

The Application of McMurry Coupling Reaction in the Synthesis of Poly(arylene vinylene)s

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Abstract: Poly(4,4'-diphenylene diphenylvinylene), poly(4,4'-diphenylene-1,2-bis(pentafluorophenyl)vinylene, poly(1,3-phenylene diphenylvinylene) and poly(1,3-phenylene dimesitylvinylene) were synthesised via the McMurry reaction. All polymers produced are soluble in common organic solvents and thermally stable particularly poly(4,4'-diphenylene diphenylvinylene) and poly(4,4'-diphenylene-1,2-bis(pentafluorophenyl)vinylene. High molecular weight samples were obtained when the pristine polymers were subjected to equilibrium fractionation.

Abstrak: Poli(4,4'-difenilena difenilvinilena), poli(4,4'-difenilena-1,2-bis(pentafluorofenil)vinilena, poli(1,3-fenilena difenilvinilena) dan poli(1,3-fenilena dimesitilvinilena) telah disintesis melalui tindak balas McMurry. Semua polimer yang dihasilkan larut dalam pelarut organik lazim dan stabil terhadap haba terutamanya poli(4,4'-difenilena difenilvinilena) dan poli(4,4'-difenilena-1,2-bis(pentafluorofenil)vinilena. Sampel dengan berat molekul yang tinggi diperolehi apabila fraksinasi keseimbangan dijalankan ke atas polimer asal.

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Introduction

Since the last 10 years poly(arylene vinylene)s have been the material of interest in the area of optoelectronics. This is due to the possibility of using such materials in electronic devices. The use of such materials in device configurations has been demonstrated in light emitting diodes [1,2], field-effect transistors [3,4], optically pump lasers [5] and sensors [6,7]. The synthetic routes have been intensively developed so as to provide access to a wide range of poly(arylene vinylene)s. Amongst others are the so-called precursor route [8,9], Wittig reaction [10,11], Knoevenagel condensation [12,13], Heck reaction [14,15] and also ring opening metathesis polymerisation (ROMP) [16,17]. However, all these routes have some deficiencies such as lack of post-synthesis processing due to insolubility of the polymers, the presence of impurities as well as limited availability of monomers. The application of low-valent titanium species in reductive coupling reaction of aldehydes and ketones to form alkenes was reported in 1970s [18,19]. The reaction has been extensively elaborated by McMurry and co-workers and is now generally known as the McMurry reaction. The application of this reaction was extended to the preparation of poly(arylene vinylene)s and the polymer produced was reported to be soluble in common organic solvent, thus allows post-synthesis processing [20]. In this paper, we report the synthesis and characterisation of a few poly(arylene vinylene)s prepared via the McMurry reaction. The polymers produced were characterised using GPC, FTIR, DSC and TGA.

Experimental

The synthesis of poly(4,4'-diphenylene diphenylvinylene), poly(4,4'-diphenylene-1,2-bis(pentafluorophenyl)vinylene, poly(1,3-phenylene diphenylvinylene) and poly(1,3-phenylene dimesitylvinylene) from the corresponding diketone compounds were carried out according to the general procedure described below.

Dry THF was added to TiCl_3 (4 mole equiv.) in a three-necked round bottom flask (250 mL). LiAlH_4 (2 mole equiv.) was transferred to the mixture at about 0°C under positive pressure of nitrogen. The mixture was then stirred at room temperature for 30 minutes and refluxed for an hour. Diketone (1 mole equiv.) was added to the mixture at room temperature. The mixture was then refluxed for about 20 hours. After slow addition of HCl (60 – 80 mL, 2 M) at about 0°C , the product was extracted into chloroform (3 x 50 mL). The combined extracts were washed with brine, dried over MgSO_4 and filtered. After evaporating the solvent, the residue was dried under vacuum. The product was then re-precipitated from chloroform into methanol (three times) giving the expected polymers as powders or granules.

Results and discussion

Poly(4,4'-diphenylene diphenylvinylene)

A yellow granular solid of poly(4,4'-diphenylene diphenylvinylene), (PDPV), was obtained with 69% material recovery (Figure 1). The FTIR spectrum (Figure 2) shows peaks at 1599cm^{-1} and 1660cm^{-1} . These peaks can be assigned to aryl carbon skeleton

breathing vibration mode and conjugated ketone stretching mode respectively. The intensity of ketone peak decreased tremendously compared to the corresponding peak in the spectrum of the monomer, and was shifted slightly to higher frequency. The decrease in intensity means that carbonyl units were consumed in the polymerisation and the shift in frequency is consistent with the decrease in conjugation for a chain end carbonyl on polymerisation. The broad

peak centred at 3450cm^{-1} is assigned to hydroxyl groups. This could be pinacol formed during incomplete coupling or benzhydrol groups resulting from chain termination by LiAlH_4 reduction of a carbonyl group. Prolonged drying of the polymer under vacuum resulted in no decrease in intensity of this peak indicating that the peak is not due to the residual methanol from the re-precipitation step.

