*Macromolecules* **1998,** *31,* 1819−1826

# Synthesis of Novel Poly[(2,5-dimethoxy-*p*-phenylene)vinylene] Precursors Having Two Eliminatable Groups: An Approach for the Control of Conjugation Length

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*Received September 8, 1997; Revised Manuscript Received December 2, 1997*

ABSTRACT: Poly[(2,5-dimethoxy-*p*-phenylene)vinylene] (DMPPV) of varying conjugation length was synthesized by selective elimination of organic soluble precursor polymers that contained two eliminatable groups, namely, methoxy and acetate groups. These precursor copolymers were in turn synthesized by competitive nucleophilic substitution of the sulfonium polyelectrolyte precursor (generated by the standard Wessling route) using methanol and sodium acetate in acetic acid. The composition of the precursor copolymer, in terms of the relative amounts of methoxy and acetate groups, was controlled by varying the composition of the reaction mixture during nucleophilic substitution. Thermal elimination of these precursor copolymers at 250 °C, yielded partially conjugated polymers, whose color varied from light yellow to deep red. FT-IR studies confirmed that, while essentially all the acetate groups were eliminated, the methoxy groups were intact and caused the interruption in conjugation. Preliminary photoluminescence studies of the partially eliminated DMPPV samples showed a gradual shift in the emission maximum from 498 to 598 nm with increasing conjugation lengths, suggesting that the color of LED devices fabricated from such polymers can, in principle, be fine-tuned.

## Introduction

Poly(*p*-phenylenevinylene) (PPV) and its derivatives have attracted a great deal of attention in recent years because of their interesting electroluminescent properties and their potential for application as the active emitting layer in light emitting diodes (LED).[1,2] The demonstration that both their photoluminescence and electroluminescence spectra are essentially identical suggests that the state from which the emission occurs is the same in both cases.[3,4] Thus, the interest in the control of conjugation length in these polymers stems from the desire to control the color of the emission in such LED devices, which in turn would be related to the absorption maximum in their electronic absorption spectra. Furthermore, the efficiency of luminescence was shown to be significantly enhanced, when isolation of short conjugated segments is achieved, because of exciton confinement.[5−7] Several approaches to achieve control of conjugation length of PPV have been reported. For instance, in the case of PPV homopolymer, partial elimination of both the sulfonium polyelectrolyte precursor[7] and the methoxy precursor[8] by varying the temperature of elimination have been attempted. The success of these approaches is limited by their inability to achieve precise control over the entire range of conjugation lengths, using just temperature as the handle. In copolymer systems, Burn et al.[9] have exploited the relatively higher lability of the sulfonium group, adjacent to the dialkoxyphenyl unit in the polyelectrolyte precursor, toward nucleophilic substitution to generate precursor copolymers containing both sulfonium and methoxy groups. Further, the greater ease of elimination of the sulfonium groups, when compared to the methoxy groups, provided some control of the conjugation lengths in such copolymer systems. Similarly, precursor copolymers of poly[(dialkoxy-*p*-phenylene)vinylene] containing both chloride and methoxy groups, prepared by partial substitution of the chloroprecursor, have also been demonstrated.[6] The high lability of the methoxy groups in the presence of even traces of acid,[10] such as HCl, is a limitation of both these approaches, because the HCl that is released upon elimination of the sulfonium (or chloro) group could, in principle, catalyze further elimination of the methoxy groups. Furthermore, while the authors have demonstrated the feasibility of this approach, its versatility in terms of achieving controlled variation over the entire composition window was not reported. More recently, a step growth condensation strategy to prepare PPV copolymers with statistically controllable conjugation length has been explored.[11] An alternative approach, wherein well-defined oligomeric segments of PPV are incorporated in a nonconjugated polymer backbone, has also been demonstrated.[12] In such an approach, while precise control of conjugation length is achievable, it suffers from the limitation that increasing the conjugation length becomes synthetically cumbersome. In this paper, we describe a novel approach to synthesize DMPPV precursors, by competitive nucleophilic substitution of the sulfonium polyelectrolyte precursor, using methanol and sodium acetate as nucleophiles. The composition of the precursor copolymer, in terms of the relative amounts of methoxy and acetate groups, is controlled by varying the composition of the reaction mixture during nucleophilic substitution. The facile elimination of the acetate groups, leaving the methoxy groups intact, permitted a controlled variation of the conjugation length, which is reflected in both their UV−visible and photoluminescence spectra.

## Experimental Section

**Instrumental Methods.** NMR spectra of all polymers were recorded on a Bruker 200 MHz spectrometer using $CDCl_3$ as the solvent and TMS as reference. UV−visible spectra of

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S0024-9297(97)01324-7 CCC: $15.00

the polymer films, spin-coated onto quartz plates, were recorded on a Hitachi U-3400 spectrophotometer. Photoluminescence of the same films was recorded using a Hitachi F-2000 fluorescence spectrophotometer. IR spectra of the polymer films coated on KBr pellets were recorded on a Bruker Equinox 55 FT-IR spectrometer. TGA was done using a Du Pont 2000 data station and TGA 951 instrument.

