Synthesis of electrically conducting copolymers with short alternating conjugated and non-conjugated blocks

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Six copolymers with short alternating conjugated and non-conjugated blocks were synthesized using the Wittig reaction. The conjugated block consists of two and one-half units of *p*-phenylene vinylene with methoxy groups substituted at the 3 and 5 positions of the flanking phenyl rings. These rigid blocks are linked to flexible linear alkyl chain spacers by ester groups. The polymers, characterized by ^{13}C n.m.r., *FT*i.r., elemental analysis, g.p.c. and d.s.c. are soluble and fusible. Free-standing films were cast from chloroform solutions and showed electrical conductivities ranging from 10^{-3} to 10^{-2} S cm^{-1} upon doping by iodine vapour at room temperature.

(Keywords: poly(*p*-phenylene vinylene); block copolymer; synthesis)

INTRODUCTION

Most electrically conducting polymers possess an extended conjugated skeleton, which is believed to be not only a basic condition for electrical conductivity but is also a major cause of the characteristic intractability and poor mechanical properties of these macromolecules. Over the years progress has been made in enhancing the processibility of electrically conducting polymers by synthesizing these conjugated polymers via precursor polymers or by attaching solubilizing substituents[1–5]. Further, Thakur[6] challenged the prerequisite of long conjugation, by doping natural rubber with oxidizing agents and demonstrating that a polymer with a non-conjugated, predominantly σ-bonded backbone can apparently become conductive upon doping with iodine.

The dependence of electrical conductivity on the conjugation length in a polymer is an important topic and has been approached in different ways by various authors. For example, Yang and Geise[7] studied the blending, iodine doping and conductivity of poly(*p*-phenylene vinylene) (PPV) model compounds containing two and one-half PV repeat units and differing substituents on the phenyl rings. They demonstrated that the model compounds blended with polystyrene or poly(methyl methacrylate) become electrically conducting when doped with iodine. These blends showed a stable conductivity in the range of 10^{-2} to 10^{-1} S cm^{-1}. Spangler and Hall[8] investigated oxidative doping of PV oligomers with $SbCl_5$ in solution and indicated that polaron and bipolaron-like species were formed in the process. Gregorius and Karasz[9,10] studied the iodine doping of poly(thienylene vinylene) (PTV)–PPV copolymers; they showed that PTV segments are the dopable components in the copolymers and estimated that they must have a minimum length of four or more repeat units in order to obtain significant conductivity upon doping. Earlier, Hörhold and Bergmann[11] investigated the u.v. absorption of PV oligomers with chain lengths ranging from the dimer to a heptamer and suggested that the conjugation in high-molecular-weight PPV does not extend over the entire length of the molecule. Kossmehl[12] tried to rationalize the correlation between the molecular structure of small conjugated oligomers and their conductivities, a subject that has recently been studied in more detail by others[13].

Molecules containing short conjugated chains are considered to be dopable and consequently conducting. However, blends of doped small molecules with conventional thermoplastics are generally immiscible and phase separation takes place. Furthermore, it is unlikely that copolymers such as PTV–PPV, which contain only rigid components, will lead to the major improvements in processibility, mechanical properties and stability of the doped species. It is conceivable, however, that linking conjugated rigid molecular blocks with non-conjugated flexible molecular chains will provide improved systems. Our approach has been to link short conjugated rigid segments having a substituted oligomeric PV structure with non-conjugated flexible segments having a hydrocarbon structure of a specific length in a linear multiblock architecture. The rigid components are

