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Intrinsically Soluble Copolymers with Well-Defined Alternating Substituted *p*-Phenylenevinylene and Ethylene Oxide Blocks

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ABSTRACT: Three new copolymers with well-defined alternating substituted *p*-phenylenevinylene (PV) and ethylene oxide (EO) blocks were studied. The multiblock copolymers were synthesized using the Wittig reaction and characterized with GPC, IR, elemental analysis, and ^{13}C and ^{1}H NMR. Thermal properties were studied with DSC and the results compared with those of blends of a model compound and poly(ethylene oxide). The copolymers are intrinsically soluble and fusible, and free-standing films can be cast from chloroform solutions. Iodine doping of the films from vapor or in solution yields materials with electrical conductivities in the range of 10^{-3} S cm^{-1}.

Introduction

Poly(*p*-phenylenevinylene) (PPV) and its derivatives have been synthesized and studied as electrically conducting polymers for about 2 decades.[1-5] During this period, many significant improvements have been made, including the rationalized doping of the polymer with a variety of dopants,[6-8] the synthesis of the polymer *via* a precursor route,[3,4] orientation and alignment of the molecular chain by stretching the film or fiber to achieve anisotropic electrical conductivity,[9] and the modification of PPV by substituting different groups on the phenyl rings[10] or on the olefinic carbons.[5,10] PPV model compounds are also being studied in an attempt to understand their structure–property relations.

Doping the low molar mass model compounds yields electrically conducting materials.[11,12] Furthermore, blends of PPV derivatives and of the model compounds with conventional polymers can also be doped conveniently to yield conducting materials. However, these blends are characteristically inhomogeneous.[13] To improve the homogeneity of such blends, we initiated a study of novel multiblock copolymers that consist of substituted PV blocks and conventional polymer blocks. The PV blocks can be doped and produce electrically conducting species[14] and can be used as light-emitting chromophores.[15] The flexible blocks increase the solubility of the copolymer and provide a film-forming capability. They also provide some protection for the doped species against ambient conditions. Changing the flexible blocks, therefore, may well affect the overall properties of the copolymer. With respect to the present study, different flexible blocks may also provide different permeabilities in the copolymer for the dopant and some variation in the stability of the conductivity to the atmosphere. In previous publications[14,15] we reported on copolymers that consisted of short blocks of substituted PV (rigid blocks) and of methylenes (flexible blocks), joined by ester and ether links. In the present study, we present a study of electrically conducting copolymers containing the same rigid blocks but with ethylene oxide (EO) as the flexible blocks (Figure 1). Compared with the other two series of copolymers, these present materials also facilitate the study of property differences between the copolymers and blends of a model low molar mass compound in a matrix of PEO. In conjunction with the results derived from an earlier study of similar blends,[12] the comparison not only provides more evidence for the proposed molecular structure of the copolymers but also extends the understanding of the functions of rigid conjugated and flexible nonconjugated blocks in doping and electrical conduction processes.

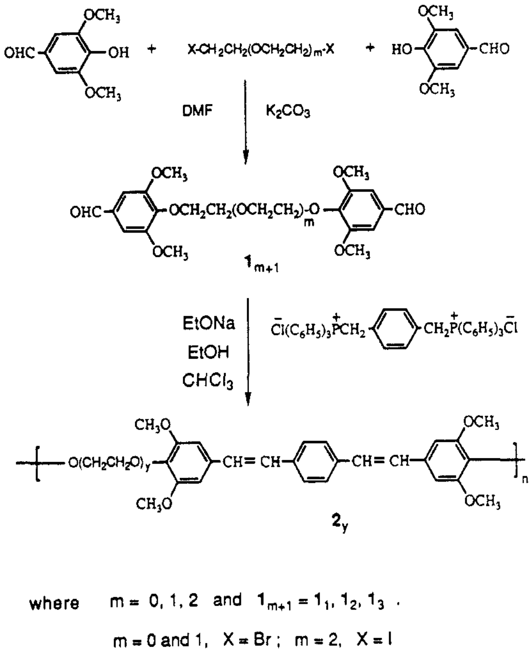

Figure 1. Synthetic route for producing dialdehydes (1_1, 1_2, and 1_3) and block copolymers (2_1, 2_2, and 2_3).

