

Thermal properties and processability of dialkoxy-PPV precursors

Ann Delmotte*, Monique Biesemans† and Marcel Gielen

General and Organic Chemistry, Free University of Brussels, Pleinlaan 2,
1050 Brussels, Belgium

and Jun Gu and Bruno Van Mele

Physical Chemistry and Polymer Science, Free University of Brussels, Pleinlaan 2,
1050 Brussels, Belgium

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A homologous series of ring-substituted dialkoxy-PPV precursors have been synthesized and characterized. By increasing the number of methylene units in the side groups up to six, a linear decrease of the glass transition temperature is found, with a span of ca. 100°C, going from 92°C down to -11°C. T.m.a. experiments reveal high stretchability of thin films at temperatures just above T_g without elimination. The thermal conversion of the precursor polymer into the conjugated materials was studied and with controllable amounts of catalytic acid in the thin films, a well-defined processing window can be established in order to prepare stretched, conjugated thin films of dialkoxy-PPV material. Copyright © 1996 Elsevier Science Ltd.

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INTRODUCTION

The use of conjugated polymers such as poly(*p*-phenylenevinylene) (PPV) and its derivatives as semi-conductors is well established and boosted since the discovery of the electroluminescence properties of these materials¹. In order to fully exploit those properties, one needs stable and strong materials. The rigid backbone of conjugated polymers, however, implies poor processability and low molecular weights when synthesized in a direct way, because of the limited solubility². The synthesis of high molecular weight PPV-precursor polymers however is possible via the Wessling–Zimmerman polymerization route in water³. The conversion of these precursor polymers into the final conjugated polymer proceeds through thermal elimination of small molecules⁴ and the processing of the material has to be performed before or during this elimination reaction.

Many different modifications of PPV have been studied and in the case of dialkoxy ring-substituted PPV-derivatives, the effect of the modification is a decrease in band gap of about 0.3 eV compared to PPV⁵ and an improvement in solubility and processability. The synthesis of these precursor polymers is executed in methanol and the conversion can be established in several ways such as heating in the presence of an acid⁶ or illumination of a solution^{7,8}.

In order to optimize the mechanical properties,

the purity and the chain structure of the conjugated polymers, a careful study of the properties of the synthesized precursors (T_g , molecular weight and molecular weight distribution) and the conversion conditions is necessary. The knowledge of the optimum stretching and elimination temperature should lead to highly oriented, fully conjugated thin films.

In this paper some physico-chemical data of a homologous series of ring-substituted dialkoxy-PPV-precursors and the results of some conversion studies are presented.

EXPERIMENTAL

The synthesis of the monomers (disulfonium salts) was performed similar to the method described earlier for the 1,4-dibutoxy-substituted material⁷. Some data of the synthesized compounds following the route described in *Scheme 1*, are listed in *Table 1*.

The precursor polymers [II] were prepared by polymerization of the corresponding disulfonium salts [I] in methanol, according to *Scheme 2*, as described before^{7,8}. The obtained white, gum-like precipitates are soluble in common organic solvents and can be purified by reprecipitation in methanol.

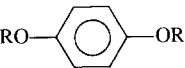
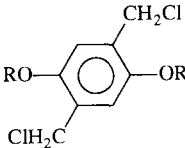
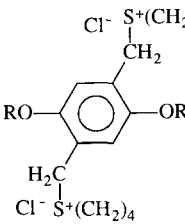
G.p.c.-measurements in THF at room temperature, d.s.c. and t.g.a./FTi.r. experiments were performed on pure samples of precursor polymer and for t.m.a. experiments thin films were cast by evaporation of a solution on glass surfaces followed by soaking in water in order to remove the films.

G.p.c. was recorded on a Waters low temperature g.p.c. in THF using polystyrene sample standards. D.s.c.

* To whom correspondence should be addressed

† Also at High Resolution NMR Centre, Free University of Brussels, Pleinlaan 2, 1050 Brussels, Belgium

Table 1 Physical properties of the synthesized compounds: yield (%), m.p. (°C) and recrystallization solvents

R =	-CH ₃	-C ₂ H ₅	-C ₃ H ₇	-C ₄ H ₉	-C ₆ H ₁₃
	^a	73%	77%	71%	80%
	-	70–71°C	49–50°C	44–45°C	42–43°C
		MeOH	MeOH	MeOH	MeOH
	83%	84%	70%	62%	66%
	163–164°C	152–153°C	83–84°C	85–86°C	70–72°C
	CH ₂ Cl ₂	CH ₂ Cl ₂	CH ₂ Cl ₂	CH ₂ Cl ₂	CH ₂ Cl ₂
	79%	87%	68%	70%	63%