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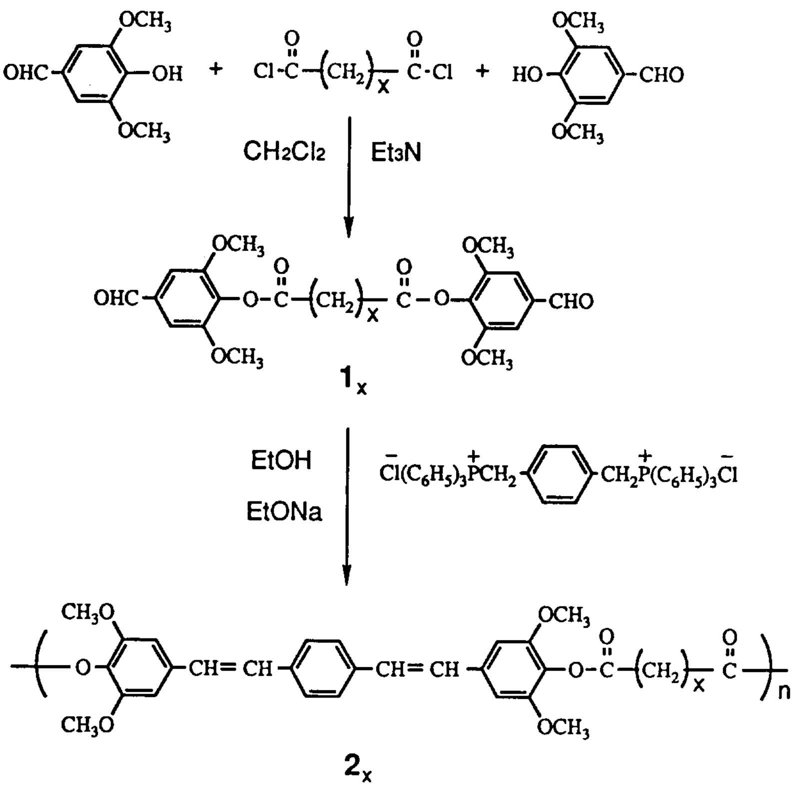

1_x x=2, 3, 4, 5, 6, 7, 8

2_x x=3, 4, 5, 6, 7, 8

Figure 1 Synthetic route yielding dialdehydes (1_2, 1_3, 1_4, 1_5, 1_6, 1_7 and 1_8) and block copolymers (2_3, 2_4, 2_5, 2_6, 2_7 and 2_8)

dopable because of their conjugated and (usually) electron-donating substituents, whereas the flexible components provide the copolymer with increased solubility, fusibility, film-forming properties, and some mechanical strength and a protective coating for the doped segments. The covalent bonds between the rigid and the flexible blocks, and their short length, inhibit large-scale phase separation during the film formation and doping process.

In this contribution, copolymers based on these concepts were synthesized using the Wittig reaction between a bisphosphonium salt and a dialdehyde, as depicted in *Figure 1*. As expected, the polymers are soluble in certain organic solvents, for example, chloroform and tetrahydrofuran (THF). Free-standing films were cast from solution and doped with iodine vapour at room temperature to give materials with electrical conductivities ranging from 10^{-3} to 10^{-2} S cm^{-1}.

EXPERIMENTAL

Synthesis of dialdehydes and polymers

Bis(4-formyl-2,6-dimethoxyphenyl)butanedioate, compound 1_2. To a stirred solution of 3.64 g (0.02 mol) 4-hydroxy-3,5-dimethoxybenzaldehyde in 100 ml of methylene chloride were added, dropwise, a solution of 1.55 g (0.01 mol) butanedioic dichloride in 10 ml of methylene chloride and a solution of 1.74 g (0.022 mol) pyridine in 5 ml of methylene chloride at room temperature. The mixture was stirred overnight, and the solvent was removed by rotary evaporation. The solid was washed thoroughly with distilled water followed by ether, recrystallized from chloroform/hexane (1:1 v/v), and dried in vacuum to give 1.22 g (27.3%) greenish yellow crystals; m.p. 194–195°C.

Table 1 Yields and melting points of the monomers

			Elemental analysis			
			C		H	
Monomer, 1_x	Yield (%)	Melting point (°C)	calc.	found	calc.	found
1_2	27.3	195	59.2	58.9	4.97	4.99
1_3	81.2	145	60.0	59.7	5.25	5.35
1_4	80.1	185	60.8	60.3	5.52	5.70
1_5	73.7	129	61.5	61.2	5.78	5.90
1_6	39.8	136	62.1	62.0	6.02	6.11
1_7	35.8	124	62.8	62.5	6.24	6.30
1_8	92.8	114	63.4	63.2	6.46	6.55

The other dialdehyde monomers with ester bonds (compounds 1_3, 1_4, 1_5, 1_6, 1_7, 1_8) were synthesized in the same way from corresponding dicarboxylic acid chlorides. Yields, melting points and elemental analyses are listed in *Table 1*.