**Poly[2,5-dimethoxy-1,4-(α-hydroxy)xylylene-*co*-2,5-dimethoxy-1,4-(α-methoxy)xylylene] (C).** In a typical experiment, 30 mL of ice-cold, $N_2$-purged methanolic NaOH (0.4 M) was added in a slow stream to the ice-cold, $N_2$-purged methanolic solution of the bis(sulfonium) monomer **A** (5 g, 12.16 mmol in 35 mL of MeOH). The polyelectrolyte **B** was obtained by stirring the reaction mixture at 0−5 °C for 1 h. The polymer solution was then added to 60 mL of water and stirred for 5.5 h. The polymer, which was obtained as a residue after centrifugation of the reaction mixture, was washed with MeOH and redissolved in chloroform, and this solution was filtered (to remove inorganic salts), concentrated and precipitated out by adding it to methanol. The polymer, thus obtained, was once again purified by redissolving in chloroform and reprecipitating from MeOH and then dried under vacuum. Yield: 339 mg.

The hydroxyl content in this copolymer was changed by varying the relative amount of water added to the methanolic reaction mixture after polymerization.

**Poly[2,5-dimethoxy-1,4-(α-methoxy)xylylene-*co*-2,5 dimethoxy-1,4-(α-acetoxy)xylylene] (D). Method I. Acetylation of the hydroxy precursor (C).** In the first method, a mixture of 1 mL of acetic anhydride and 2.5 mL of pyridine was added to 20 mL of chloroform solution containing 232 mg of the precursor **C**. The mixture was stirred at room temperature for 2 h and heated to 60 °C for 11 h. The chloroform solution was then filtered and concentrated, and a precipitate was obtained by adding to methanol. The resulting polymer was purified by redissolving in tetrahydrofuran and reprecipitating from water. The polymer was washed with MeOH and dried under vacuum. Yield: 78 mg.

**Method II. Competitive Nucleophilic Substitution.** In the second method, the sulfonium precursor **B** was prepared (as previously described) using 3 g of the monomer, and methanol was removed completely under reduced pressure. The polymerization time was limited to 30 min (instead of 1 h, as in the previous case), and the solvent removal, typically, took about 40−45 min. The residue was dissolved in a solution of sodium acetate in acetic acid containing 2% (by volume) acetic anhydride and the required amount of methanol. The mixture was heated to 40−45 °C for a few minutes and then stirred at room temperature for 8 h. The polymer that precipitated out was centrifuged; the residue was washed with MeOH, filtered, and dissolved in chloroform. The chloroform solution was filtered and concentrated, and precipitation was induced by methanol. The product was filtered, washed with MeOH, and purified once again by redissolving in chloroform and reprecipitating in methanol. The purified product was dried under vacuum. The yield of the precursor polymer varied from 290 to 450 mg.

The copolymer compositions were determined from their $^1$H NMR spectra. The maximum mole fraction of acetate in the copolymer, when no methanol was used during the nucleophilic substitution step, was found to be 67%. When the same reaction was done on a 1 g monomer scale, the precursor copolymer contained 78% acetate, and a yield of 150 mg was obtained.

**Thermal Elimination Studies.** The polymer films for thermal elimination studies were prepared by coating 0.2 wt % solutions of the precursors in chloroform onto KBr pellets for IR studies. For UV−visible and photoluminescence studies, they were spin-coated on quartz plates. These films were heated under an $N_2$ atmosphere for 1 h at 250 °C for partial elimination and under a slow stream of HCl and $N_2$ atmosphere for a further 1 h at 220 °C for effecting complete elimination. For TGA, 5−10 mg of the sample was taken and heated at 10 °C/min under an $N_2$ atmosphere (40 mL/min).