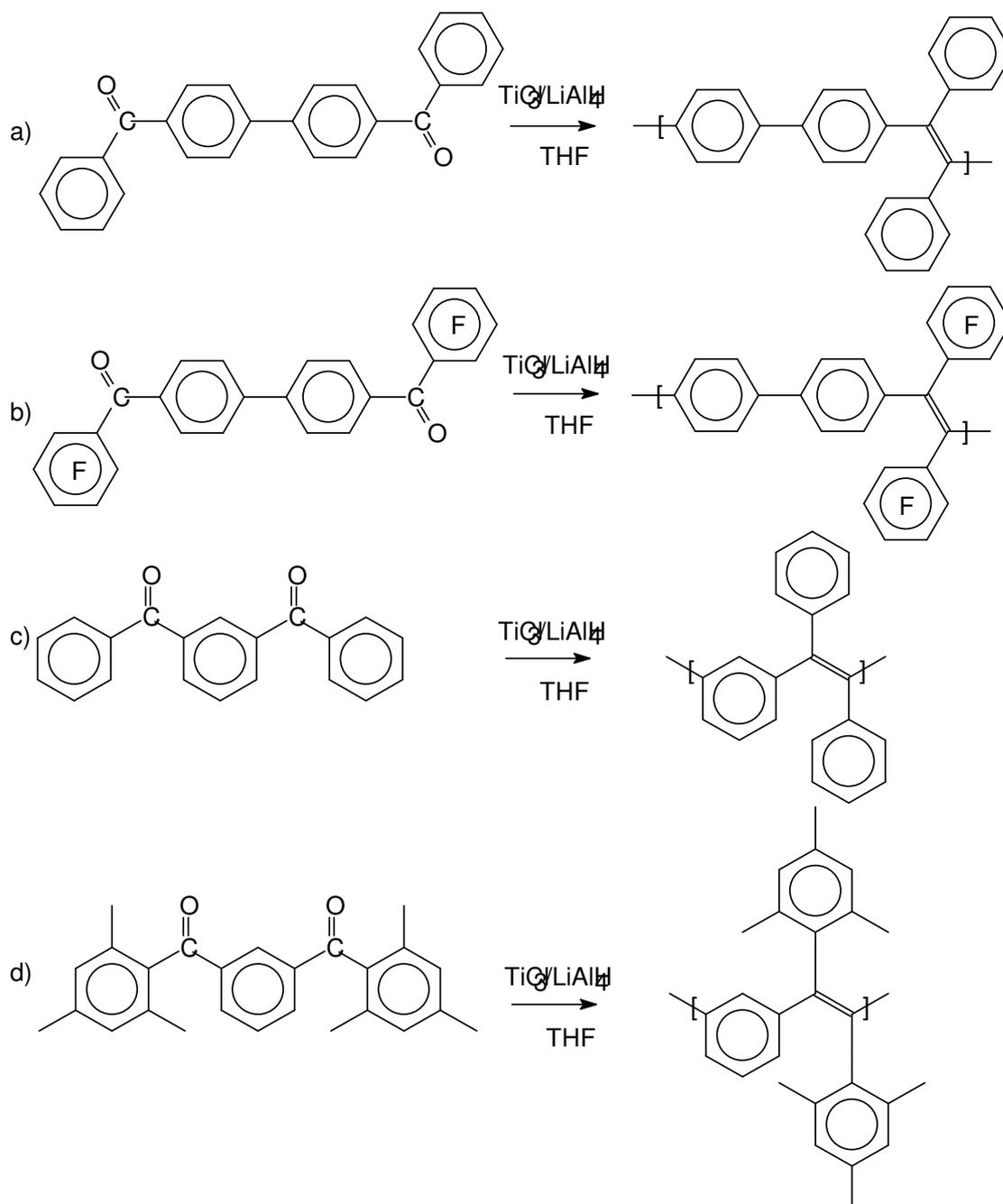


Fig. 1. The McMurry route to a) PDPV, b) PDPV-DF, c) *m*-PPV-DP and d) *m*-PPV-DM