Poly[oxy-pentanedioyloxy-(2,6-dimethoxy-1,4-phenylene)(1,2-ethenylene)(1,4-phenylene)(1,2-ethenylene)(3,5-dimethoxy-1,4-phenylene)], compound 2_3. To a stirred solution of 0.92 g (0.002 mol) compound 1_3 and 1.40 g (0.002 mol) 1,4-xylylene-bis(triphenylphosphonium chloride) in 50 ml of mixture (3/2 w/v) of anhydrous ethanol and molecular-sieve-dried chloroform, a solution

Table 2 Yields, relative molecular weights, glass transition temperature (T_g) and elemental analysis results of the polymers

Polymer, 2_x	Yield (%)	Unit weight	M_w	Polydispersity	T_g (K)	Elemental analysis			
						C		H	
						calc.	found	calc.	found
2_3	90	530	3.5×10^4	1.6	400	70.2	69.7	5.70	5.78
2_4	90	544	1.8×10^4	2.2	396	70.6	70.0	5.92	5.96
2_5	91	558	2.1×10^4	3.3	383	71.0	70.4	6.13	6.20
2_6	88	572	4.2×10^4	1.4	367	71.3	71.1	6.34	6.41
2_7	92	586	1.8×10^4	3.4	359	71.7	71.3	6.53	6.70
2_8	91	600	2.3×10^4	2.9	359	72.0	71.7	6.71	6.80

Table 3 Chemical shifts of ^1H n.m.r. of the diester monomers

	Chemical shift (ppm)[a]						
x	H_1	H_2	H_3	H_4	H_5	H_6	H_7
2	9.92(2H)	7.16(4H)	3.89(12H)	3.14(s; 4H)			
3	9.92(2H)	7.16(4H)	3.91(12H)	2.85(t; 4H)	2.26(q; 2H)		
4	9.91(2H)	7.15(4H)	3.90(12H)	2.72(t; 4H)	1.95(t; 4H)		
5	9.91(2H)	7.15(4H)	3.89(12H)	2.68(t; 4H)	1.86(m; 4H)	1.63(m; 2H)	
6	9.91(2H)	7.15(4H)	3.90(12H)	2.66(t; 4H)	1.83(m; 4H)	1.54(m; 4H)	
7	9.91(2H)	7.15(4H)	3.89(12H)	2.64(t; 4H)	1.80(m; 4H)	1.46(m; 4H)	1.40(m; 2H)
8	9.91(2H)	7.15(4H)	3.90(12H)	2.64(t; 4H)	1.79(m; 4H)	1.46(m; 4H)	1.42(m; 4H)

[a] s, singlet; t, triplet; q, quintet; m, multiplet; the resolution is not high enough for counting the splittings. ^3J coupling constants in the methylene segments are all 7–8 Hz

of 0.11 g (0.0048 mol) sodium in 10 ml anhydrous ethanol was added, dropwise, at 25°C. The mixture was stirred for 2 h, and a solution of 2 ml of hydrochloric acid in 10 ml of distilled water was added to quench the reaction and to dissolve any sodium chloride present. The paste-like product was collected by filtration and then dissolved in chloroform. This solution was washed thoroughly with water/ethanol (5:1 v/v) to eliminate triphenylphosphine oxide and sodium chloride. Then the solution (0.05 g polymer in 4 ml chloroform) was used to cast films on a clean glass surface pretreated with dichlorodimethylsilane. The solvent was evaporated in a hood; the dried film was peeled off the glass and further dried *in vacuo* at 50°C for 8 days to give 1.06 g (90% yield) of a yellow film.

