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SYNTHETIC METALS

Selective elimination in dialkoxy-PPV precursors yielding polymers with isolated tetraalkoxy-stilbene units

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Abstract

In the polymerization of 2,5-diethoxy-1,4-phenylenedimethylene-bis(tetrahydrothiophenium chloride) leading to the 2,5-diethoxy-poly(phenylenevinylene) (2,5-diethoxy-PPV) precursor we have varied the NaOH concentration from equimolar to a five-fold excess. Elimination to the conjugated form is observed during polymerization by using concentrations higher than equimolar. Suprisingly, this elimination is very selective, yielding tetraethoxy-stilbene units only. Almost no delocalization over more than two benzene rings, i.e. hexaethoxy-distyrylbenzene units, is observed in polymers with as much as 35% elimination (determined by ^{1}H NMR spectroscopy). This selectivity is explained by the preference of an E_2-elimination yielding products with the highest gain in resonance energy at every step: tetraalkoxy-stilbenes. Absorption and emission spectroscopies reveal that significant energy transfer from benzene to stilbene units occurs and that a blue photoluminescence with $\lambda_{max} = 415$ nm is present.

Keywords: Poly(phenylenevinylene); Stilbene; Selective elimination

1. Introduction

Poly(2,5-dialkoxy-1,4-phenylenevinylene)s are amongst the most important conjugated polymers, primarily due to their ability to emit electroluminescence with high quantum yields in polymer-based light-emitting diodes [1–4]. Many of the properties of these poly(phenylenevinylene)s (PPVs) can be modified by adjusting the molecular structure. One of the most striking examples in this area is the ability to cover the whole visible spectrum from blue to red in the (electro)luminescence of these modified PPVs [1,5–7]. Shortening of the conjugated units in the polymer gives rise to a decrease in effective conjugation length and, hence, to materials with hypsochromic-shifted emission. Several approaches have been undertaken to obtain full control of the effective conjugation length in these PPV-type polymers; Holmes and co-workers [5–7] reported on the partial elimination of leaving groups in the Wessling–Zimmerman precursor copolymers, leading to polymers with a statistical distribution of double bonds and materials that emit light with a maximum at 508 nm. Non-statistical approaches are presented by Yang et al. [8] and McNamara and Wudl [9]. Yang et al. [8] studied the synthesis and optical properties of a copolymer with rigid conjugated and flexible aliphatic blocks, furnishing a blue-emitting material. McNamara and Wudl [9] reported on the ring-opening metathesis polymerization of [2,2]*para*-cyclophane-1-ene, yielding an insoluble polymer with an alternating structure. In principle this very elegant approach can be extended to substituted PPVs. However, the synthesis of the substituted monomers is time-consuming. The problem of solubility may be circumvented by the stereoselective polymerization of [2,2]*para*-cyclophane-1-ene yielding the soluble *cis*-derivative first; however, the stability of the products is low [10].

In this paper we report on our findings concerning the formation of a controlled number of tetraalkoxy-stilbene units in soluble PPV precursors, without ap-

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preciable amounts of units with a higher conjugation length.

2. Experimental

2.1. Methods

^1H NMR spectra were recorded on a Bruker AC 250 using concentrations of 2 mg in 0.5 ml of $CDCl_3$. All spectra were baseline corrected prior to integration. Absorption and emission spectra were recorded on a Perkin-Elmer Lambda 3B and Perkin-Elmer LS 50, respectively. GPC analysis was performed on a Waters Ultrastyragel using polystyrene standards and estimated $K = 2.89 \times 10^{-4}$ and $a = 0.7$ values. T_g measurements were performed on a Perkin-Elmer DSC-7 with a heating rate of 20 °C/min.