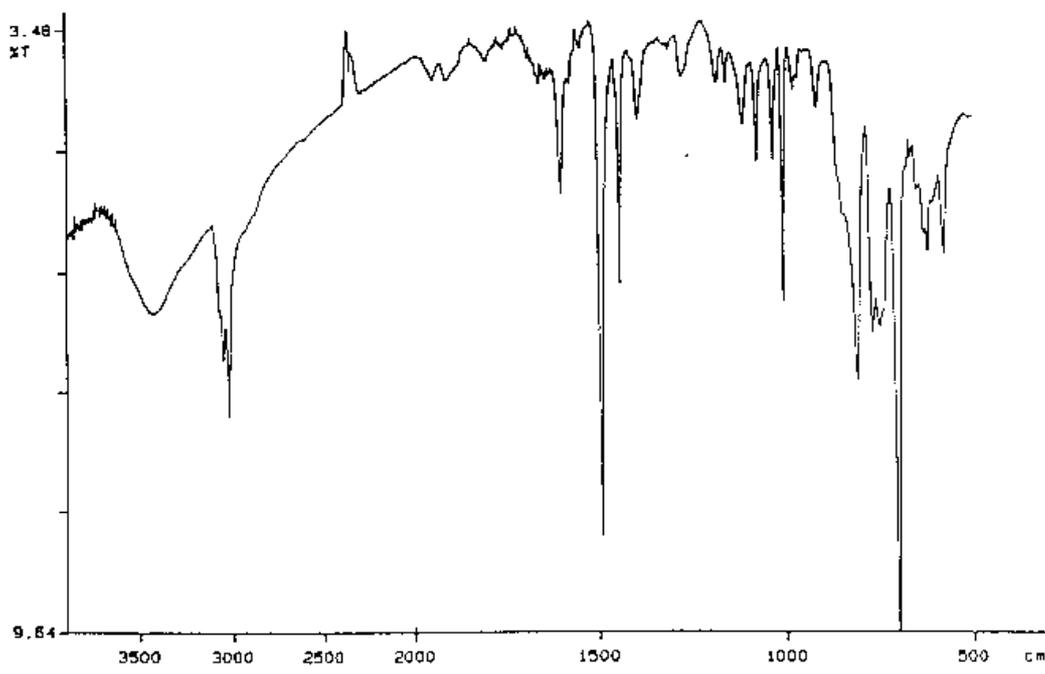


Fig. 2. FTIR spectrum of PDPV

Molecular weight determination was made on this polymer using GPC in chloroform with monodisperse polystyrene as standard (Figure 3). The number average molecular weight (\bar{M}_n) and weight average

molecular weight (\bar{M}_w) obtained were 3,100 and 30,000 respectively with a polydispersity index of about 10.

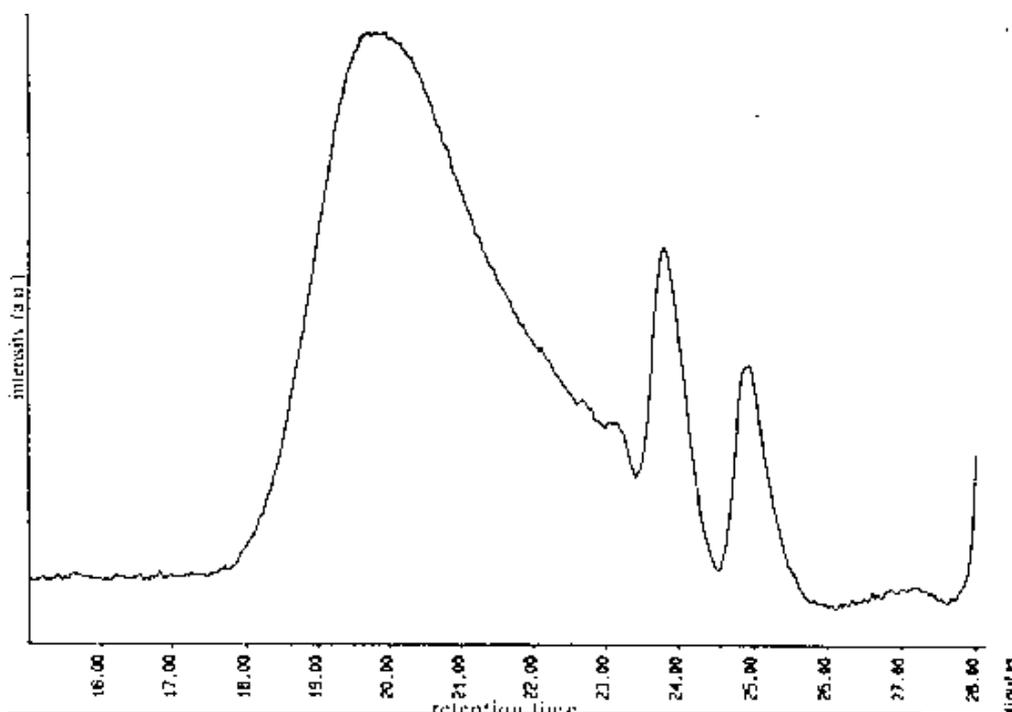


Figure 3. Gel permeation chromatogram of PDPV

Fractions	$^1\overline{M}_n$	$^1\overline{M}_w$	PDI	^2DP
pristine	3,100	30,000	9.6	9
1	88,100	166,900	1.9	267
2	49,900	225,400	4.5	151
3	42,900	78,100	1.8	130
4	19,300	28,100	1.5	58
5	16,500	22,400	1.4	50
6	13,600	16,600	1.2	41
7	9,850	11,600	1.2	30
8	7,040	8,800	1.3	21
9	5,740	7,100	1.2	17
10	4,160	5,900	1.4	13
11	3,840	5,200	1.4	12
12	3,620	5,000	1.4	11
13	3,100	4,100	1.3	9
14	2,470	3,260	1.3	7
15	1,970	2,515	1.3	6
16	1,765	2,330	1.3	5
17	1,150	1,560	1.4	3

¹ values are based on polystyrene standard

² degree of polymerisation

Table 1. Results from the fractionation of PDPV

Materials for use in electro-optic devices should ideally be well defined and of high purity. In this case, the relatively high molecular weight and telomeric molecules are present in the sample produced and the nature of telomeric molecules is not known. The presence of telomeric molecules may also be the reason for low \overline{M}_n since it is very sensitive to the amount of low molecular weight molecules present in the sample. Attempts have been made to rectify these deficiencies by undertaking a careful equilibrium fractionation of the pristine polymer at 20°C using chloroform and heptane as solvent and non-solvent respectively. As a result, a series of 17 fractions was collected varying from $\overline{M}_n \sim 88,000$ down to $\overline{M}_n \sim 1,000$ with polydispersity indices of about 1.3 (Table 1). The first fraction shows a degree of polymerisation of more than 260 which corresponding to the reaction conversion, for this fraction of sample, of more than 99.6%. This implies that the McMurry coupling reaction has a great potential as a condensation polymerisation method for the synthesis of poly(arylene vinylene)s, as long as a procedure to extract the high molecular weight fractions from the pristine polymer is available. Samples of the first three fractions do not show any carbonyl peak at all in the FTIR spectra, suggesting that, for these fractions of sample, the polymerisation reaction proceeded to completion or at least to extent that the presence of the carbonyl groups is reduced to

only a trace thus it can not be detected by FTIR. However, for the rest of the fractions the carbonyl peak increases as the molecular weight decreases. Therefore, it is possible to conclude that some chain ends are carbonyls.