^a Janssen, used as received

experiments were performed on a Perkin-Elmer DSC 7 using perforated aluminium pans. The furnace was purged with nitrogen at a flow rate of 30 ml min⁻¹ and the heating rate in all experiments was 10°C min⁻¹. T.g.a./FTi.r. experiments were performed on a Perkin-Elmer TGA 7 coupled to a Perkin-Elmer 1760 X FTi.r. spectrophotometer. The measuring unit was purged with helium at a total flow rate of 100 ml min⁻¹. The transfer line and the i.r. gas cell were heated to 180°C and all experiments were performed at a heating rate of 20°C min⁻¹. T.m.a. experiments were performed on a Perkin-Elmer TMA 7 with a quartz extension probe. The furnace was purged with helium with a flow rate of 30 ml min⁻¹ and all experiments were performed at a heating rate of 5°C min⁻¹. Thin films were cast by evaporation of a CHCl₃ or CH₂Cl₂ solution and film thickness was typically 30 μm. In order to acidify these, the free standing films were kept in the presence of hydrogen chloride gas during several seconds. Films of about 5 mm long were submitted to an extension force of 14 mN in the t.m.a. experiments.

RESULTS AND DISCUSSION

As the obtained white gum-like precipitates are soluble in common organic solvents, it is possible to perform g.p.c. measurements on THF solutions, d.s.c. experiments on the solids and t.m.a. measurements on thin films. *Table 2* summarizes the results obtained.

Using identical reaction conditions in the homologous series leads to the formation of precursor polymers of very similar molecular weights and molecular weight distributions which allows reliable *T_g* measurements. A study of the relationship between the molecular weight

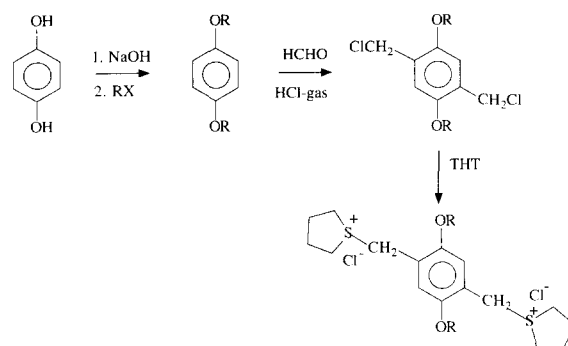
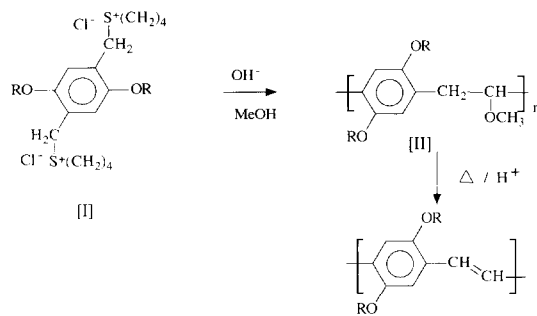
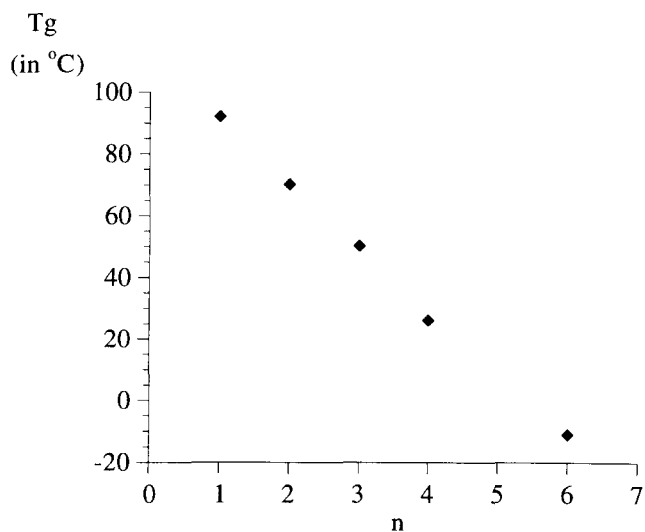