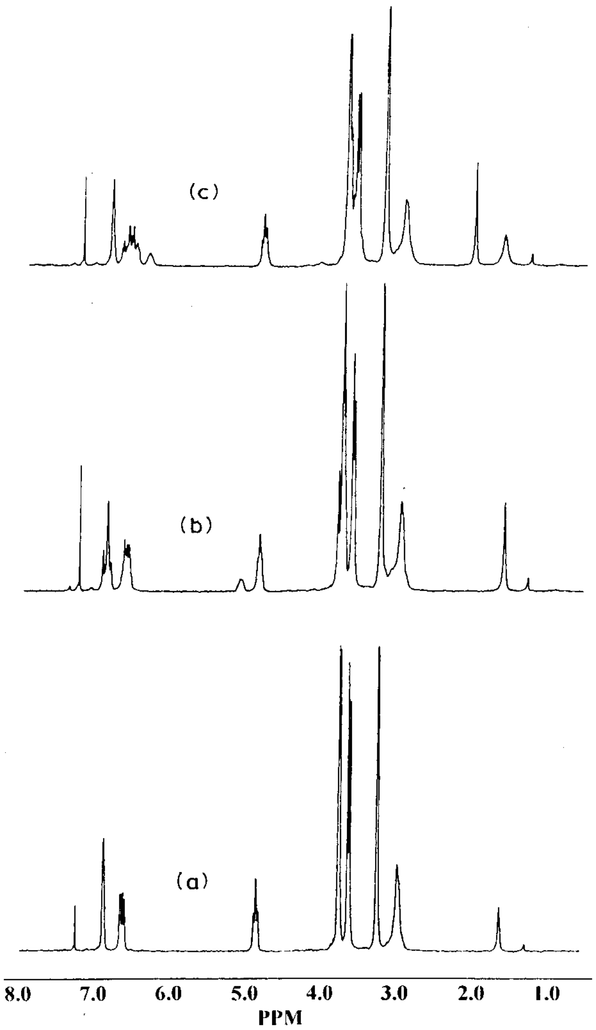


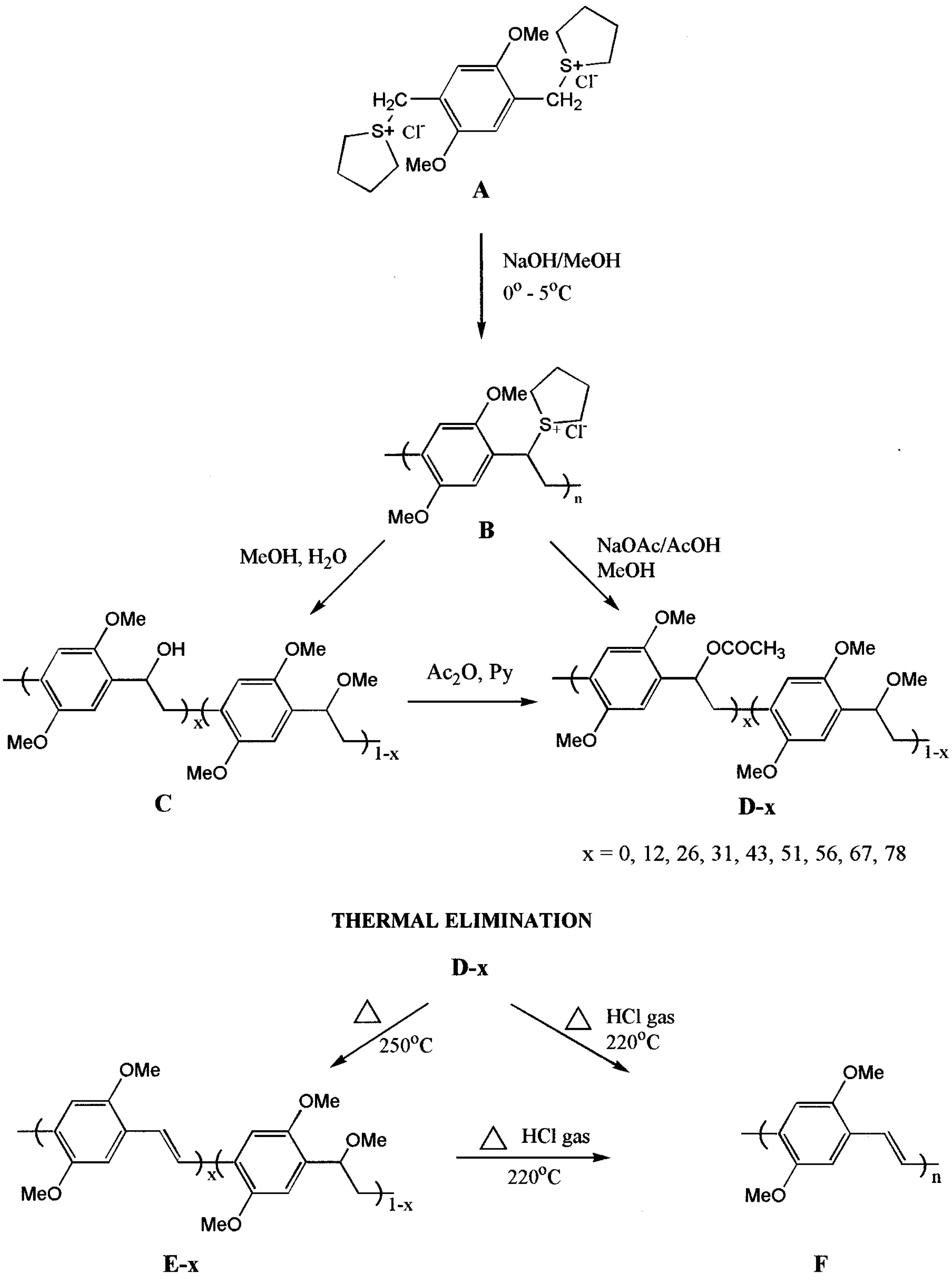
**Figure 1.** $^1$H NMR spectra of the precursor copolymers **D-0** (a), **C** (b), and **D-33** (c).

## Results and Discussion

Poly(phenylenevinylene) and its derivatives have been mostly synthesized via the Wessling route,[13] wherein a sulfonium polyelectrolyte precursor **B** is thermally eliminated to give the final conjugated polymer. Treating the sulfonium precursor with methanol[14] and even carrying out the polymerization directly in methanol[15] were shown to be effective methods for generating an organic-soluble methoxy precursor. In an effort to prepare precursors that have both methoxy and acetate groups, two approaches were attempted (Scheme 1).

In one case, the polymerization was carried out in methanol at 0 °C and varying amounts of water were added to it after completion of the polymerization (ca. 1 h). The reaction mixture was then warmed to room temperature. The copolymer **(C)** that precipitated out was found to contain both −OH and −OMe groups, as was seen from its $^1$H NMR spectra (Figure 1b). The backbone methine (−C***H***OH) proton appears at 5.1 ppm, while the corresponding methine proton adjacent to the methoxy group (−C***H***OMe) appears slightly upfield at 4.9 ppm. The relative intensities of these protons yielded the composition of the copolymer. The hydroxyl groups were further converted to acetates using pyridine/acetic anhydride. Upon acetylation of the hydroxyl groups, the methine proton (−C***H***OAc) moves considerably downfield to 6.4 ppm (Figure 1c). The relative

**Scheme 1. Synthetic Scheme for the Preparation of the Precursor Copolymers and Conditions for Their Thermal Elimination**



intensity of this with respect to the peak at 4.9 ppm remains essentially the same, confirming that the copolymer composition after acetylation remains unchanged. This approach, however, suffered from one severe limitation, in that the maximum mole fraction of −OH groups that could be incorporated was ca. ~40%. When attempts to increase the hydroxyl content, by increasing the water to methanol ratio, were made, the resulting polymers were found to be insoluble. This may be due to further intermolecular nucleophilic displacement of the sulfonium groups by the secondary hydroxyl groups that are already generated on the polymer backbone, which would lead to the formation of ether cross-links.