The other polymers (compounds 2_4, 2_5, 2_6, 2_7, 2_8) were synthesized in a similar way. The results, including yields, relative molecular weight (g.p.c.), glass transition temperatures (T_gs) and elemental analyses are listed in *Table 2*.

Characterization

*FT*i.r. spectra were taken on an IBM system IR/3X type 913X *FT*i.r. spectrometer equipped with Nicolet PC/IR Operation software.

^1H n.m.r. spectra were recorded on a Varian XL-300 spectrometer, using 32 f.i.d. accumulation and a pulse width of 10.2 μs. ^{13}C n.m.r. spectra were recorded on a Varian XL-200 spectrometer, using 512 transients and a 10.2 μs pulse width. In all cases samples were dissolved in $CDCl_3$; the chemical shifts were measured relative to those of tetramethylsilane (TMS).

G.p.c. was performed, using THF as the solvent, on a Waters model 500 with a Waters 416 differential refractometer and a Waters 730 data module. Polystyrene standards (Polymer Laboratories Ltd, UK) were used in the calibration.

D.s.c. measurements were carried out on an indium-calibrated Perkin–Elmer DSC-4 under helium with a heating rate of 20°C min^{-1}.

Elemental analyses were performed by the Microanalysis Lab at the University of Massachusetts at Amherst.

Film doping and electrical conductivity measurements

Films (10–30 μm thick) were prepared as described above. The film doped with iodine vapour at room temperature slowly became black. Electrical conductivities were measured by the standard four-probe method, using spring press-contact electrodes at room temperature in air.

RESULTS AND DISCUSSION

Characterization of dialdehydes

The melting points of the dialdehyde monomers decrease with increasing length n (n = number of carbon atoms) of the methylene chain, with an alternating odd–even effect caused by packing differences in the crystalline structure that are due to the different symmetries of the molecules (*Table 1*). Assigned ^1H n.m.r. data are summarized in *Table 3*; *Figure 2* shows one example. The numbers of hydrogen atoms, their position (see *Figure 3*), and the coupling pattern of the signals unequivocally prove the structure of the compounds.

An example of a dialdehyde i.r. spectrum is given in *Figure 4*; *Table 4* summarizes the relevant assignment.

Characterization of polymers

The i.r. and ^{13}C n.m.r. spectra (*Table 5*) establish the structure of the polymers $\mathbf{2}_3$ to $\mathbf{2}_8$, as expected from the Wittig reaction mechanism[14]. In the i.r. spectra (see *Figure 4* for an example), the aldehyde C=O stretch absorption near 1700 cm^{-1} was no longer present, while the ester C=O near 1760 cm^{-1} remained; between 957 and 965 cm^{-1} a new band emerged as a result of the out-of-plane bending of the *trans* CH=CH moieties. However, the latter does not prove the absence of *cis* configurations, whose absorptions are weak because the out-of-plane vibration of the *cis* CH=CH group causes very little change in dipole moment, a property the polymers share with the *cis/trans* mixture of the model compound 1,4-bis[2-(3,4,5-trimethoxyphenyl)ethylene] benzene[15].

In the ^{13}C n.m.r. spectra of the polymers in $CDCl_3$ solution, there was a satisfactory agreement between observed and calculated chemical shifts of the ω,ω'-alkanedioate carbons. Furthermore, a striking correspondence exists between the rigid segments of the polymer and the *cis/trans* mixture of the model compound (*Table 5*). The assignment and discussion of the model spectrum has been given previously[16]. In fact, as expected, the spectra display two peaks for every carbon atom, with the largest *cis:trans* splittings at the V_1, V_2, and A_2 carbons and the smallest at M_3, whereas the pure all-*trans* configuration of the model obviously displays only one peak per carbon atom (see *Table 5* for locations of specific carbon atoms).