As mentioned earlier, telomers were present in polymer sample and as a result of the fractionation experiment, one of low molecular weight components was isolated and was proved by ^1H nmr, ^{13}C nmr (Figure 4), FTIR and MALDI-TOF (Figure 5) spectroscopies to be the cyclic trimer shown in Figure 6. Thermogravimetric analysis of the sample of run 3 in Table 1 shows the onset decomposition temperature at 370°C, and even at 490°C the polymer only loses less than 5% of its weight, indicating a very good stability against heat. The polymer was found to have a glass transition temperature of 231°C as measured by DSC.

Poly (4, 4'-diphenylene-1, 2-bis (pentafluorophenyl) vinylene)

Poly (4,4'-diphenylene-1,2-bis (pentafluorophenyl) vinylene), PDPV-DF, was prepared from the corresponding diketone, namely 4,4'-bis (pentafluorobenzoyl) biphenyl (Figure 1). An orange solid of poly (4,4'-diphenylene-1,2-bis (pentafluorophenyl) vinylene) was produced in 70% material recovery.

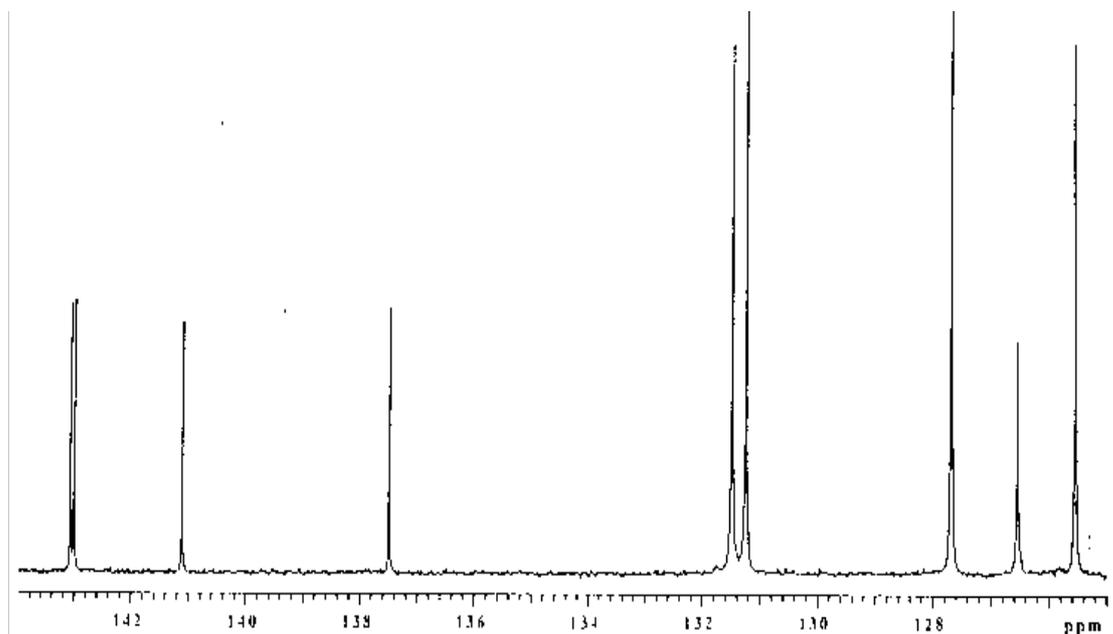


Fig. 4. ¹³C nmr spectrum of the cyclic trimer

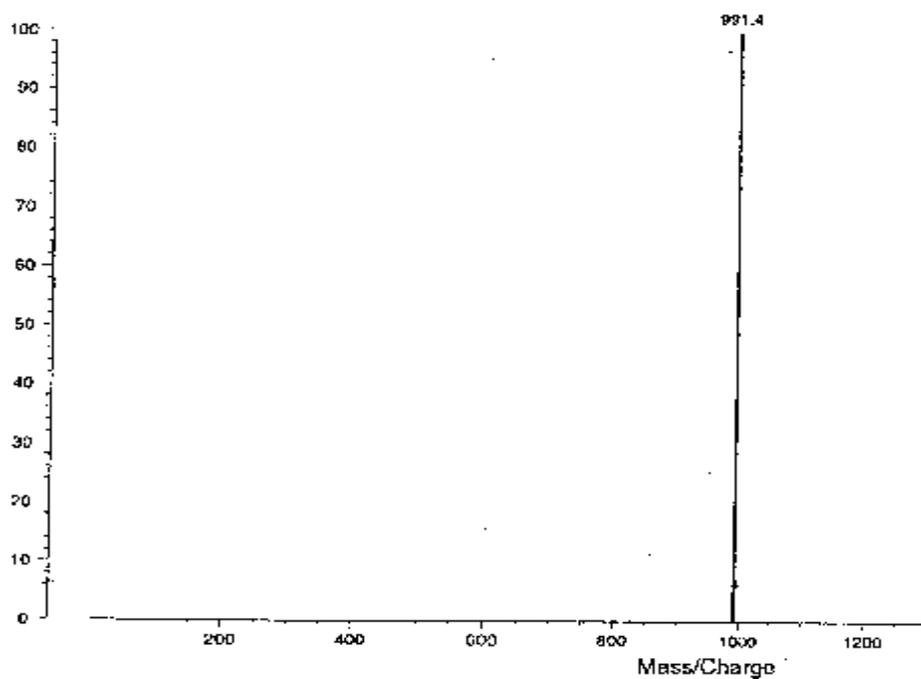


Fig. 5. MALDI-TOF mass spectrum of the cyclic trimer

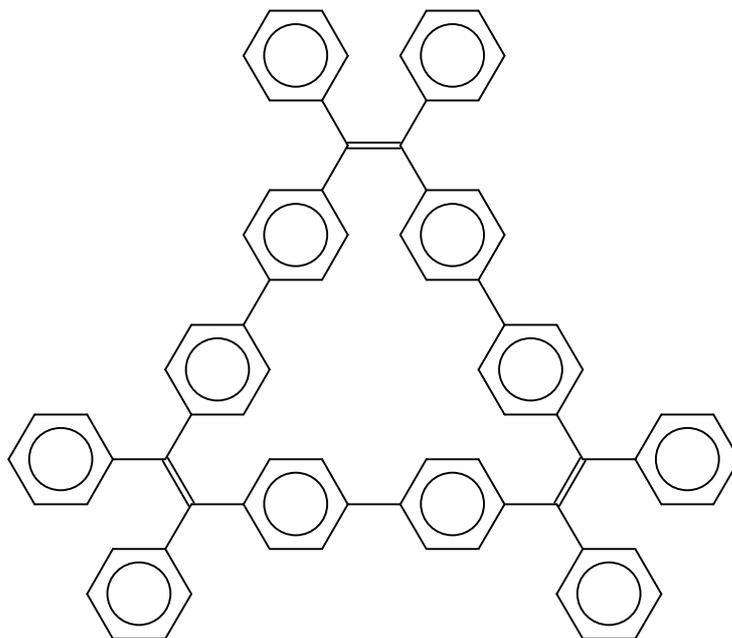


Fig. 6. Molecular structure of the cyclic trimer

The FTIR spectrum (Figure 7) shows major peaks at 1499cm^{-1} and 1522cm^{-1} , the assignment is uncertain but they are probably due to carbon-fluorine vibrations. The carbonyl peak has almost disappeared compared to the corresponding peak in the FTIR spectrum of the monomer. This means that the carbonyl is almost

completely consumed in the polymerisation. The broad peak centred at 3422cm^{-1} can be assigned to the hydroxyl group. This could be either the pinacol formed during incomplete coupling or benzhydrol groups resulting from chain termination by LiAlH_4 reduction of carbonyl groups.