In an attempt to overcome this limitation, we carried out a direct displacement of the sulfonium groups by

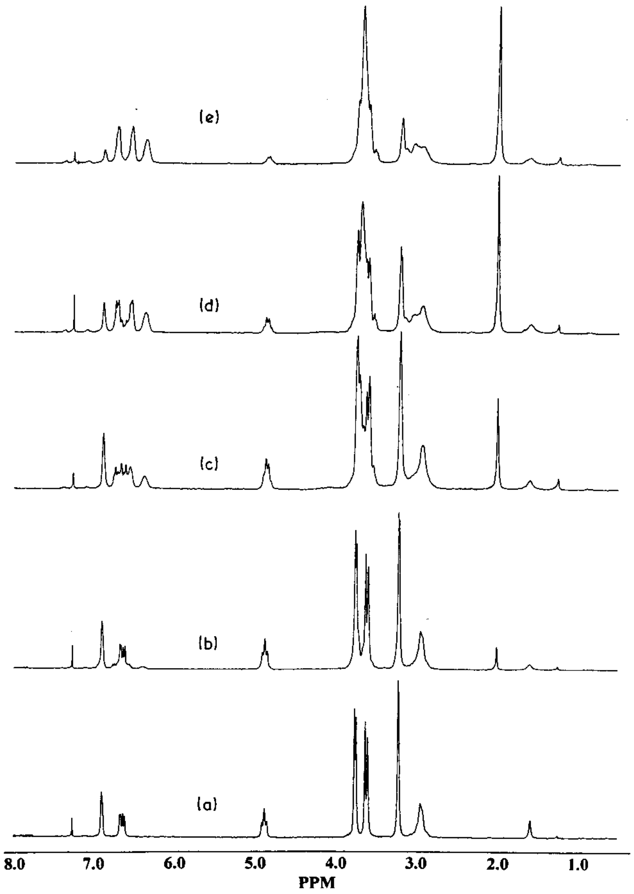


**Figure 2.** $^1$H NMR spectra of the precursor copolymers **D-0** (a), **D-12** (b), **D-31** (c), **D-67** (d), and **D-78** (e).

sodium acetate in acetic acid. The polymerization was first carried out in methanol at 0 °C, after which the solvent was removed under reduced pressure. The residue was then redissolved in acetic acid containing various mole fractions of sodium acetate and methanol. Two percent (by volume) of acetic anhydride was added to the acetic acid to remove any inadvertent water that might have been present.[16] Upon completion of the reaction, the polymer that precipitated out was purified by dissolution in chloroform and reprecipitation. $^1$H NMR spectra (Figure 2) of the precursor copolymers (**D-*x***) (where *x* represents the mole percent of the acetate groups) generated in this manner clearly indicate the presence of both methoxy and acetate groups. The relative intensities of the backbone methine protons, C***H***OMe (at 4.9 ppm) and C***H***OAc (at 6.4 ppm), were used to calculate the composition of the copolymers (see Table 1). The variation in the relative intensities of these two peaks is also proportionally reflected in the intensities of the aliphatic methoxy protons (3.2 ppm) and the methyl protons (2.01 ppm) of the acetate groups. Additionally, the fine structure of the aromatic protons and the chemical shifts of the aromatic methoxy protons were found to vary with the copolymer composition. It may be added here that the acetoxy precursor copolymer prepared by the first approach, i.e., via the hydroxy precursor **C**, also exhibited an essentially identical spectrum (compare Figures 1c and 2c).

**Table 1**

| copolymer | yield (%) | mole fraction of NaOAc in the mixture | mole fraction of OAc in the copolymer[a] |
|---|---|---|---|
| **D−0** | 32 | 0.00 | 0.00 |
| **D−12** | 32 | 0.04 | 0.12 |
| **D−26** | 20 | 0.08 | 0.26 |
| **D−31** | 21 | 0.12 | 0.31 |
| **D−43** | 21 | 0.21 | 0.43 |
| **D−51** | 22 | 0.35 | 0.51 |
| **D−56** | 21 | 0.62 | 0.56 |
| **D−67** | 29 | 1.00 | 0.67 |
| **D−78**[b] | 28 | 1.00 | 0.78 |

[a] Values were determined from $^1$H NMR spectra. [b] Reaction was carried out at smaller (one-third) scale.

