Phase-transfer catalysed synthesis of disubstituted poly(phenylene vinylene)

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An attempt to synthesize a series of phenyl ring disubstituted poly(*o*-, *m*- and *p*-phenylene vinylene) is reported. In this 'one-pot' reaction, a phase-transfer catalyst was used to promote the extraction of strong base deprotonated bischloromethyl aromatic anions from the aqueous to the organic phase to sustain a nucleophilic substitution reaction with the remaining bischloromethyl monomers. The polymers obtained were characterized for their chemical compositions and physical properties by elemental, i.r. and u.v. spectroscopic, and thermal analyses. The *o*-substituted polymers were found to have low melting temperatures, good solubilities and high molecular weights, but low yields. The *m*-substituted monomers, however, produced only non-conjugated poly-*m*-xylylenes. The *p*-substituted polymers offered the best combination of yield and physical properties. Films cast from soluble poly(2,5-dibutoxy-*p*-phenylene vinylene) have electrical volume resistivity in the range 300–500 ohm cm when doped with concentrated sulfuric acid.

(Keywords: phase-transfer catalyst; conducting polymer; phenyl ring disubstituted poly(*o*- and *p*-phenylene vinylene); poly-*m*-xylylene)

INTRODUCTION

Inherently conducting polymers typically have a conjugated backbone structure. Since the first report in the early seventies[1] of conducting polymers which can be switched from a semiconducting to a conducting state upon doping, their applications are still very limited because these rigid polymers are difficult to process and are chemically unstable at elevated temperatures[2–4]. Techniques employed to enhance their processability have been reported[2,3]. These include the electrochemical method[2,3,5], blending or grafting the conducting polymer with another processable polymer[6,7], the precursor method[8–10], the use of a special dopant-carrier like AsF_3[2,3], etc. In the electrochemical synthesis method, the conducting polymer with the desired geometry and properties is fabricated directly on an electrode or substrate in the doped state. In the precursor method, a high-molecular-weight yet highly processable non-conducting polymer precursor is first prepared. The precursor then undergoes either a thermal or chemical elimination process to generate the conjugated product. A reduction in the conjugation length may result if the elimination process does not go to completion. The most studied conducting polymer precursors are those producing polyacetylene[8] or poly(phenylene vinylene) (PPV)[9,10] upon elimination.

PPV is a conjugated polymer composed of alternating repeating units of polyacetylene and poly(phenylene). Upon doping, PPV exhibits reasonably good electrical conductivity and thermal stability[9,10]. Processable poly(*p*-phenylene vinylene) (*p*-PPV) has been synthesized mostly through the precursor route[9–12], although equivalent structures and their copolymers have been prepared directly via the Wittig reaction[13]. Both synthetic methods employed a multistep reaction process involving stringent reaction conditions as well as air-sensitive and relatively expensive chemicals. The polymer from the Wittig method has a molecular weight limited by its solubility in the reaction medium. Various techniques have since been developed to prepare the same phenylene vinylene-type polymer using simpler chemistry. Examples are the catalytic McMurry reaction process[14], a strong-base-promoted reaction using potassium *t*-butoxide[15,16], the employment of a phase-transfer catalyst (PTC)[17] and dehydrochlorination[18]. The solubility as well as the molecular weight of the final product was increased in some of these studies by attaching bulky side groups to the main-chain structure. Recent reports[19,20] on the photo- and electroluminescent properties of PPV have demonstrated that the conjugated polymer has promising practical optoelectronic applications such as light emission diodes by simply modifying its structure. In this report, the effects of the phenyl ring substituent on the preparation as well as the physical properties of a series of poly(*o*-, *m*- and *p*-phenylene vinylene) were studied. A PTC was employed in this one-step polymerization process in which the conjugated polymers were generated directly from their respective starting monomers without going through the intermediate precursor step.