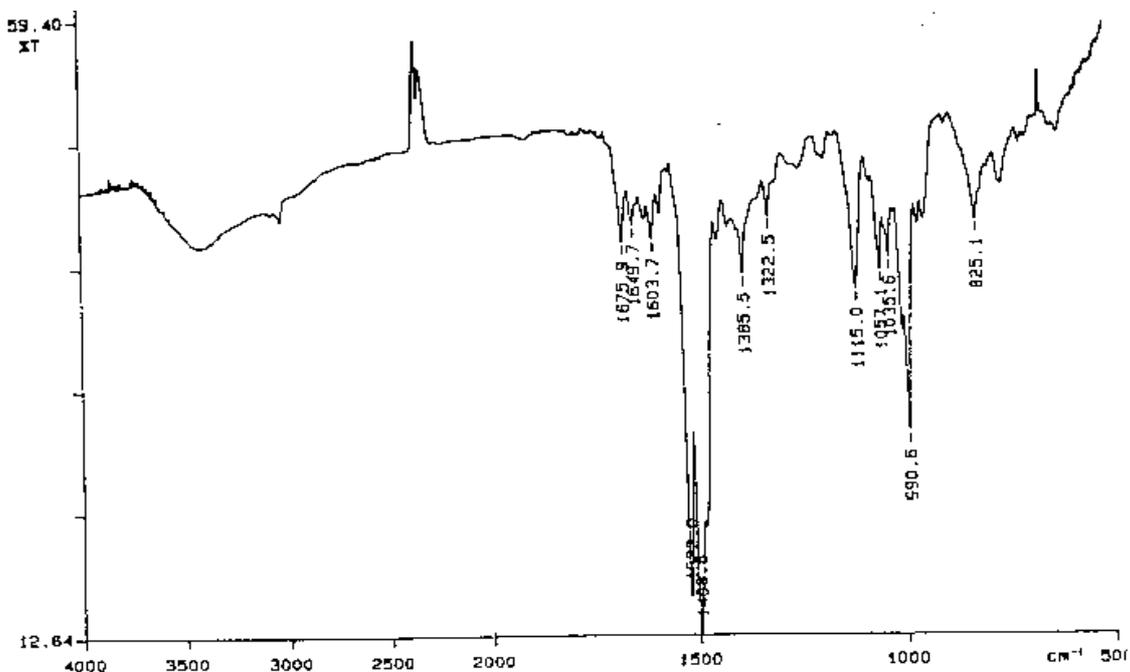


Fig. 7. FTIR spectrum of PDPV-DF

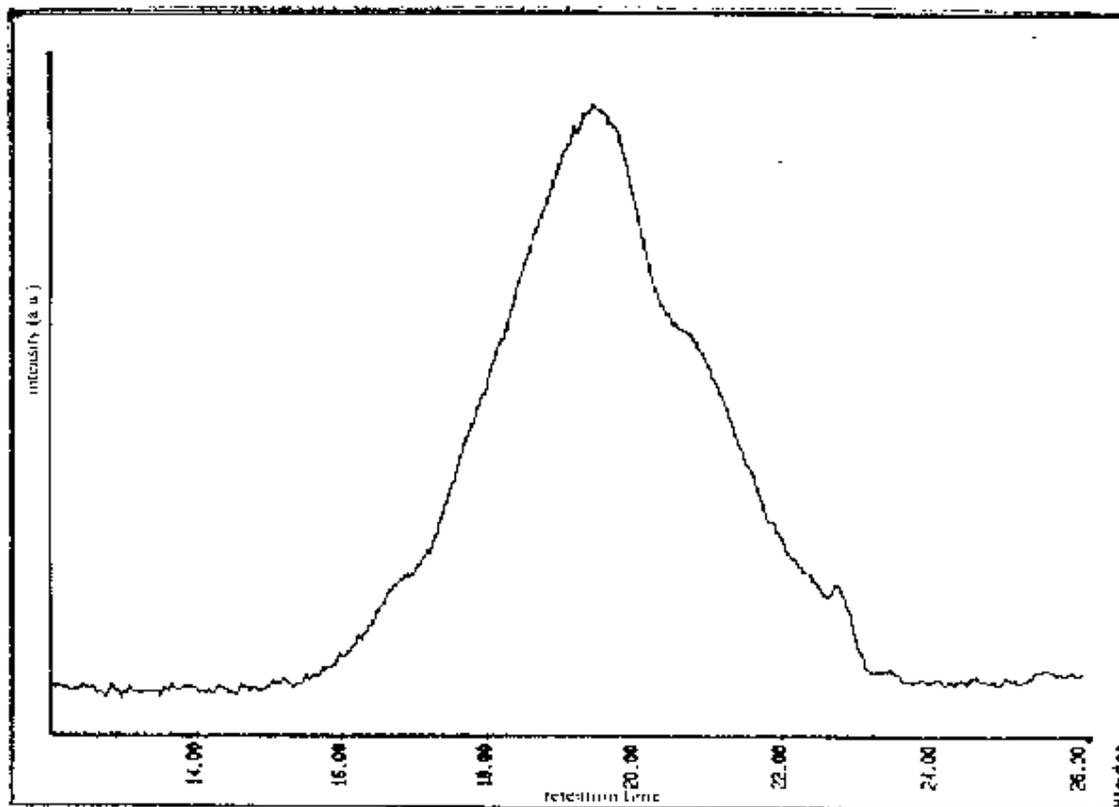


Fig. 8. Gel permeation chromatogram of PDPV-DF

Molecular weight determination was made on this polymer using GPC. The chromatogram obtained (Figure 8) shows a broad peak with partially resolved peaks on the trailing edge, possibly corresponding to telomeric units. The number average molecular weight and weight average molecular weights obtained were 13,800 and 45,800 respectively, with a polydispersity index of 3.3.

It was found that the polymer shows an orange fluorescence when illuminated with u.v. radiation and is soluble in common organic solvents including dichloromethane, chloroform, toluene and THF.

Thermogravimetric analysis shows that this polymer is remarkably thermally stable. It loses 2% of its weight at 400°C and even at 490°C the polymer shows only 5% weight lost. The polymer was shown to have a glass transition temperature of 222°C as measured by DSC.

Poly(1,3-phenylene diphenylvinylene)

Poly(1,3-phenylene diphenylvinylene), *m*-PPV-DP was recovered as a pale yellow solid which gave a faint yellow fluorescence when illuminated with u.v. radiation. The FTIR spectrum (Figure 9) shows strong peaks at 1442, 1491 and 1596 cm^{-1} . The first two peaks have been attributed to aromatic carbon-hydrogen bending modes and the later peak can be attributed to

aromatic carbon skeleton breathing mode. The peak corresponding to the aromatic hydrogen stretching mode can be seen at 3051 cm^{-1} .

The gel permeation chromatogram of the polymer is presented in Figure 10. Low molecular weight molecules are clearly present as partially resolved peaks on the trailing edge. The number average and weight average molecular weights obtained for this polymer are 7,500 and 45,800 respectively, with a polydispersity index of 6.1.

The polymer was found to be soluble in organic solvents such as chloroform, toluene and THF, thus allows the solution processing. As a result of equilibrium fractionation carried out on the pristine polymer, a series of fractions of various molecular weights was collected, varying from a \overline{M}_n of 27,300 down to a \overline{M}_n of 1,400 with polydispersity indices of the order of about 2 (Table 2). The degree of polymerisation obtained for the first fraction, which constitutes about 33% of the pristine polymer, was 107. This corresponding to a reaction conversion of 99% in this sample, again underlining the potential of the McMurry reaction as an approach to poly(arylene vinylene)s.