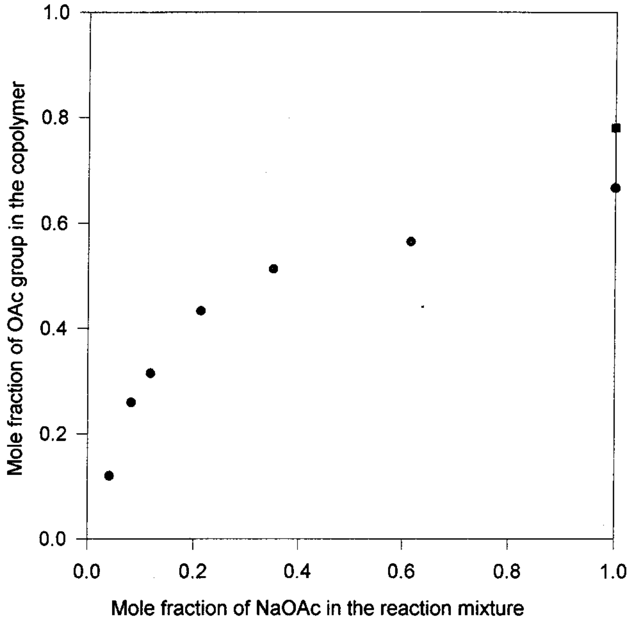


**Figure 3.** Plot of composition of the precursor copolymers versus the mole fraction of NaOAc in the reaction mixture. ■ indicates the data point for the reaction that was carried out on a smaller scale.

A plot of the composition of the copolymers **D-*x*** versus the mole fraction of NaOAc in the reaction mixture is shown in Figure 3. As seen from the plot, the maximum achievable acetate content was found to be 67%, even when the reaction mixture contained no methanol during the nucleophilic substitution step. This suggests that partial substitution of the sulfonium groups does occur during the polymerization in methanol and also, probably, during the period when the solvent is being removed (typically, about 40−45 min). In an attempt to increase the acetate content further, the polymerization was carried out on a smaller scale so that the time for removal of methanol after polymerization could be reduced. This resulted in a slightly lower extent of premature substitution and a copolymer containing 78% acetate groups was obtained. Control experiments carried out, in the absence of both NaOAc or acetic acid, confirmed that NaOAc is indeed the nucleophile and also that the substitution occurs effectively only when acetic acid is used as the reaction medium. One limitation of this approach, however, is that the precursor containing only acetate groups could not be prepared because of the high lability of the sulfonium groups in the dimethoxy PPV precursor. The FT-IR spectra of some representative precursor copolymers **D-*x***, along with those of the eliminated samples **E-*x***, are shown in Figure 4. These spectra are normalized with respect to the peaks at 1406 and 1464 cm$^{-1}$, which were found to be invariant with composition. The intensities of the peaks at 1741 and 1094 cm$^{-1}$, due to the carbonyl stretching and aliphatic $OCH_3$ (asymmetric C−O−C

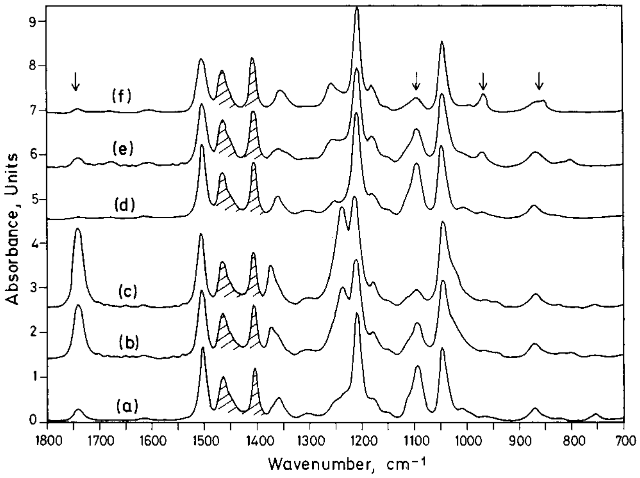


**Figure 4.** FT-IR spectra of the representative precursor copolymers **D-12** (a), **D-51** (b), **D-78** (c), **E-12** (d), **E-51** (e), and **E-78** (f) before and after elimination.

stretching),[5] respectively, are in accordance with the varying contents of acetate and methoxy groups in the precursor copolymers.

**Thermal Elimination.** The thermal elimination of the precursor copolymer films was carried out at 250 °C under a slow stream of dry purified nitrogen. The FT-IR spectra of the copolymers indicated that the elimination of the acetate groups is essentially complete in about 1 h. It is clear from the spectra of the eliminated copolymers **E-*x*** (Figure 4) that the carbonyl peak at 1741 cm$^{-1}$ due to the acetate groups has essentially disappeared. Also, as expected, the intensities of the peak at 1094 cm$^{-1}$ due to the residual methoxy groups are clearly higher in the eliminated copolymers with lower acetate content, i.e., when the extent of elimination is smaller. Furthermore, the intensities of the trans C−H out-of-plane bending vibration at 968 cm$^{-1}$ and the vinylic C−H stretching band at 3054 cm$^{-1}$ (not shown in the figure) are also seen to increase with the extent of elimination. The thermal elimination of acetate is known to give rise to both cis and trans double bonds.[17] Son et al.[18] have shown that the pure xanthate precursor, when eliminated, does yield PPV containing some amount of cis double bonds, which in the case of unsubstituted PPV gave a signature peak at 840 cm$^{-1}$, due to the cis C−H out-of-plane bending vibration. The observation of this cis peak in our samples is hampered by the presence of a peak at 869 cm$^{-1}$ even in the uneliminated precursor. However, upon careful observation, it appears that a shoulder at 850 cm$^{-1}$ begins to appear in the spectra resulting from samples with higher acetate content and is fairly resolved in the copolymer **E-78** (Figure 4f). At first sight, it appeared that this may indicate the presence of cis double bonds in these partially eliminated copolymers, as was observed in PPV generated from the xanthate precursor. However, control elimination experiments indicated that this peak is also present in the fully eliminated DMPPV sample prepared by thermal elimination (in the presence of HCl gas) of the pure methoxy precursor. Furthermore, all the fully eliminated DMPPV samples, irrespective of the precursor copolymer structure, exhibited this peak. Hence, at this point the exact origin of this peak remains unclear and further experiments are required to unequivocally establish its origin. The interest in the generation of cis units, of course, stems from the fact that PPV with higher cis content was shown to exhibit enhanced electroluminescence efficiencies.[18]