EXPERIMENTAL

Monomer preparation

All chemicals and solvents used were reagent grade unless specified otherwise. The monomers used to

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synthesize the conjugated polymers were the following:

α,α′-dichloro-*o*-xylene (*o*-DCX);
α,α′-dichloro-*m*-xylene (*m*-DCX);
α,α′-dichloro-*p*-xylene (*p*-DCX);
1,2-bis(chloromethyl)-4,5-dimethylbenzene (*o*-MeDCX);
1,3-bis(chloromethyl)-4,6-dimethylbenzene (*m*-MeDCX);
1,4-bis(chloromethyl)-2,5-dimethylbenzene (*p*-MeDCX);
1,4-bis(chloromethyl)-2,3,5,6-tetramethylbenzene (*p,p*′-MeDCX);
1,2-bis(chloromethyl)-4,5-dimethoxybenzene (*o*-MeODCX);
1,3-bis(chloromethyl)-4,6-dimethoxybenzene (*m*-MeODCX);
1,4-bis(chloromethyl)-2,5-dimethoxybenzene (*p*-MeODCX);
1,2-bis(chloromethyl)-4,5-dibutoxybenzene (*o*-BuODCX);
1,3-bis(chloromethyl)-4,6-dibutoxybenzene (*m*-BuODCX);
1,4-bis(chloromethyl)-2,5-dibutoxybenzene (*p*-BuODCX).

o-DCX, *m*-DCX, *p*-DCX, *o*-MeDCX and *p,p*′-MeDCX were reagent-grade chemicals obtained from Aldrich (USA) or Fluka (Switzerland) and were used without further purification. *m*-MeDCX and *p*-MeDCX were prepared from chloromethylation of *m*-xylene and *p*-xylene using paraformaldehyde and 85% phosphoric acid[21]. Syntheses of *o*-MeODCX, *m*-MeODCX and *p*-MeODCX were attempted by chloromethylation of 1,2-dimethoxybenzene, 1,3-dimethoxybenzene and hydroquinone dimethyl ether, respectively, using formalin and hydrogen chloride[22]. *o*-BuODCX, *m*-BuODCX and *p*-BuODCX were obtained by first converting veratrol, resorcinol and hydroquinone to their respective aromatic butyl ethers by reaction with *n*-butyl bromide[22]. The aromatic butyl ethers were then chloromethylated using the procedures described in ref. 22.

The monomers synthesized were recrystallized from petroleum ether or chloroform. Their purities were confirmed by ^{1}H n.m.r. and capillary melting point measurements. All the monomers had reasonably good yields with the exception of *m*-MeODCX and *m*-BuODCX. These two monomers were found to be highly reactive and infusible polymeric products were obtained instead of the bischloromethyl compounds in the chloromethylation step[23]. A small quantity of the unstable *m*-MeODCX monomer, as characterized by ^{1}H n.m.r., was obtained after lowering the chloromethylation temperature using an ice–water bath. The monomers, however, were unstable even in storage at room temperature. *m*-MeODCX converted to a purple-coloured insoluble solid and *m*-BuODCX was obtained as a low-melting-temperature dark green product that was soluble in petroleum ether. Instead of going through the polymerization procedures, solid residues from the chloromethylation step of *m*-MeODCX and *m*-BuODCX were used directly for comparison with the other disubstituted PPVs.

Polymerization

A typical phase-transfer catalysed synthetic procedure is as follows. Some 0.5 to 1 mmol of the monomer and 0.5 mmol of tetrabutylammonium bromide (TBAB) were added, respectively, into a vigorously stirred mixture of 10 ml 55–60 wt% sodium hydroxide aqueous solution (with 2 mmol NaCl added) and 20 ml dimethylsulfoxide (DMSO) in a hot water bath and allowed to react for 24 h. The products that had not already precipitated out in the reaction medium were collected by precipitation using methanol. The polymers were filtered and washed with hot water several times until the filtrate was pH neutral. They were then dried in a vacuum oven before further analysis.