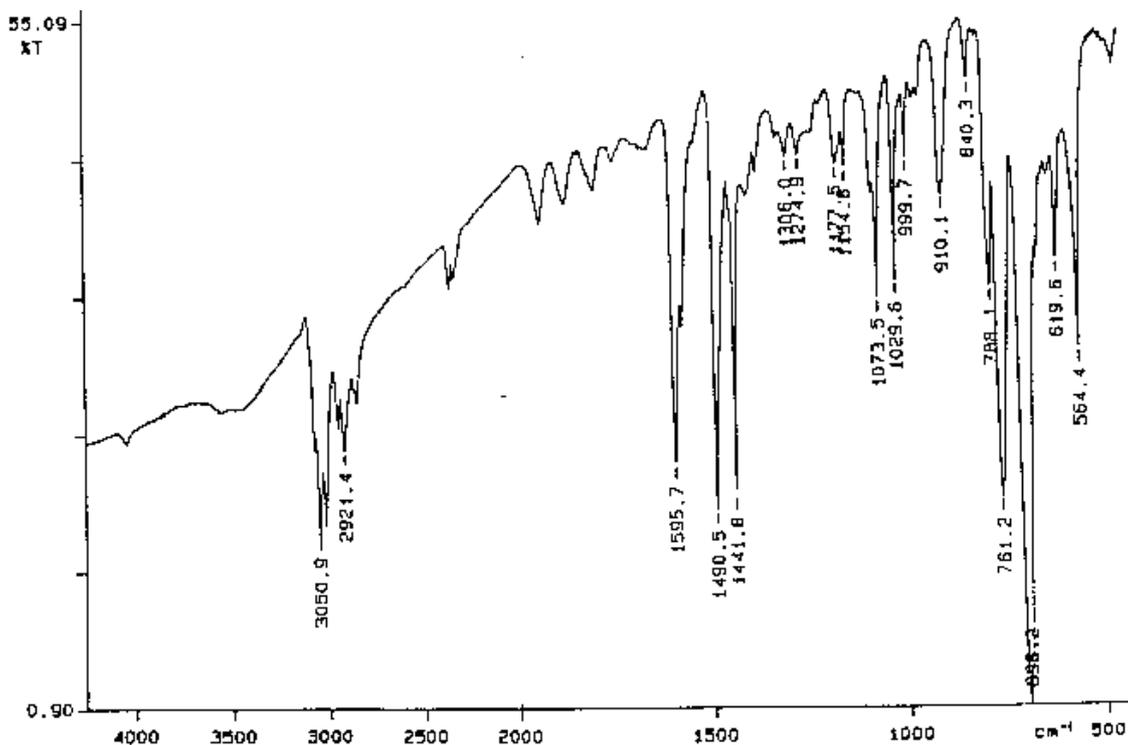


Fig. 9. FTIR spectrum of *m*-PPV-DP

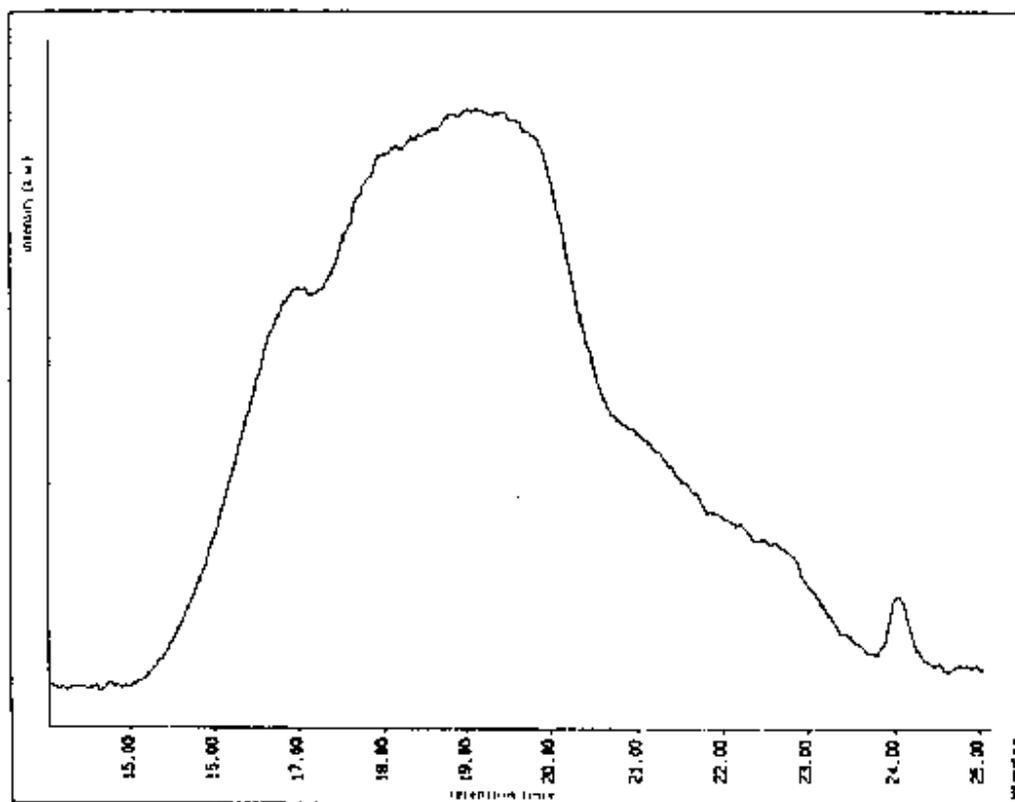


Fig. 10. Gel permeation chromatogram of *m*-PPV-DP

Fractions	$^1\overline{M}_n$	$^1\overline{M}_w$	PDI	^2DP
pristine	7,500	45,800	6.1	29
1	27,300	70,800	2.6	107
2	19,000	53,700	2.8	75
3	17,400	49,900	2.9	69
4	14,600	35,000	2.4	57
5	12,700	29,300	2.3	50
6	8,000	15,400	1.9	31
7	5,200	6,800	1.3	20
8	2,500	3,370	1.3	10
9	2,060	2,580	1.3	8
10	1,740	2,250	1.3	7
11	1,400	1,800	1.3	6