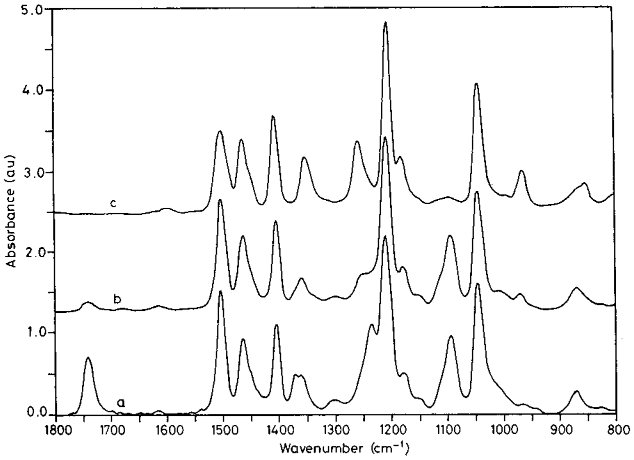


**Figure 5.** FT-IR spectra of the partially and completely eliminated precursor copolymers **D-31** (a), **E-31** (b), and **F** (c).

To confirm that the methoxy groups remain intact during the elimination process, the spectra of the films prior to elimination and after elimination at 250 °C, for the typical precursor copolymer **D-31**, are compared in Figure 5. After normalization of the invariant peaks at 1406 and 1464 cm$^{-1}$, it is clearly seen that while the intensity of the carbonyl peak essentially disappears, the intensity of the OMe peak at 1094 cm$^{-1}$ remains largely unaltered. This confirms that under these elimination conditions only the acetate groups are eliminated, leaving the methoxy groups intact. However, upon subjecting these partially eliminated films to further thermal elimination in the presence of HCl gas at 220 °C, elimination of the methoxy groups also occurred, yielding completely eliminated DMPPV (Figure 5c). As expected, the spectra of all the copolymers subjected to elimination under these acidic conditions were found to be essentially identical. We also found that elimination of the methoxy groups can be catalyzed by pyridinium hydrochloride; when elimination was carried out in the presence of 2 wt % of pyridinium hydrochloride, the spectra were found to be identical with that of the completely eliminated sample generated under HCl purge. The use of pyridinium hydrochloride as the catalyst makes the elimination process more readily accessible and hence may be used as a routine alternative to elimination of methoxy PPV precursors under HCl. It must be added here that, upon elimination, two very weak peaks (most prominent in Figure 4e) due to inadvertent oxidation are seen at 1681 and 1614 cm$^{-1}$. These peaks have also been previously observed under standard elimination conditions and were precluded only when the elimination was carried out under a reducing atmosphere.[19]

The TGA curves of some representative precursors are shown in Figure 6. From these curves it is clear that, while the pure methoxy precursor undergoes very little elimination (ca. 4 wt % loss at 315 °C), the extent of elimination is higher in the case of the acetate precursors (ca. 18 wt % loss at 315 °C for **D-56**). Furthermore, the TGA's also indicate that the weight loss at 315 °C, in the case of **D-31**, **D-56**, and **D-67**, are essentially the same. While this percentage weight loss in the case of **D-67** is almost equal to the expected value (of 19%) considering the loss of only the acetate groups, it is much higher in the other two cases. This is contrary

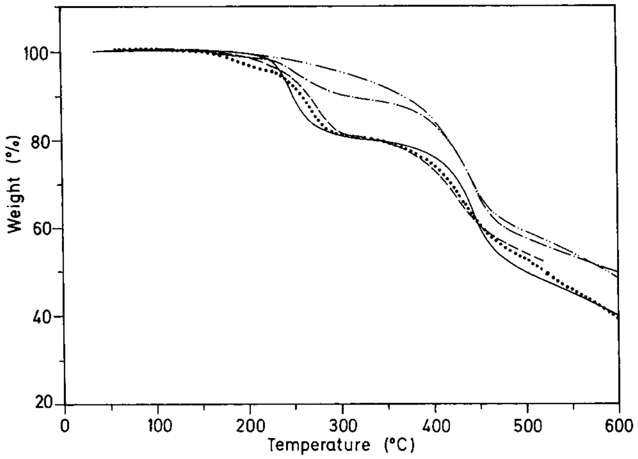


**Figure 6.** TGA curves of the precursor copolymers **D-0** (− ·· −), **D-12** (− · −), **D-31** (—), **D-56** (···) and **D-67** (---).

to what may be expected on the basis of FT-IR studies on thin films, which suggest that the acetate groups are lost selectively, leaving behind the methoxy groups intact. This discrepancy is possibly due to the fact that the elimination process in thick films and bulk samples differs considerably from that in the thin films used for spectral studies. The residual occluded acid plays a more significant role in catalyzing the elimination in thick films and bulk solid samples, causing the weight loss to be much higher than expected. Such observations of differing extents of elimination in thick versus thin film samples have been made before, and explanations of a similar nature have been put forward.[10] This behavior is also visually observable, in that even pure methoxy precursor samples, when heated at 250 °C, acquire an orange color in the interior, while oftentimes retaining a light yellow external appearance. This suggests that even the trace amount of inadvertent acid that remains occluded in the bulk of the sample causes its elimination. Thus, TGA analyses of bulk samples in these cases do not provide quantitative information inasmuch as the extent of elimination is concerned, although the onset of elimination (~220 °C) is suggestive of the temperatures that would be effective for carrying out the elimination of these precursors.