Another noteworthy point is that the peak intensities corresponding to *cis* and *trans* configurations are nearly equal in the polymer n.m.r. spectra. Under the experimental conditions employed, the peak intensities correlate strongly with composition[17], therefore the *cis:trans* ratio was determined by using the pairs of peaks of A_2, A_3, and M_3. The results, also shown in *Table 5*,

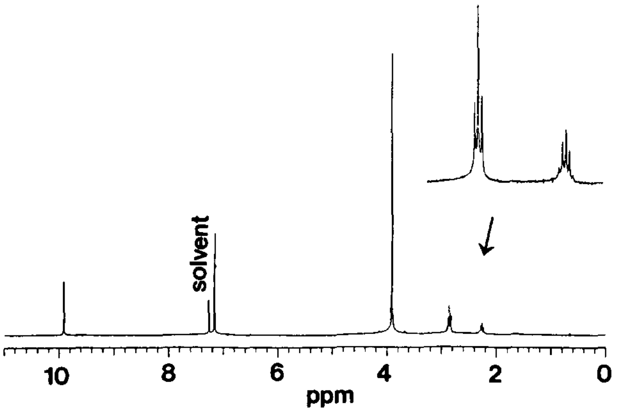

Figure 2 ^1H n.m.r. spectrum of dialdehyde compound $\mathbf{1}_3$ in $CDCl_3$ solution. Expanded section shows the coupling patterns of the signals from the aliphatic segment

Table 4 Infra-red spectra of the diester dialdehydes

	Absorption						
Absorbing group	$\mathbf{1}_2$	$\mathbf{1}_3$	$\mathbf{1}_4$	$\mathbf{1}_5$	$\mathbf{1}_6$	$\mathbf{1}_7$	$\mathbf{1}_8$
ν(CH) of Ph	3007	3007	3007	3007	3007	3007	3007
ν_{as}(CH)	2946	2946	2946	2946	2946	2946	2946
ν_s(CH)	2849	2849	2849	2849	2849	2849	2849
ν(C=O) (–COO–)	1789	1757	1759	1763	1763	1763	1763
ν(C=O) (–CHO)	1697	1701	1700	1698	1698	1696	1698
Ph breathing	1604	1605	1605	1607	1603	1603	1605
	1502	1501	1501	1501	1501	1501	1499
δ(C–H) CH_2	1469	1468	1472	1462	1466	1466	1472
δ(C–H) CH_3	1388	1391	1391	1387	1389	1383	1387
ν(C–O) of	1338	1331	1333	1333	1333	1337	1331
(Ph–O–C)	1128	1125	1120	1121	1130	1130	1127
(CO–O–Ph)	1236	1237	1242	1237	1237	1238	1240
γ(C–H) of Ph with 1,2,3,5 substitution	838	835	835	833	835	843	830

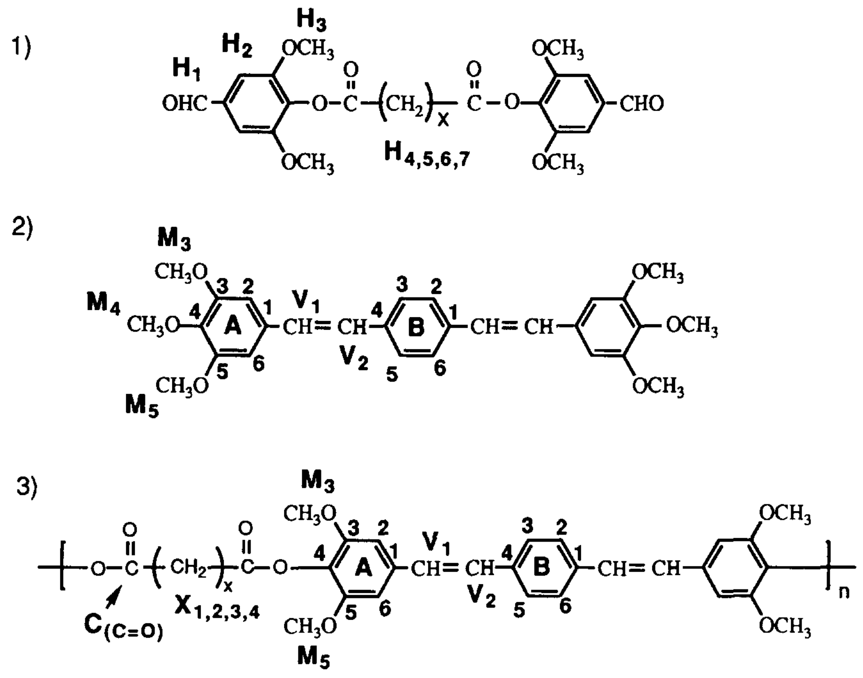

Figure 3 Atom numbering scheme used in n.m.r. assignments for the dialdehydes (1), the model compound (2) and the copolymers (3)