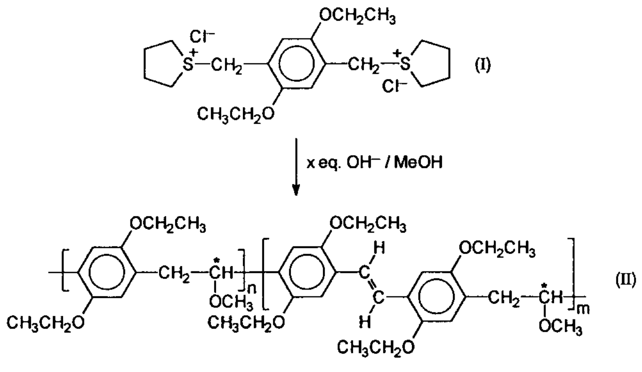
2.2. Materials

In a typical polymerization reaction (e.g. three equivalents of base), 0.66 g (1.5 mmol) of 2,5-diethoxy-1,4-phenylenedimethylene-bis(tetrahydrothiophenium chloride) (**I**) is dissolved in 15 ml of methanol, cooled to temperatures between 0 and -15 °C and purged with nitrogen. 15 ml of a cooled and purged suspension of sodium hydroxide in methanol (0.3 M) is added to this solution at once. After 30 min of reaction the mixture is diluted with methanol and transferred to a dialysis tube. Dialysis with methanol/H_2O (99:1) is continued for 24 h and the obtained precipitate is filtered and rinsed with methanol, yielding 0.24 g of material. Further purification can be performed by dissolving the precipitate in methylene chloride and reprecipitating in methanol. ^1H NMR ($CDCl_3$) δ: 7.42–6.52 (arom. + vinyl. H), 4.94–4.92 (*CH), 4.12–3.72 (OCH_2), 3.23–2.29 (Φ-CH_2 + OCH_3), 1.48–1.22 (CH_3) ppm. IR (neat): 3060, 2973, 2930, 2901, 2814, 1503, 1481, 1416, 1394, 1257, 1199, 1098, 1047, 979, 939, 874, 769, 747 cm^{-1}.

3. Results and discussion

3.1. Synthesis of the polymers

The synthesis of the methoxy-pendant precursor of poly(2,5-diethoxy-1,4-phenylenevinylene) (**II**, DEOPPV precursor) is carried out by the polymerization of 2,5-diethoxy-1,4-phenylenedimethylene-bis(tetrahydrothiophenium chloride) (**I**) in methanol using 0.3 M solutions of **I** and NaOH in a molar ratio varied from 1:1 to 1:6 at reaction temperatures between 0 and -15 °C, as described before [11] (see Scheme 1). Two series of experiments have been performed: in one the total amount of base is added at once at the start of the polymerization, while, in the second, one equivalent of base is added first and the excess of base is added after 30 min of reaction. In all cases, a highly viscous reaction product is obtained which is yellow coloured when an excess of NaOH is used. Upon dialysis at room temperature of the viscous reaction product against methanol containing 1% of water, a coloured gum-like precipitate is formed which is soluble in common organic solvents. The precipitated polymers so obtained are isolated, washed, dried and characterized in detail and the most important results are listed in Table 1.



Scheme 1. The reaction.

Table 1
Results for the precipitated polymers (all base added at once)

Equiv. NaOH	Yield (%)	M_w (daltons)	T_g (°C)	Conj. (%)
1	40	9.7×10^5	70.3	0
2	40	6.4×10^5	75.6	17
3	36	5.0×10^5	78.6	21
4	22	3.3×10^5	84.1	24
5	20	3.3×10^5	84.9	27
6	17	2.1×10^5	82.6	34

Similar to other reports [11,12], the precusor polymer is entirely methoxy-group pendant by substitution of the sulfonium group by methoxides. By increasing the amount of base used in the polymerization, several striking trends are observed. First, the yield decreases steadily from 40% at an equimolar ratio of base and monomer to 17% at six equivalents of base. This decrease in yield is accompanied by a decrease in molecular weight of the precursor polymers formed. The gradual decrease in molecular weight of the polymers precipitated is also presented in Fig. 1. A gradual increase in T_g is observed despite the fact that there is a decrease in molecular weight, going from equimolar to five-fold excess NaOH over monomer. This increase in T_g is attributed to an increase in chain stiffness due to partial elimination (see below). Similar results are found for the other series of experiments, although the concentration of the alkaline solution, i.e. the volume added,