Characterization

Elemental analyses were performed at the Shanghai Institute of Organic Chemistry of the Chinese Academy of Sciences, Shanghai PRC. Thermal analyses were effected on a differential scanning calorimeter (Shimadzu DSC50 with LTC-50 cooling unit) at a heating rate of 20°C min^{-1} from -80 to 200 or 250°C and on a thermogravimetric analyser (Shimadzu TGA-40) at a scan rate of 5°C min^{-1} from room temperature to 550°C all under nitrogen purge. U.v. (Shimadzu UV-240, with optional interface OPI-1) and i.r. spectra (Hitachi Model 270-30 and DigiLab FTS45 FTIR) were obtained for samples in the format of either KBr pellet, solution or thin film (solvent cast). The purity of the intermediates and monomers prepared was monitored using a melting-point apparatus (Electrothermal) and by ^{1}H n.m.r. (60 MHz, JEOL NM-PMX 60SI).

RESULTS AND DISCUSSION

Polymer structure and reaction mechanism

Figure 1 shows the chemical structures of the disubstituted polymers and their respective starting monomers. Only the *o*- and *p*-disubstituted monomers yielded conjugated polymer structures similar to PPV. The presence of conjugated double-bond structures was evidenced by the colours of the products which are given in *Table 1*. Their colours ranged from bright yellow to dark brown and were related to the degree of conjugation as well as the electron-donating effects of the substituted side groups. Comparing the i.r. spectra of the monomers and their respective polymers, the C–Cl absorption peak at 660 to 700 nm^{-1} diminished or disappeared in the i.r.

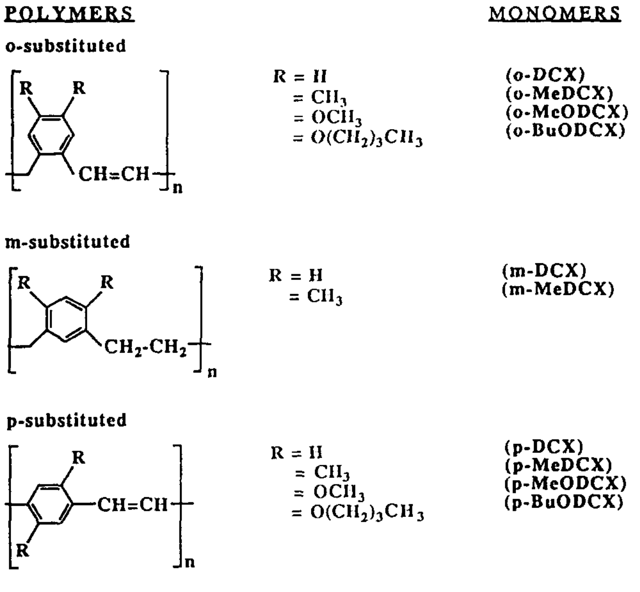

Figure 1 Repeating unit structure for disubstituted poly(phenylene vinylene), poly(xylylene) and their starting monomers

spectra for the final polymers. The other i.r. absorptivities that were pertinent to the given polymer structures were at 955 to 990 nm^{-1} due to the *trans* –CH=CH– structure and 750 or 850 nm^{-1} due to the *o*- and *p*-disubstituted benzene groups respectively[11,17].