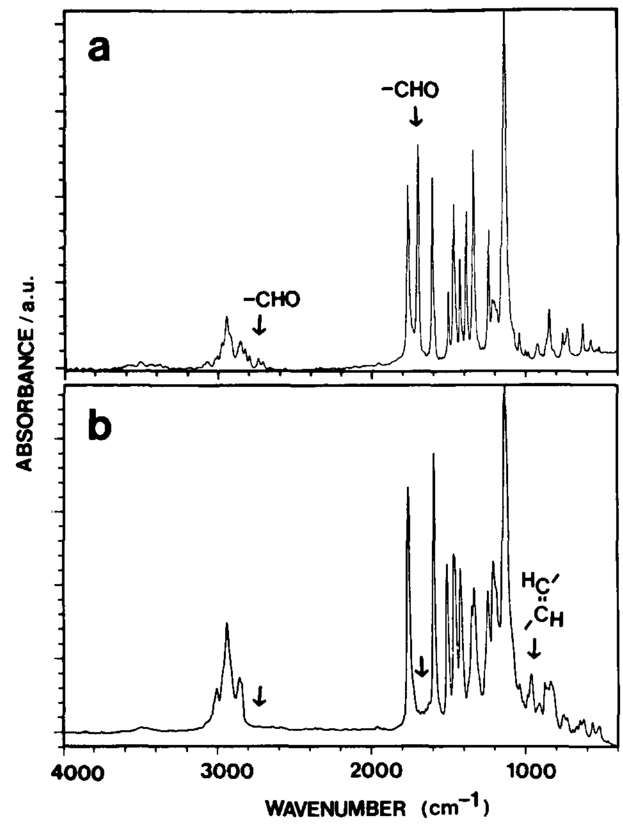

Figure 4 I.r. spectra of dialdehyde 1_7 (a) and polymer 2_7 (b)

reveal a high *cis*:*trans* ratio of about 1. It suggests that the betaine formation is the step that dominates the stereochemical outcome of the Wittig reaction (*Figure 5*). The formation rates of *erythro*- and *threo*-betaine should be equal, because of their nearly equal energy content, while betaine formation should be quasi-irreversible ($k_1 \sim k'_1 > k_{-1} \sim k'_{-1}$; *Figure 5*). The alternative — about equal decomposition rates of *erythro*- and *threo*-betaine ($k_3 \sim k'_3$) — seems unlikely with unstabilized ylids; the observed *cis*:*trans* ratios suggest little stabilization in the ylids employed. Normally, PPV derivatives containing *cis*-olefinic links can be isomerized to the all-*trans* form by refluxing in toluene for 4 h in the presence of a catalytic amount of iodine. This procedure applied to the *cis*/*trans* mixture of $\mathbf{2}_3$ to $\mathbf{2}_8$ led to incomplete conversion because iodine and polymer immediately formed a black complex that precipitated from the solution. Thus we have not yet been able to isolate either a pure *cis* form or a pure *trans* form of these polymers. Model compounds of *cis* and *trans* configurations have recently been separated and studied[18].

An attempt to use dialdehyde monomer $\mathbf{1}_2$ in the synthesis of polymer $\mathbf{2}_2$ was not successful. This failure may be due to the fact that the alkyl chain in $\mathbf{1}_2$ contains only two carbons and the protons on the carbons are much more acidic because they are influenced by both of the C=O groups. The relatively high acidity of the protons allows them to compete with the phosphonium salt in reacting with the strong base in the reaction.