From the newly synthesized dialdehydes 1_1, 1_2, and 1_3, the multiblock copolymers 2_1, 2_2, and 2_3 were prepared using the Wittig reaction. The dialdehydes and the copolymers were characterized by elemental analysis, IR, and NMR. The copolymers are soluble in organic solvents (e.g., chloroform and tetrahydrofuran) and have, as shown by gel permeation chromatography, weight-average molecular weights in the range (2–3) × 10^4. Differential scanning calorimetry (DSC) was used to study the copolymers as well as blends which consisted of PEO and the model compound of the conjugated block, i.e., *trans*, *trans*-1,4-bis[2-(3,4,5-trimethoxyphenyl)ethenyl]ben-

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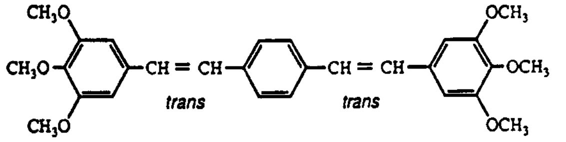


Figure 2. Structure of the model compound (M), *trans,trans*-1,4-bis[2-(3,4,5-trimethoxyphenyl)ethenyl]benzene.

Table I. Characterization of the Dialdehydes

			elem anal. (%)			
			C		H	
dialdehyde	yield (%)	mp (°C)	calcd	found	calcd	found
1_1	41.0	188–189	61.5	61.5	5.68	5.68
1_2	86.4	75–77	60.8	60.8	6.03	5.92
1_3	79.5	107–109	60.2	60.1	6.32	6.28

zene (Figure 2), henceforth, designated as M. In the blends, the ratio of crystallization enthalpy of M to melting enthalpy decreases from nearly unity in PEO-rich blends to nearly zero in PEO-poor blends, a result suggesting that a high degree of crystallinity is already present in freshly prepared PEO-poor blends, whereas in PEO-rich blends the originally dispersed state of M requires annealing to crystallize. In the copolymers, however, despite the high molar ratios of conjugated to flexible, nonconjugated blocks (which are comparable to the PEO-poor blends of the model compound and PEO) neither crystalline nor liquid crystalline behavior was observed. DSC shows the copolymers undergo a glass transition at T_g's ranging from 64 to 121 °C. The copolymers can be cast into free-standing films, which upon doping by iodine vapor display electrical conductivities of about 10^{-3} S cm^{-1}.

Experimental Section

Syntheses of Dialdehydes and Copolymers. 1,2-Bis(4-formyl-2,6-dimethoxyphenoxy)ethane, compound 1_1: a solution of 3.64 g (0.02 mol) of 3,5-dimethoxy-4-hydroxybenzaldehyde and 1.88 g (0.01 mol) of 1,2-dibromoethane in 150 mL of DMF was stirred and heated at 60 °C while 3.0 g (0.022 mol) of potassium carbonate was added slowly. After the addition, the solution was stirred and kept at 60 °C overnight, and the mixture was then poured into 2 L of distilled water. After 2 h, the precipitate was collected, dried in air at ambient temperature, and then recrystallized from ethanol/water (5/1). The yield of 1_1 was 1.6 g (41%) with a melting point of 188–189 °C.

The two other dialdehydes, namely, 1.5-bis(4-formyl-2,6-dimethoxyphenoxy)-3-oxapentane (compound 1_2) and 1,8-bis-(4-formyl-2,6-dimethoxyphenoxy)-3,6-dioxaoctane (compound 1_3), were synthesized in the same way from corresponding starting materials. The yields, melting points, and elemental analyses are listed in Table I.