Scheme 1 Synthesis of the monomers

Scheme 2 Synthesis and conversion of ring-substituted dialkoxy-PPV precursors

Table 2 G.p.c., d.s.c. and t.m.a. results

R	M_w (Da)	M_w/M_n	T_g (°C)	ΔC_p (J g ⁻¹ °C ⁻¹)	T_s (°C) ^b
-CH ₃	- ^a	- ^a	92.0	0.22	100.0
-C ₂ H ₅	1.6 × 10 ⁶	3.0	70.0	0.21	79.0
-C ₃ H ₇	1.5 × 10 ⁶	2.1	50.5	0.20	55.0
-C ₄ H ₉	2.4 × 10 ⁶	2.4	26.0	0.21	36.0
-C ₆ H ₁₃	2.6 × 10 ⁶	2.4	-11.0	0.25	- ^c

^a Insoluble in THF^b Stretching temperature of thin films measured in t.m.a. experiments as the onset of extension^c Not processable at room temperature**Figure 1** Glass transition temperature of the precursor polymer as a function of the number n of methylene units in the alkoxy side groups $-\text{O}(\text{CH}_2)_n\text{H}$

and the glass transition temperature showed that for M_w values of 3×10^5 Da and more a constant value of T_g is observed⁸. As expected, the values of ΔC_p are comparable and are an indication that the samples are solvent-free. The values of ΔC_p are reproducible within a range of 5% and the calculated value of T_g in consecutive runs varies no more than 0.5°C.

The influence of the side group length on the T_g value, however, is much more important since the difference in glass transition temperature between a methoxy and a hexyloxy side group is in the order of 100°C. When the T_g values are plotted graphically as a function of the number (n) of $-\text{CH}_2-$ units in the side group, a linear relation is found (see Figure 1). Several examples exist in literature where the number of methylene units in a spacer in the *main* chain influences the T_g value in a linear fashion⁹. Considering homologous series with alkyl spacers in *side* groups of more or less rigid polymers such as alkyl-substituted polythiophenes¹⁰ and poly-(alkyl methacrylate)s¹¹, this linear relationship is not observed. In general, the influence of a bulky methyl group on T_g is an increase in T_g value when compared to the unsubstituted material. This effect is diminished by adding more methylene units to the alkyl side groups, so that T_g now decreases. This decrease in T_g is rather sharp when going from one to two or three additional methylene units whereas longer side groups do not seem

to influence T_g significantly any more. In this work, however, a linear relationship is observed up to six methylene units and T_g decreases by 20°C per additional methylene unit on average.

Tokito *et al.*¹² report a T_g value of 110°C for the dimethoxy-PPV precursor [II] instead of 92°C in this work. This difference can be explained by considering the synthesis route, which in the case of Tokito *et al.* consists of a polymerization in water followed by anion exchange and a substitution reaction in methanol. This route leads to material which is probably partly conjugated. In a previous paper¹³ we demonstrated that partial conjugation leads to a higher T_g value, e.g. 21% of conjugation represents an increase in T_g of 8°C in the case of diethoxy-PPV precursors. Moreover, the material obtained by Tokito *et al.* is described to be slightly coloured and the drawability of the fibres starts well below their measured T_g , whereas we obtain white material which stretches in a narrow temperature range above T_g (see also later, Table 2 and Figure 2).

Han *et al.*¹⁴ on the other hand describe a dibutoxy-PPV precursor with a butoxy leaving group, having a T_g of 2.6°C, which is about 23°C lower than the value of the dibutoxy-PPV precursor containing a methoxy leaving group of this work. For diethoxy-PPV precursors containing an ethoxy leaving group, we observed a decrease in T_g of 6°C compared to the precursor containing a methoxy leaving group¹⁵. So, a more important decrease in T_g when going from a methoxy to a butoxy leaving group seems plausible. This effect could still be enhanced due to the plasticizing effect of residual solvent and pyridine as mentioned by Han *et al.*¹⁴. So, the measured T_g values of this work seem not in contradiction with the foregoing literature values.

It can be concluded that it is possible to tune the glass transition temperature of the precursor polymer [II] by choosing the length of the alkoxy-side groups. Table 2 also shows that the stretching temperature T_s , as measured by t.m.a., confirms the observed T_g as calculated from d.s.c. experiments. The values of T_s , measured with an extension force of 14 mN, are up to 10°C higher than those found for T_g by d.s.c. With extension forces of 120 mN, T_s values are found to be 5°C higher than T_g . At temperatures higher than T_s , the precursor material can be stretched at least 20 times its initial length as is shown in Figure 2. Measurements of those macroscopic drawing ratios are limited by the geometry of the extension probe and the t.m.a. furnace, as the stretching experiment is interrupted when the probe is extended for more than 2.8 cm.