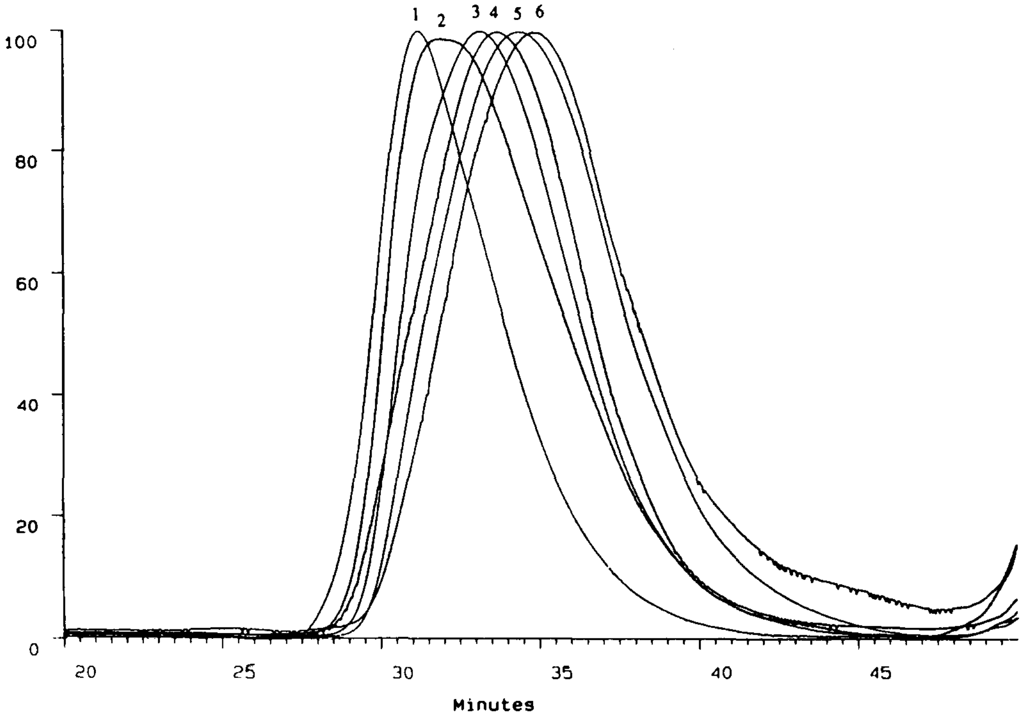


Fig. 1. GPC chromatograms of the precipitates obtained after polymerization with excess of base. The numbers represent the total amount of equivalents of NaOH used in the polymerization.

has a marked influence on the molecular weight distributions. High dispersion ratios and bimodal distributions are found when volumes larger than 15 ml of base are added.

^{1}H NMR spectroscopy shows that, next to the complete substitution of all the sulfonium groups by methoxy groups, an increasing number of vinylic units is formed as a result of the increasing concentration of NaOH. As much as 35% elimination is found in the case of six equivalents of base. The percentage elimination is defined as the number of vinylic units divided by the number of benzene rings present. From ^{1}H NMR spectroscopy, however, it is not possible to determine the nature of the unsaturated units in our case. Therefore, electronic absorption spectra of the polymers obtained are recorded in chloroform. In Fig. 2 we compare the data of the polymers obtained in this study with the polymers obtained in the acid-catalysed elimination of methanol from the methoxy-pendant precursor polymers as published before [11]. The acid-catalysed elimination of the precursor polymer only shows a broad distribution of different conjugation lengths (Fig. 2(a)). From Fig. 2(b) it is evident that, in the case of the polymerization with an excess of NaOH, a non-statistical distribution of elimination products is found. In all cases the major absorption, accompanying the absorption of the localized benzene ring at $\lambda_{max} = 299$ nm, is found at $\lambda_{max} = 360$ nm; this electronic transition is assigned to the tetraethoxystilbene unit. Only a small absorption at longer wavelength ($\lambda_{max} = 410$ nm) is observed, corresponding to the hexaethoxy-distyrylbenzene unit. The absorption maxima found in this study at 299, 360 and 410 nm are in close agreement with the data reported by Manecke and Zerpner [13] on well-defined dialkoxy-PPV oligomers.