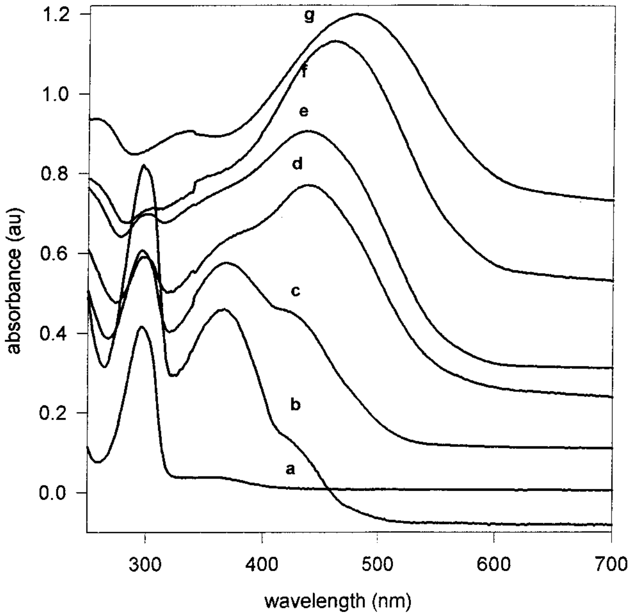


**Figure 7.** UV−vis spectra of the partially eliminated precursor copolymers **E-0** (a), **E-12** (b), **E-31** (c), **E-51** (d), **E-67** (e), **E-78** (f), and **F** (g). The spectra have been offset along the *y* axis for clarity.

**Table 2**

| copolymer | UV−vis $\lambda_{max}$ (nm)[a] | photoluminescence $\lambda_{max}$ (nm) |
|---|---|---|
| **E-0** | 298 (366) | 459 |
| **E-12** | 366 (431) | 500 |
| **E-26** | 367 (431) | 534 |
| **E-31** | 362 (431) | 536 |
| **E-43** | (372) 419 | 553 |
| **E-51** | (370) 438 | 563 |
| **E-56** | (360) 437 | 587 |
| **E-67** | (360) 437 | 589 |
| **E-78** | (360) 460 | 598 |
| **F** | 487 | 598 |

[a] The values listed in parentheses represent either a shoulder or a weaker absorption.

The color of the partially eliminated films of the various copolymers varied from light yellow (for **E-12**) to deep red (for **E-78**) as the acetate content in the precursor copolymers increased, suggesting a variation of conjugation length. Typical UV−visible spectra of the partially eliminated copolymer (**E-*x***) films are shown in Figure 7. Table 2 lists the $\lambda_{max}$ values of the various partially eliminated copolymers. These spectra clearly indicate the evolution of conjugation lengths with increasing acetate content in the precursor copolymers. A similar variation in the UV−visible spectrum was indeed noticed in the solution spectra of the 2,5-dibutoxy PPV precursor,[20] when a chloroform solution of the precursor was photolyzed for varying durations. Recently, well-defined oligomers of dialkoxy PPV were synthesized and careful analysis of their spectral characteristics in solution suggested that both the absorption and emission maxima reach limiting values when the number of repeat units becomes 11.[21] On the basis of these investigations by Meier and co-workers, the evolution of conjugation lengths in our partially eliminated polymers may be discussed as follows. First, one observes that **E-0**, which is expected to have only isolated tetraalkoxy stilbene units, exhibits a $\lambda_{max}$ value of 366 nm compared to 354 nm measured for the two-ring model compound;[21] suggesting that there is possibly a bathochromic shift when the measurement is done in the solid state compared to solution studies. Bearing this in mind, one may conclude that as the extent of elimination increases, the concentration of four-ring oligomers (~438 nm) increases until the case of **E-78**, where a significant concentration of six-ring oligomers (~460 nm) is present.[22] Quantitative estimates of the relative populations of the various oligomeric units is difficult to obtain, because of the presence of unknown amounts of cis olefinic units, which have distinctly shifted (hypsochromic) absorption bands. Upon complete elimination (Figure 7g), the $\lambda_{max}$ value shifts to about 487 nm, along with a significant broadening of the peak, suggesting the presence of a broader distribution of conjugation lengths.

The photoluminescence spectra (Figure 8) of these partially eliminated copolymers show that the emission maximum of **E-*x*** samples varies from 498 to 598 nm with increase in conjugation length. These spectra were recorded at room temperature using an excitation wavelength of 360 nm. It may be added here that the pure methoxy precursor, after a similar thermal treatment, also exhibited a photoluminescence spectrum with an emission maximum at around 440 nm (Figure 8a).