Poly[oxyethyleneoxy(2,6-dimethoxy-1,4-phenylene)(1,2-ethenylene)(1,4-phenylene)(1,2-ethenylene)(3,5-dimethoxy-1,4-phenylene)], compound 2_1: to a stirred solution of 1.56 g (0.004 mol) of compound 1_1 and 2.80 g (0.004 mol) of 1,4-xylylenebis-(triphenylphosphonium chloride) in 100 mL of anhydrous ethanol and molecular-sieve-dried chloroform (3/1) was added, dropwise, at ambient temperature a solution of 0.23 g (0.01 mol) of Na in 15 mL of anhydrous ethanol. After the addition, the mixture was stirred for 4 h and then 5 mL of 2% hydrochloric acid was added. The pastelike product, collected on the wall of the flask, was thoroughly washed with ethanol/water (3/1) to remove the byproducts triphenylphosphine oxide and NaCl. It was subsequently isomerized to the *all-trans* configuration by refluxing for 4 h in toluene in the presence of a catalytic amount of iodine. After removal of the toluene, the product was dissolved in 30 mL of chloroform and the solution was used to cast a film on clean glass pretreated with dichlorodimethylsilane. The solvent was evaporated in a hood, and the dried film was peeled off the glass and further dried *in vacuo* at 40 °C for 2 weeks to give 1.67 g of a yellow polymeric product.

Table II. Characterization of the Copolymers

					elem anal. (%)			
					C		H	
copolymer	yield (%)	$M_w \times 10^{-4}$	M_w/M_n	T_g (°C)	calcd	found	calcd	found
2_1	91	2.3	4.2	123	73.0	72.3	6.13	6.20
2_2	95	2.9	2.7	97	71.4	71.0	6.39	6.45
2_3	92	2.8	4.3	66	70.1	69.5	6.61	6.72

The other polymers, compounds 2_2 and 2_3, poly[oxy-3-oxapentyleneoxy(2,6-dimethoxy-1,4-phenylene)(1,2-ethenylene)-(1,4-phenylene)(1,2-ethenylene)(3,5-dimethoxy-1,4-phenylene)] and poly[oxy-3,6-dioxaoctylene(2,6-dimethoxy-1,4-phenylene)(1,2-ethenylene)(1,4-phenylene)(1,2-ethenylene)(3,5-dimethoxy-1,4-phenylene)], respectively, were synthesized in the same way from the corresponding dialdehydes. The yields, relative molecular weights (obtained by GPC), and elemental analysis results are listed in Table II.

The model compound, *trans,trans*-1,4-bis[2-(3,4,5-trimethoxyphenyl)ethenyl]benzene, was synthesized in the same way as discussed in ref 16.

Blends of Model Compound (M) with PEO. The model compound and PEO (Aldrich; MW 200 000) were weighed according to the selected weight ratio and dissolved in chloroform with a solid/solvent ratio of 0.5 g/40 mL. The solution was poured onto a glass surface pretreated with dichlorodimethylsilane. After the solvent was evaporated in a hood, the film was peeled off and further dried *in vacuo* at 40 °C for 2 weeks.

Characterization. FTIR spectra were obtained on an IBM IR/3X Type 913X FTIR spectrometer equipped with Nicolet PC/IR Operation software.

^{1}H NMR spectra were recorded using a Varian XL-300 spectrometer in $CDCl_3$ with 32 FID accumulation using a pulse width of 10.2 μs, and chemical shifts were referred to TMS. ^{13}C NMR spectra were recorded on a Varian XL-200 spectrometer in $CDCl_3$ with 2048 transients and a pulse width of 10.2 μs, and chemical shifts were referred to TMS. GPCs were performed using THF as solvent on a Waters Model 500 with a Waters 416 differential refractometer and a Waters Data Module 730. Polystyrene standards (Polymer Laboratories Ltd., U.K.) were used in the calibration.