The ^{1}H NMR data in combination with the UV–Vis spectra show that, up to 35% elimination, tetraalkoxystilbene units are almost exclusively found. The reason for this selectivity in the base-induced elimination during polymerization is speculative. It has been proposed that the acid-catalysed elimination of methanol in a chloroform solution proceeds through an E_1-mechanism and the carbenium ion intermediate is then stabilized by conjugation [11]. Increasing the conjugation length will lead to an increase in the stabilization of the intermediate, leading to delocalized units. Hence the formation of conjugated arrays is preferred. Although this preference cannot be concluded from Fig. 2(a), there is experimental evidence available from the elimination of HCl from PVC [14]. In the base-catalysed elimination of the sulfonium group and HCl, however, no carbenium ion intermediate is expected (E_2-mechanism). Hence, the resonance energy gained in this elimination is higher for the formation of a stilbene unit than it is for units with higher conjugation length. This selectivity in the E_2-mechanism will yield polymers with primarily stilbene units. Early publications propose an E_1cB-mechanism for the (base-catalysed) elimination of sulfonium groups [15], but this mechanism involves the presence of a

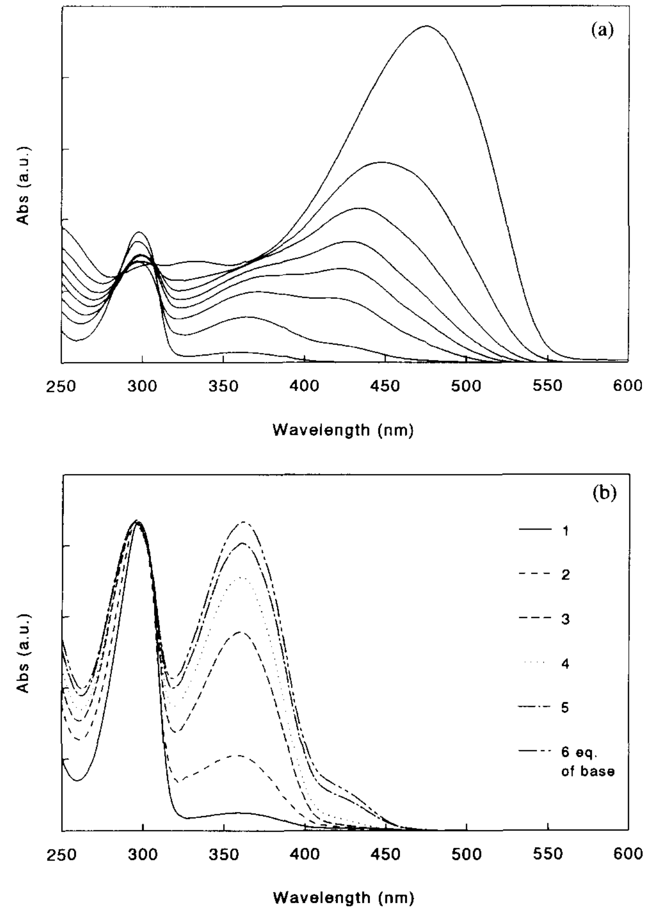


Fig. 2. (a) Selection of UV–Vis spectra obtained during the irradiation experiment in chloroform [11]. (b) UV–Vis spectra of the precipitates obtained after polymerization with excess of base.

carbanion which can be stabilized by the phenyl rings and, thus, favouring longer conjugated units in the elimination reaction. Hence, this E$_1$cB-mechanism does not agree with the selectivity which is found experimentally here and elsewhere [16]. To the best of our knowledge no specific reports on the presence of isolated stilbene units in PPVs have been published; only Halliday et al. [17] report on some isolated stilbene and distyrylbenzene units in PPV precursors made by a delayed addition of base. However, it is proposed to be randomly distributed [17].

The nucleophilic substitutions of $^-$OH or $^-$OCH$_3$, the latter being the better nucleophile [7,18], with the sulfonium group of the polymer accompany the elimination. Therefore, it is not feasible to comment on a possible relation between degree of elimination and the excess of NaOH used. The decrease in both the molecular weight and the yield is explained by side reactions as well. It is reasonable to assume that nucleophilic substitutions of $^-$OH or $^-$OCH$_3$ can occur with the sulfonium group at the monomer or at the growing chain end.