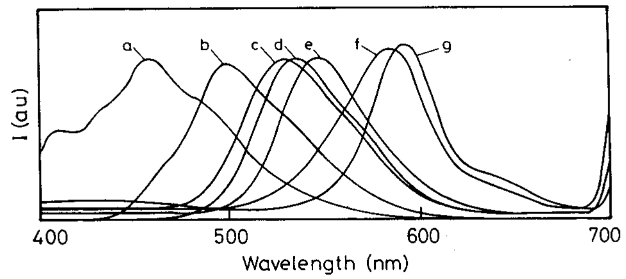


**Figure 8.** Photoluminescence spectra of the partially eliminated precursor copolymers **D-0** (a), **E-12** (b), **E-26** (c), **E-31** (d), **E-43** (e), **E-56** (f), and **E-78** (g).

This is probably from the isolated tetraalkoxy stilbene segments that results from inadvertent elimination. This value is also slightly red-shifted compared to the solution measurements that were carried out for the two-ring model compound.[21] The presence of such partial eliminated units is also noticeable in the UV−visible spectrum (Figure 7a), shows a weak absorption at 366 nm. Furthermore, the nascent precursor film (before thermal treatment) also exhibited essentially the same photoluminescence spectra. This reconfirms that little change, if any, has occurred to the pure methoxy precursor upon thermal treatment in the absence of HCl gas. The emission maximum, upon complete elimination in the presence of an acid, occurs at 598 nm, which is in agreement with previously observed values for DMPPV.[23] It is interesting to note that the emission maximum of completely eliminated DMPPV occurs at the same wavelength as that of sample **E-78**, even though the $\lambda_{max}$ value in the absorption spectra is higher for the former (Table 2). A similar observation of the invariance of the PL maximum, in dialkoxy PPV polymers that contain above 85% conjugated units, has been reported earlier.[6] In all cases, varying the excitation wavelength does not appear to affect both the emission maximum and the overall shape of the spectrum, although their intensities appear to vary. This in turn suggests that selective excitation of shorter segments does not lead to selective emission from those segments alone. As previously suggested,[24] the emission appears to occur from the segments with the longest conjugation length because of migrations of the excitons prior to radiative decay. This explains the invariance of the PL $\lambda_{max}$, both with the excitation wavelength and also with increase in conjugation length (for > 78%).

In conclusion, we have shown that a novel precursor to DMPPV, containing both methoxy and acetate groups, can be prepared by competitive nucleophilic substitution of the sulfonium polyelectrolyte precursor, using methanol and NaOAc in acetic acid medium. The composition of the precursor can be varied by changing the relative concentrations of the two nucleophiles in the reaction mixture. This method is fairly straightforward and has the potential to affect continuous variation in composition. The acetate groups in the precursor copolymers are found to be more thermally labile and are readily eliminated at 250 °C, giving polymers in which the methoxy groups remain intact. From their FT-IR and UV−visible spectra, it was shown that the extent of conjugation increases with an increase in the mole fraction of eliminatable acetate groups in the precursor. The emission maximum in the photoluminescence spectra of the partially eliminated copolymers is also seen to shift to longer wavelengths with increase in conjugation length. In comparison with previous approaches to PPV precursors containing two types of eliminatable groups, this approach presents two distinct advantages: (a) the precursor does not possess any ionic groups, unlike some of the previous cases where the two eliminatable groups are methoxy and sulfonium groups,[9] and (b) the elimination of the acetate groups results in the release of only a mild acid, namely acetic acid, which does not catalyze the elimination of the methoxy groups. The former aspect, namely the generation of purely nonionic precursors, allows one to prepare a wide range of compositions which is rather difficult when dealing with polymers with ionic groups, as the solubility of the polyelectrolyte precursors varies drastically with composition, often yielding precursors which are very difficult to dissolve in a single solvent. The latter aspect becomes important in exercising precise control of conjugation length, in that HCl, which is one of the products of elimination in the precursors containing either sulfonium or chloro groups, is known to catalyze the elimination of the methoxy groups, when present even in very small quantities. In essence, therefore, the present approach is ideally suited to generate DMPPV species of varying conjugation lengths that may be potentially useful as the active emitting layer in LED devices, wherein the fine-tuning of the emission wavelength, over a fairly wide range from 498 to 598 nm, is readily achievable. One limitation of this approach is its inability to prepare precursor copolymers having only acetate groups, because of premature nucleophilic substitution that occurs during the polymerization and during removal of the solvent, methanol. However, in terms of their application, the severity of this limitation is largely mitigated when one notes that the emission maxima of **E-78** and fully eliminated DMPPV are essentially identical. In unsubstituted PPV, the problem of premature substitution of the polyelectrolyte precursor is unlikely to be this severe, as it is known that nucleophilic substitution by methanol, in this case, occurs only upon heating to 50 °C.[15] Hence, in the unsubstituted PPV case it should be possible to exercise a greater control of composition and prepare the complete range of precursor copolymers, using essentially the same approach. Work along these lines is currently in progress and will reported shortly. Furthermore, alternative polar nonnucleophilic solvents to carry out the polymerization are also being examined in an effort to develop an approach to exercise greater control of the precursor copolymer composition. Efforts to use other nucleophiles to affect this substitution are also being made, in an attempt to impart other useful functional characteristics to the final conjugated polymer.

**Acknowledgment.** We thank the CSIR, New Delhi, India, for providing us the financial support for carrying out this research. We also thank Prof. K. Kishore for help in carrying out the TGA analysis of our samples.

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MA971324J