Table 5 $CDCl_3$ solution chemical shifts (ppm) of ^{13}C n.m.r. and *cis* isomer percentages of the model compounds and the polymers

			x					
Carbon atoms[a]	All-*trans* model	*cis*–*trans* model	3	4	5	6	7	8
$C(A_1)$	133.1	133.0	130.1	130.1	130.1	130.1	130.1	130.1
		132.6	129.4	129.4	129.4	129.5	129.4	129.4
$C(A_2, A_6)$	103.8	103.8	103.1	103.1	103.1	103.2	103.1	103.1
		106.2	105.6	105.6	105.6	105.7	105.6	105.6
$C(A_3, A_5)$	153.5	153.5	152.2	152.3	152.2	152.4	152.3	152.3
		153.0	151.8	151.8	151.8	151.9	151.8	151.9
$C(A_4)$	138.0	137.9	136.5	136.5	136.5	136.5	136.5	136.5
		137.2	136.0	136.0	136.0	136.1	136.0	136.0
$C(V_1)$	128.6	128.5	128.4	128.4	128.4	128.7	128.4	128.4
		130.2	129.0	128.8	130.1	130.1	130.1	130.1
$C(V_2)$	127.7	127.7	128.2	128.4	128.4	128.5	128.4	128.4
		129.5	128.8	128.7	128.8	128.9	128.8	128.8
$C(B_1B_4)$	136.6	136.6	135.6	135.6	135.6	135.6	135.6	135.6
		136.0	135.2	135.2	135.2	135.2	135.5	135.2
$C(B_2, B_3, B_5, B_6)$	126.8	126.8	126.9	126.9	126.9	127.0	126.9	126.9
		126.2	126.3	126.3	126.3	126.4	126.3	126.3
$C(M_3, M_5)$	56.1	56.1	56.1	56.1	56.1	56.2	56.1	56.1
		55.9	55.9	55.9	55.9	56.0	55.9	55.9
$C(M_4)$	60.9	60.8						
$C(C{=}O)$			170.9	171.2	171.3	171.6	171.5	171.6
$C(X_1)$			32.8	33.5	33.7	33.9	33.8	33.9
$C(X_2)$			20.7	24.4	24.7	25.0	25.0	25.1
$C(X_3)$					28.3	28.7	28.8	29.0
$C(X_4)$							28.8	29.2
cis percentage	0	35	55	52	52	61	47	51

[a] A_n, caromatic carbons; B_n, aromatic carbons; M_n, methoxy carbons; V_n, vinylene carbons, see *Figure 4*