¹ values are based on polystyrene standard

² degree of polymerisation

Table 2. Results from the fractionation of *m*-PPV-DP

Thermogravimetric analysis shows that the pristine polymer decomposes very slowly when heated under nitrogen. It loses 2% of its weight at 215°C but only by 3% at 490°C. It was found that the glass transition temperature of the polymer was 188°C as measured by DSC.

Poly(1,3-phenylene dimesitylvinylene)

Poly(1,3-phenylene dimesitylvinylene), *m*-PPV-DM, was synthesised from the corresponding diketone, namely 1,3-dimesitylbenzene (Figure 1). A pale yellow polymer was recovered and found to emit faint yellow fluorescence when illuminated with u.v. radiation. However, the number average and weight

average molecular weights obtained were only 1,040 and 1,300 respectively. The degree of polymerisation achieved in this attempt is only 3 and this is possibly due to the bulky pendant groups that might have been inhibited further condensation reaction.

In the FTIR spectrum (Figure 11), there is a strong peak at 1610 cm^{-1} that can be ascribed to the aromatic carbon skeleton vibration mode, and both peaks at 1419 and 1481 cm^{-1} are attributed to the aromatic hydrogen vibration modes. The peak of methyl hydrogen stretching absorption can be seen at 2981 cm^{-1} .

It was found that the polymer decomposes at about 240°C and loses its weight rapidly when heated beyond 270°C.

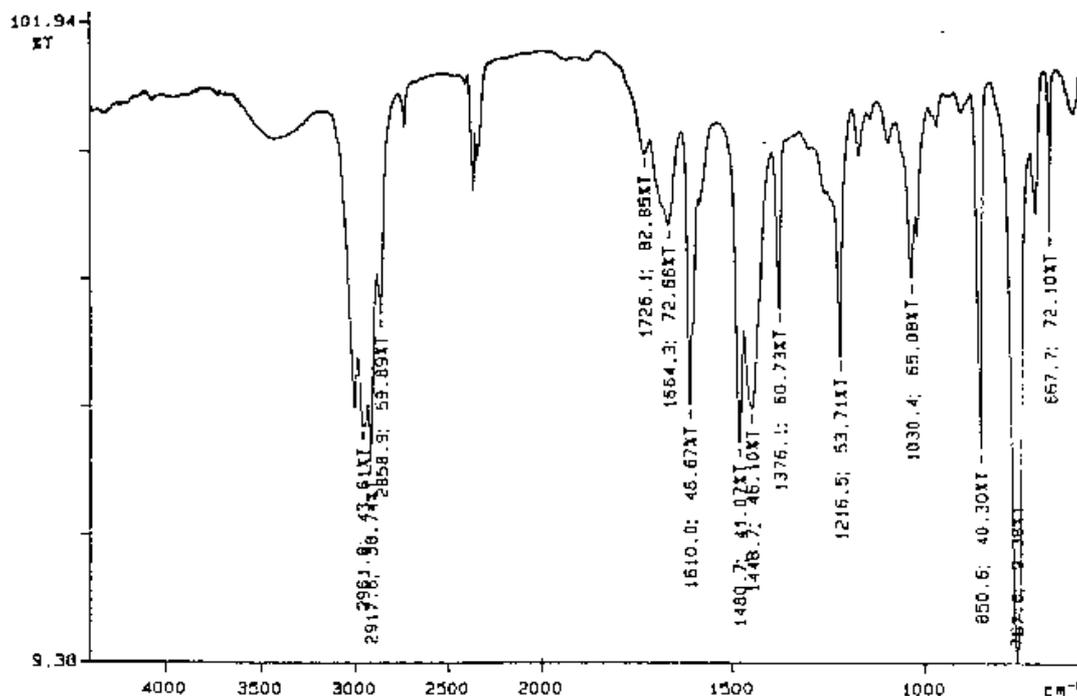


Fig. 11. FTIR spectrum of *m*-PPV-DM

Conclusion

It has been shown that a few poly(arylene vinylene)s, namely poly(4,4'-diphenylene diphenylvinylene), poly(4,4'-diphenylene-1,2-bis(pentafluorophenyl) vinylene), poly(1,3-phenylene diphenylvinylene) have been synthesised successfully via the McMurry reaction. However, only oligomers was produced in the case of poly(1,3-phenylene dimesitylvinylene) that might due to the bulkiness of its pendant groups. The fractionation procedure has been shown to allow high molecular weight samples with small polydispersity indices to be obtained from the pristine polymers. All polymers produced have been shown to have good solubility in common organic solvents as well as good thermal stability, especially poly(4,4'-diphenylene diphenylvinylene) and poly(4,4'-diphenylene-1,2-bis(pentafluorophenyl) vinylene).

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