A suggested phase-transfer catalysed polymerization mechanism using the *p*-substituted monomer as an example is presented in *Figure 2*. The bischloromethyl aromatic compounds were deprotonated in the aqueous phase by the strong base. After coupling with the cations from the dissociated phase-transfer catalyst (Q^+, y^-), the deprotonated anions were extracted into the organic phase. The efficiency of a PTC is described by an extraction constant. The extraction constant is related to the structure of the PTC cation and anion as well as the solution pH and solvent dielectric value[24]. Optimization of the reaction conditions has been reported[17] and a detailed mechanism for the PTC transport process in a similar reaction has been discussed[25]. The extracted anions then underwent a nucleophilic substitution reaction with other benzyl chloride moieties to produce poly(α-chloro-*p*-xylene). Elimination of the α-chloride was effected by the strong base resulting in the final conjugated structure. The exhausted PTC cations were returned to the aqueous phase to continue the extraction process. The stepwise propagation reaction continued for as long as the anions could be extracted and the propagating polymeric species remained soluble in the reaction medium. Results from elemental analyses and i.r. studies indicated a low chlorine content in the final *p*- and *o*-PPV. Elimination of the α-chlorides was, therefore, expected to occur as soon as the substitution reaction had been completed, so that a majority of the unreacted chlorine atoms would be at the chain ends. The formation of conjugated products at an early stage of the reaction process was evidenced by a colour change as soon as the monomer and PTC were added into the strong base solution. In the strong base medium employed for this reaction, hydrolysis of the alkyl halide was also possible. An alkoxide anion resulting from the hydroxymethyl group would produce an ether linkage instead of the desired conjugated product. No evidence of ether formation was observed from the i.r. spectrum of products starting from monomers containing no alkoxy-substituted side groups. Any abundant ether linkage formation would also result in a non-conjugated polymer.

Table 1 Physical and chemical properties of substituted poly(phenylene vinylene)

		Elemental analysis			
Monomer	Product colour	Cl[b]	C[b]	H[b]	$\bar{X}n$[c]
o-DCX	brown	1.10	82.60	6.00	54
o-MeDCX	light brown	0.36	70.93	6.56	115
o-MeODCX	brownish–yellow	0.56	54.61	4.52	56
o-BuODCX	brown	0.21	68.20	7.53	121
m-DCX	white	0.32	75.32	5.87	173
m-MeDCX	white	0.39	78.22	7.58	119
m-MeODCX[a]	(purple)	5.97	65.60	6.11	(6)
m-BuODCX[a]	(dark green)	[d]	[d]	[d]	[d]
p,p'-MeDCX	white	0.73	78.07	9.30	52
p-DCX	bright yellow	1.65	83.25	6.16	36
p-MeDCX	yellow	2.03	79.64	7.61	23
p-MeODCX	bright red	0.98	66.40	6.09	39
p-BuODCX	bright red	1.54	68.34	8.11	16

[a] The products indicated are from the chloromethylation step, not from the phase-transfer catalysed polymerization process (see text for explanation)
[b] Weight percentage for the elements as determined from elemental analysis
[c] Number-average number of repeating unit calculated from C element
[d] Not determined

All monomers with *m*-substituted groups (*m*-DCX, *m*-MeDCX and *p,p'*-MeDCX) produced polymers with no conjugated structure at all. This was manifested by their overall white colour appearance as well as from i.r. studies. The low chlorine content determined from elemental analysis and the i.r. spectra also suggested that the polymers have the structure of poly(*m*-xylylene) as shown in *Figure 1* instead of incompletely eliminated poly(α-chloro-*m*-xylylene) as suggested in the past[16]. This was because the bischloromethyl groups in the *m*-substituted monomers were highly activated by being at the *para* and *ortho* positions of an electron-releasing pendant group. A highly reactive intermediate similar to the resonance structure of the carbanion shown in *Figure 2* was thought to produce the final polymer structure, although the exact mechanism is unknown. The only conjugated products obtained for the *m*-substituted monomers were oligomers from the chloromethylation step for *m*-MeODCX and *m*-BuODCX. None of the dialkoxy-substituted monomers was a stable compound as reported earlier[23]. The strong electron-releasing alkoxy substituent allowed deprotonation (or dechlorination) of the bischloromethyl