3.2. Photoluminescence of the polymers

In order to gain insight into the photophysical properties of this new series of stilbene polymers, we have investigated the excitation and emission characteristics of the polymers in CHCl$_3$ solutions. The emission and excitation spectra of the polymer (35% elimination) with the highest number of stilbene units is given in Fig. 3. The fluorescence maximum is centred around 415 nm and some vibrational fine structure is observed. The excitation spectrum of the emission at 415 nm shows two absorption bands corresponding to both the tetraethoxy-stilbene π–π^* transition at 360 nm and the localized 1,4-diethoxy-benzene π–π^* transition at 299 nm. Apparently, energy transfer from benzene unit to stilbene unit takes place. In order to study this energy transfer, the excitation spectra of the whole series is measured and the results are given in Fig. 4. By an increasing number of stilbene units in the polymer the contribution of the excitation of the localized benzene

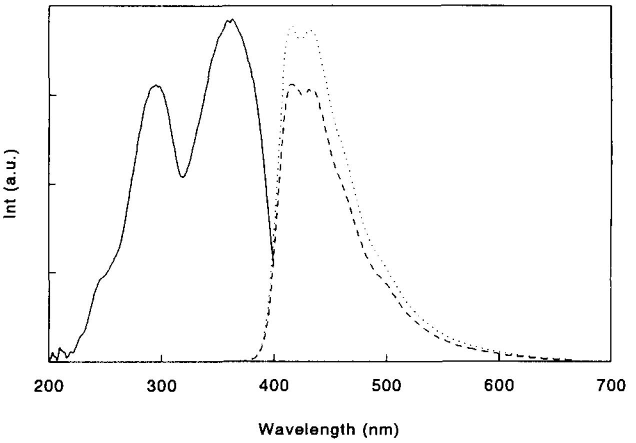


Fig. 3. Emission (broken line, λ_{exc} = 290 nm; dotted line, λ_{exc} = 360 nm) and excitation (solid line, λ_{em} = 415 nm) spectra of the material obtained after polymerization with six equivalents of NaOH.

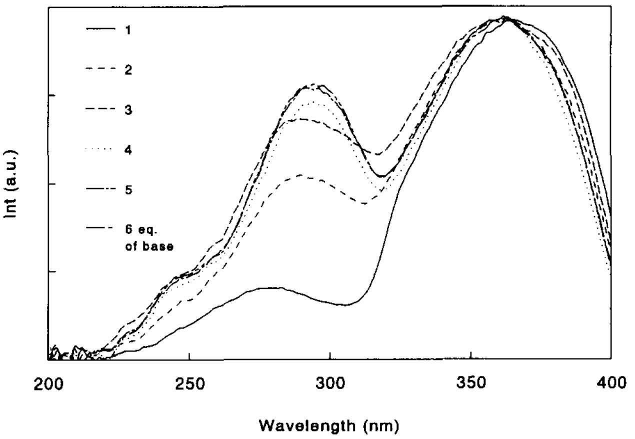


Fig. 4. Excitation spectra (emission at 415 nm) of all the precipitates obtained after polymerization with 1–6 equivalents of NaOH in methanol.

unit becomes more pronounced. Even at the lowest concentrations of stilbene, the main emission of the fluorescence still originates from the stilbene π–π^* excitation only. This increase of energy transfer by an increase of stilbene units suggests qualitatively that a fast quenching of the excitation at the localized benzene ring occurs. Therefore, it is proposed that an efficient energy transfer from benzene to stilbene can only take place efficiently at high concentrations of stilbene. In order to elucidate quantitatively the photophysical events in these new polymers a more detailed analysis is under investigation.

4. Conclusions

We have described the formation of partially eliminated diethoxy-PPV precursors. The base-induced elimination during the polymerization with an excess of base is assumed to proceed by an E_2-type mechanism that strongly favours the formation of tetraethoxy-stilbene units in the precursor polymer. Even at elimination as high as 35%, as determined by ^{1}H NMR spectroscopy, no significant amounts of eliminated units with longer conjugation lengths, i.e. hexaethoxy-distyrylbenzene units, are observed in UV–Vis spectra. The photoluminescence of these stilbene polymers is centred around 415 nm and exhibits some vibronic fine structure. This approach to achieve processable blue-emitting PPV derivatives is thought to be of general use, provided that the benzene rings are substituted with two alkoxy groups. From other work it is evident that the kinetics of both the substitution and elimination reactions are strongly influenced by the presence of substituents at the benzene ring. Investigations to test the generality of the synthesis and the properties of these new types of polymers as constituents in polymer-based light-emitting diodes are in progress.

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