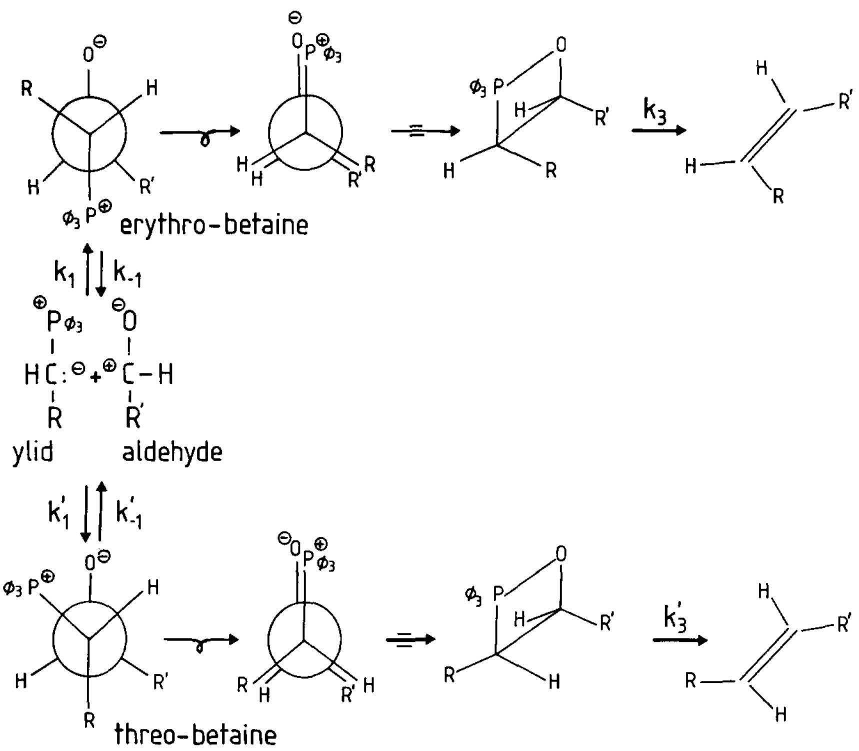

Figure 5 Part of the Wittig reaction mechanism, emphasizing the stereochemical course. *Erythro-* and *threo*-betaine are shown in their presumably lowest energy conformation

This side reaction will retard the formation of the phosphonium ylid. Therefore the expected polymer was not produced in the polymerization process.

Results of g.p.c., with polystyrene as the calibration standard, indicate molecular weights ranging from 18 000 to 35 000 (see *Table 2*). These values are much higher than those of conventional PPV synthesized using the Wittig reaction[15]. One reason is the high solubility of the monomeric reactants and intermediate oligomers in the mixture of anhydrous ethanol and chloroform. The presence of chloroform increased the solubility of the higher oligomers, which in turn allowed the polymer chain to grow before premature precipitation from the reaction medium. Prolonging the polymerization time does not increase the final molecular weight. In fact, it allowed side reactions because of the presence of ester groups and strong base. Ester hydrolysis was minimized by running the reaction for a relatively short time at room temperature or lower.

D.s.c. experiments reveal neither crystallization, melting, nor decomposition phenomena in the range 153–493 K, but each polymer shows a T_g between 359 and 400 K (see *Table 2*). The results suggest that the polymers are isotropic, homogeneous materials, a conclusion consistent with the high transparency of the polymer films. The data in *Table 2* show that the T_g decreases as the length of the flexible block increases, as expected.

Chloroform and THF solutions of the polymers show a fluorescence observable by the naked eye under ambient conditions, a property similar to that of the analogous copolymers which possess both photoluminescence (PL) and electroluminescence (EL) properties[19,20]. The ongoing study of PL and EL in this series of copolymers will be reported later.

The conductivities of the iodine-doped films are presented in *Table 6*. The length of the flexible block does not appear to affect the conductivity, although that of polymer 2_3 is about one order of magnitude larger than the other values. Previous work[7] on PV model compounds doped with iodine and blended with polystyrene showed that the highest conductivities are reached at a concentration of 20% (by weight) of the electrically active component. As *Table 6* shows, the conjugated blocks constitute 66.7–75.5% of the weight of polymers 2_3 to 2_8. On the basis of the variations that are dependent on the length of the flexible segment, we predict that copolymers with still longer flexible chains will possess comparable electrical conductivities but improved mechanical properties. The conductivities of the doped films are fairly stable when kept in air at room temperature. The black coloration remained for several months, but the conductivity decreased to a stable level of 10^{-6} S cm^{-1} over a period of 6 weeks.

Table 6 Electrical conductivities, iodine uptakes and conjugated block weight percentages of the polymers

2_x	Iodine uptake (%)	Electrical conductivity (S cm^{-1})	Content of conjugated block (wt%)
2_3	168	1.3×10^{-2}	75.5
2_4	150	1.4×10^{-3}	73.5
2_5	155	1.7×10^{-3}	71.7
2_6	134	1.5×10^{-3}	69.9
2_7	123	1.1×10^{-3}	68.3
2_8	146	1.1×10^{-3}	66.7

CONCLUSION

Copolymers with alternating conjugated and non-conjugated blocks were synthesized and characterized. They are intrinsically soluble and fusible and possess good film-forming properties, yielding transparent, yellow, free-standing films. Films doped by iodine vapour at room temperature reach electrical conductivities of 10^{-3} to $10^{-2}\,S\,cm^{-1}$.

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