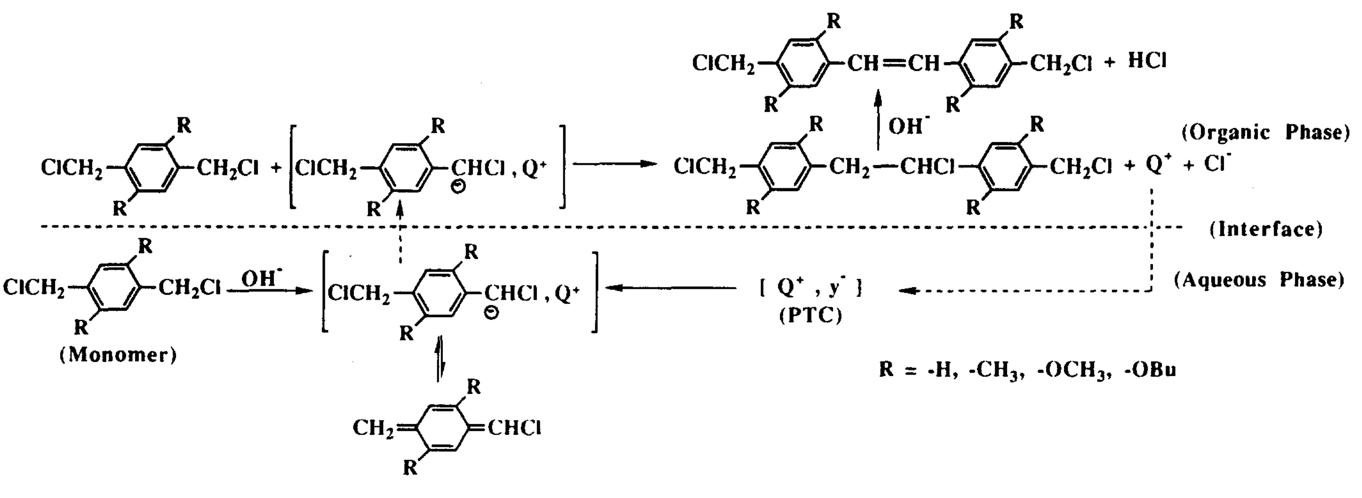

Figure 2 A PTC-aided reaction mechanism for the *p*- and *o*-substituted monomers

groups to a highly reactive methylene species even without a strong base or PTC. The oligomers resulting from the chloromethylation step were believed to have the chemical structure of poly(2,4-dialkoxy-*m*-phenylene vinylene) with a short conjugation length, as suggested by their visible-range absorptivities. Their i.r. spectra were comparable with the other coloured products, with the exception of having a higher chlorine content.

Table 1 also presents the results from the elemental analyses of the polymeric products. Residues and impurities such as the sodium salts may have caused the total percentage of the elements to be lower than 100%[17]. The low Cl content, however, was consistent with the proposed mechanism that the chloromethyl groups present were mostly at the polymers' chain-ends. By normalizing the total percentage of C, H, Cl and O elements to 100% and assuming the chain-end structure, even the molecular weights of some of the infusible polymers can be estimated. Using the ratio of the Cl and C elements, the number-average number of repeating units ($\bar{X}n$) for each of the polymers was calculated and tabulated in *Table 1*. The highest molecular weight was obtained for polymers which remained dissolved in the reaction medium during polymerization. Those were polymers derived mostly from the *o*- and *m*-substituted monomers. The lower $\bar{X}n$ values for the *p*-substituted products were expected because the rigid polymers precipitated from the reacting solution as soon as they attained a certain high molecular weight. The purple-coloured residues from the chloromethylation step of *m*-MeODCX have a high Cl content indicating it was a low-molecular-weight oligomer with the possibility of additional α-chlorine moiety in the backbone structure. Elemental analysis was not performed on the dark green residues from the chloromethylation step of *m*-BuODCX because the low melting amorphous product cannot be readily purified.

Under the prescribed and optimized reaction conditions, all of the polymers obtained have molecular weights higher than those reported earlier[17]. The yields for all of the *o*-substituted polymers were low which was probably due to steric hindrance and possible side reactions. The *m*-substituted (including the tetramethyl-substituted) monomers all gave non-conjugated products with low Cl content indicating that a different reaction route may be responsible for the reactions taking place. The formation of either conjugated phenylene vinylene, α-chloroxylylene or xylylene structures was thought to be related to the reaction conditions (such as pH) as well as the position and electron donating/withdrawing effects of the phenyl ring substituted groups. Both the *m*- and *p*-substituted monomers have reasonably good polymer yields.