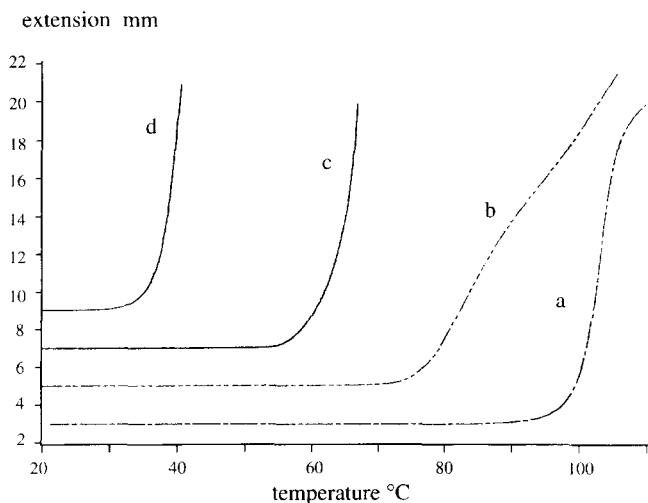


Figure 2 T.m.a. thermograms, obtained in the extension mode, of free-standing films of dialkoxy PPV-precursors as a function of the number n : (a) $n = 1$, (b) $n = 2$, (c) $n = 3$ and (d) $n = 4$

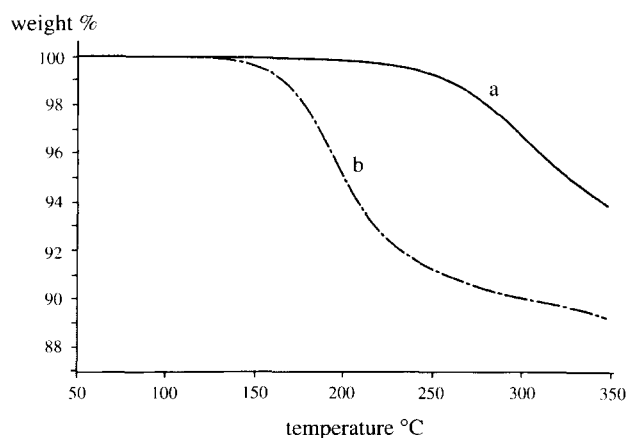


Figure 3 T.g.a. thermograms of thin films of dibutoxy-PVV ($n = 4$) precursor: (a) cast from CH_2Cl_2 and (b) cast from CH_2Cl_2 with traces of HCl gas

In view of the preparation of stretched, fully conjugated thin films, the knowledge of the stretching and elimination temperature is very important. In the case of PPV, where the precursors are water-soluble polyelectrolytes, it is known that stretching of the precursor film and elimination of the dialkyl sulfide (DMS or THT) takes place simultaneously leading to limited draw ratios¹⁶.

Using t.g.a./FT i.r. experiments it was demonstrated in a previous paper that the elimination of methanol in the conversion of the neutral precursor polymers takes place at a high temperature near degradation⁷. The length of the phenylene side group is of no influence on the elimination temperature as this is related to the leaving group, i.e. methanol. This elimination temperature, however, can be lowered by acid catalysis and the value depends strongly on the amount of acid in the thin film. The elimination temperature can be lowered by as much as 100°C for thin films which were exposed to HCl gas for 30s. This influence of the amount of hydrogen chloride in the film on the elimination behaviour is demonstrated in Figure 3.

At that point, all parameters are known to determine the exact processing window in which the alkoxy ring-substituted PPV-precursors can be converted into stretched samples of dialkoxy-PPV thin films. The lower limit of this window is determined by the glass transition temperature and/or the stretching temperature whereas the upper limit is the elimination temperature. The lower limit of the processing window can be shifted by considering a different phenylene side group and the upper limit can be shifted by varying the amount of acid in the thin film. In any case the processing window will be large enough to allow stretching of the thin film of precursor material without accompanying elimination occurring which would limit the stretching ratio.

It should be pointed out that the molecular orientation in the macroscopically stretched films was not investigated.

CONCLUSIONS

It is demonstrated that introduction of dialkoxy side groups on the phenylene ring does not influence the molecular weight of neutral precursors for PPV-derivatives. T_g values and thus the stretching conditions, however, are strongly dependent on the number of methylene units in the side group. The elimination of methanol, in order to obtain fully conjugated material, proceeds at high temperature unless acid is used in the preparation of thin films. Since thin films of precursor polymer can be stretched at temperatures well below the elimination temperature, high macroscopic draw ratios can be obtained. Controlling the amount of catalyst acid in the thin films could lead to predictable elimination temperatures, thus allowing a large processing window wherein preparation of fully stretched dialkoxy-PPV material is possible.

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