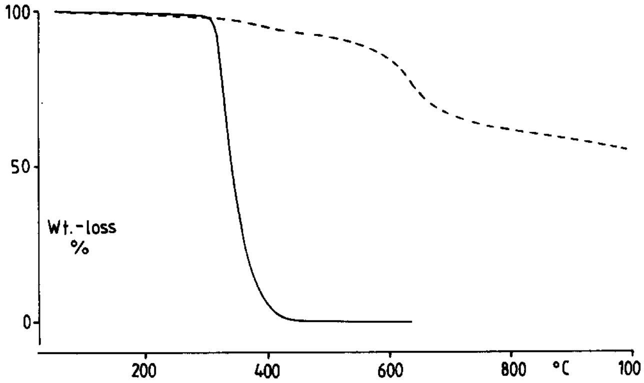


Figure 6 Thermogravimetry of II (——) and III (---) in N_2; heating rate 20°C min^{-1}

The aromatized product (III) has a 10% weight loss at 500°C with a second stronger weight loss in the range of product I (*Figure 6*). From this we conclude that the aromatization is not fully completed. Some repeat units of II are not aromatized, causing the weight loss below 600°C of III. We conclude further that the degree of aromatization in III is very high, since product III readily forms anisotropic melts.

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