Thermal analysis

In *Table 2*, results from thermal stability and transition temperature measurements for all the polymers using thermogravimetric and differential scanning calorimetric analyses are listed. The thermal stabilities of the polymers under a nitrogen atmosphere were compared using the onset temperature for degradation and the percentage weight loss associated with each degradation step. Both the conjugated *o*- and *p*-substituted polymers exhibited mostly a two-step degradation mechanism. The weight loss at the lower degradation temperature increased with the size of the substituted group for the *o*-PPVs but decreased for the *p*-PPVs. The thermal stability of the *p*-PPVs, as shown by the weight loss, was in general better than that of the *o*-PPVs with the same substituted group. Also for the *o*- and *p*-substituted conjugated polymers, their stability decreased with an increase in the electron-donating effect of the pendant group. The non-conjugated polymers were all shown to have a single

Table 2 Thermal analyses[a] of substituted poly(phenylene vinylene)

		Differential scanning calorimetry (d.s.c.)				
				Melting temperature, T_m		
PPV from monomer	Thermogravimetric analysis (t.g.a.) Onset temp.[b] in °C (% wt. loss)	T_g (°C)	ΔCp ($J g^{-1} °C^{-1}$)	Onset temp. (°C)	Peak temp. (°C)	ΔH_f ($J g^{-1}$)
o-DCX	197 (18), 338 (50)	–		46	80	27.9
o-MeDCX	193 (20), 331 (43)	48	0.29	140	149	1.6
o-MeODCX	177 (5), 285 (49)	–		123	133	27.8
o-BuODCX	188 (77), 319 (10)	–		21	37	59.3
m-DCX	336 (95)	–		51	64.5	45.8
m-MeDCX	330 (88)	–		160	193, 214	67.1
m-MeODCX[c]	142 (5), 347 (29)	[d]	[d]	[d]	[d]	[d]
m-BuODCX	[d]	[d]	[d]	[d]	[d]	[d]
p,p'-MeDCX	341 (94)	–		213	226	36.0
p-DCX	306 (41), 498 (14+)[e]	8	0.14	96	125	23.1
p-MeDCX	280 (54), 416 (25)	26	0.21	136	178	22.0
p-MeODCX	195 (6), 287 (17), 400 (32)	45	0.1	120	177	14.4
p-BuODCX	207 (9), 373 (68)	−8	0.23	127	166	4.2

[a] The heating rate for t.g.a. and d.s.c. is 5 and 20°C min^{-1} respectively, under nitrogen purge

[b] The onset temperature is defined as the intercept of the base-line and tangent of the steepest slope for a degradation step change

[c] Data are for the purple-coloured solid residue from the chloromethylation synthesis step

[d] Not determined

[e] The degradation step is incomplete at the end of the t.g.a. run at 550°C

degradation step at approximately the same degradation temperature range and the weight loss associated with it was almost 100% complete.

All the non-conjugated polymers have well-defined melting endotherms and the melting temperature increased with the size of the phenyl ring substituent (see *Table 2*). The melting range for the conjugated polymers, on the other hand, was broad with the exception of some of the higher molecular weight products. Their crystallinity, as seen from the heat of fusion (ΔH_f), decreased with the size of the pendant group for the *p*-PPVs but increased for the *o*-PPVs. A second-order transition relating to the glass transition temperature (T_g) was detected for all *p*-PPVs. This transition temperature indicated flexibility of the polymer main chain but was also dependent on the molecular weight of the polymer. The highly amorphous *p*-PPV from *p*-BuODCX has the lowest T_g (midpoint) as expected and was consistent with its good solubility in organic solvents. Since the melting temperatures for all of the polymers were near (for the alkoxy-substituted) or below their onset degradation temperatures, the conjugated polymers can be melt-processed only under a nitrogen atmosphere.

Solubility

Another important parameter in determining the processability of a polymer is its solubility and resistance to chemicals and solvents. The *o*-substituted polymers were found to be readily soluble in chlorinated solvents such as methylene chloride and chloroform. For the non-conjugated polymers, only the polymer from *m*-DCX was found to be soluble in methylene chloride and chloroform. Its intrinsic viscosity determined at 25°C in chloroform using an Ostwald viscometer was found to be 0.121 and was consistent with the molecular weight estimated from the elemental analysis. For the *p*-substituted polymers, among a series of chlorinated, aprotic and aromatic solvents tested, only 1,1,2,2-tetrachloroethane and nitrobenzene at their boiling temperatures were found to slightly dissolve the conjugated polymer from *p*-MeODCX. The *p*-PPVs from *p*-DCX and *p*-MeDCX were insoluble in all the solvents tested.

Poly(2,5-dibutoxy-*p*-phenylene vinylene) from *p*-BuODCX was found to be soluble with an increasing order of solubility in the following solvents: chloroform, 1,1,1-trichloroethane, *m*-cresol, bromobenzene, toluene and nitrobenzene, at or near their boiling temperatures. Thin polymer film can be readily cast using toluene and nitrobenzene. The polymer from *p*-BuODCX was also found to be slightly soluble in a strong acid such as concentrated sulfuric acid and MSA. A blackish solution resulted indicating that the polymer had also been oxidized or doped. Hot concentrated nitric acid was found to decompose the reddish polymer into colourless low-molecular-weight substances.

Electrical and other properties

Polymer film cast from nitrobenzene was electrically conducting after being submerged in concentrated sulfuric acid. Using a two-point probe method and an ohmmeter, the doped polymer film was found to have a volume resistivity in the range of 300 to 500 ohm cm in air. The high resistivity compared to that of the same polymer prepared via the precursor method[12] was due to the stability of the dopant in air[26]. No evidence of any sulfonation reaction was observed from i.r. studies and the doped black polymer film can be readily returned to the undoped reddish colour by washing with water. The conductivities of the other insoluble *p*-substituted polymers were determined after being grafted on an insulating substrate and are presented in a separate communication[26]. The red polymer film has a major absorption maximum at 450 nm and a minor peak at 338 nm in the u.v.–visible range. The polymer fluoresced strongly using an Excimer laser source at 308 nm. In *Figure 3*, the i.r. spectra of a poly(2,5-dibutoxy-*p*-phenylene vinylene) film cast from nitrobenzene (before doping) and after being submerged in concentrated sulfuric acid (doped) are shown. The doped polymer was noted for its absorption maximum at around 1200 cm^{-1} due to HSO_3^- and a decrease in the absorption maximum at 970 nm due to the alkene moiety.

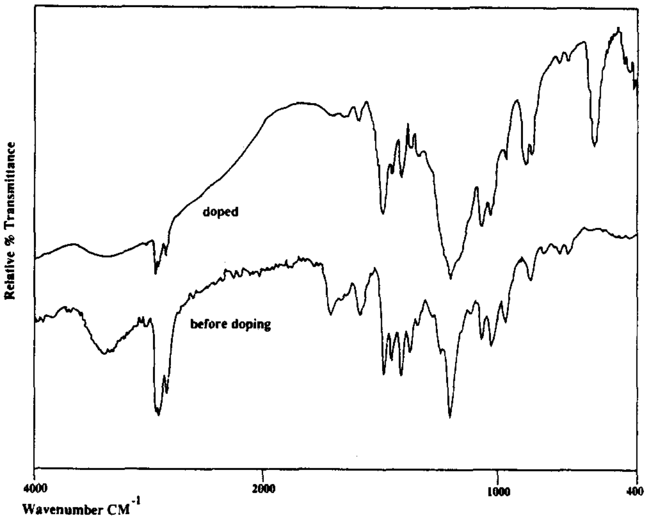

Figure 3 Infra-red spectrum of poly(2,5-dibutoxy-*p*-phenylene vinylene) before doping (lower curve) and after doping (upper curve) with concentrated sulfuric acid

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REFERENCES

1 Chiang, C. K., Druy, M. A., Gau, S. C., Heeger, A. J., Louis, E. J., MacDiarmid, A. G., Park, Y. W. and Shirakawa, H. *J. Am. Chem. Soc.* 1978, **100**, 1013
2 Skotheim, T. A. (Ed) 'Handbook of Conducting Polymers', Vols. 1 and 2, Marcel Dekker, New York, 1986
3 Kroschwitz, J. I. (Ed) 'Electrical and Electronic Properties of Polymers: A State-of-the-art Compendium', Wiley, New York, 1988
4 Wegner, G. *Angew. Chem., Int. Ed. Engl.* 1981, **20**, 261
5 Girault, N., Aldebert, P., Pineri, M. and Audebert, P. *Synth. Metals* 1990, **38**, 277
6 Schlenoff, J. B., Machado, J. M., Glatkowsky, P. J. and Karasz, F. E. *J. Polym. Sci., Polym. Phys. Ed.* 1988, **26**, 2247
7 Stowell, J. A., Amass, A. J., Beevers, M. S. and Farren, T. R. *Polymer* 1989, **30**, 195
8 Edwards, J. H., Feast, W. J. and Bott, D. C. *Polymer* 1984, **25**, 395
9 Gagnon, D. R., Capostran, J. D., Karasz, F. E., Lenz, R. W. and Antoun, S. *Polymer* 1987, **28**, 567

10 Lenz, R. W., Han, C.-C., Stengel-Smith, J. and Karasz, F. E. *J. Polym. Sci., Polym. Chem. Ed.* 1988, **26**, 3241

11 Murase, I., Ohnishi, T., Noguchi, T. and Hirooka, M. *Polym. Commun.* 1984, **25**, 327

12 Han, C.-C. and Elsenbaumer, R. L. *Mol. Cryst. Liq. Cryst.* 1990, **189**, 183

13 Huang, W. S., Jen, K. Y., Angelopoulos, M., MacDiarmid, A. G. and Cava, M. P. *Mol. Cryst. Liq. Cryst.* 1990, **189**, 237

14 Cataldo, F. *Polym. Commun.* 1991, **32**, 354

15 Swatos, W. J. and Gordon III, B. *Polym. Prepr.* 1990, **31** (1), 505

16 Gilch, H. G. and Wheelwright, W. L. *J. Polym. Sci. Part A-1* 1966, **4**, 1337

17 Yamazaki, N. and Imai, Y. *Polym. J.* 1983, **15** (12), 905

18 Hsieh, B. R. and Van Laeken, A. *Polym. Prepr.* 1992, **33** (2), 164

19 Burroughes, J. H., Bradley, D. D. C., Brown, A. R. *et al. Nature* 1990, **347**, 539

20 Burn, P. L., Holmes, A. B., Kraft, A. *et al. Nature* 1992, **356**, 47

21 Vansheidt, A. A., Mel'nikova, E. P. and Kukjareva, L. V. *Zh. Prikl. Khim.* 1960, **33**, 2151

22 Vogel, A. I. 'Practical Organic Chemistry', 3rd edn, Longman, London, 1956, pp. 533, 671

23 Wood, J. H., Perry, M. A. and Tung, C. C. *J. Am. Chem. Soc.* 1950, **72**, 2989

24 Starks, C. M. (Ed) 'Phase-Transfer Catalysis', ACS Symp. Ser. No. 326, Washington DC, 1985

25 Leung, L. M., Chan, W. H. and Leung, S. K. *J. Polym. Sci., Polym. Chem. Ed.* 1993, **31**, 1799

26 Leung, L. M. and Yam, C. M. *Polym. Bull.* in press