DSC measurements were carried out on an indium-calibrated Perkin-Elmer DSC-4. The samples were scanned at a rate of 20 °C/min under helium at 20 psi. The elemental analyses were performed by the Microanalysis Lab at the University of Massachusetts at Amherst.

Doping and Electrical Conductivity Measurement. A solution of 0.05 g of the polymer in 4 mL of chloroform was poured onto a piece of a carefully cleaned glass surface pretreated with dichlorodimethylsilane. The solvent was evaporated in a hood at room temperature to yield a transparent free-standing film with a typical thickness of 10–30 μm measured by a micrometer. The film was doped with iodine vapor at room temperature and slowly became black over 2 days. In other experiments solution doping was performed in which solutions of 0.1 g of copolymer in 5 mL of chloroform and 0.15 g of iodine in 5 mL of THF were mixed and stirred for 2 min. The mixture was then poured onto a glass surface to cast films as described above.

Electrical conductivities were measured with a standard four-probe method using spring press contact electrodes at room temperature in air every 2 h during the first 10 h of the doping process and at 8-h intervals later. The conductivities reported are the maximum conductivities obtained with an uptake of iodine of 140–170 wt % referred to the polymer.

Results and Discussion

Characterization of the Dialdehydes. The elemental analyses of the dialdehydes 1_1, 1_2, and 1_3 given in Table I show excellent agreement between calculated and experimental values (see Table I).

IR spectra (see Figure 3a) display strong absorption bands in the range 1682–1695 cm^{-1} and weak ones between 2700 and 2800 cm^{-1}, a result establishing the presence of

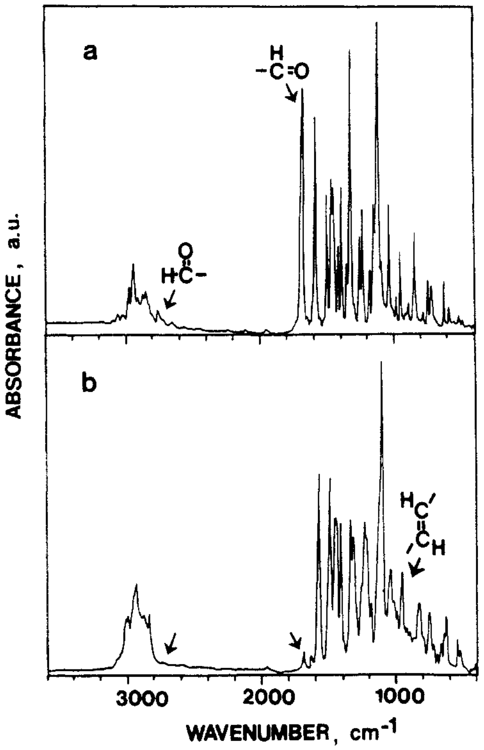
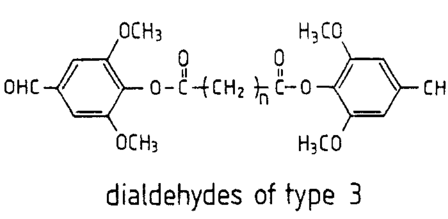


Figure 3. IR spectra of (a) dialdehyde 1_2 and (b) copolymer 2_2.

conjugated aldehyde groups. Several medium strength peaks in the range of 1450–1600 cm^{-1} can be attributed to phenyl ring stretching vibrations, and a peak near 840 cm^{-1} assigned as a C–H out-of-plane bending vibration of an isolated ring hydrogen atom agrees with the substitution pattern of the phenyl ring. A very strong peak at 1130 cm^{-1} and a medium strong peak at 1040 cm^{-1} are interpreted as C–O–C stretching vibrations, an assignment consistent with the aralkyl ether nature of the compounds.[17]

High-resolution ^{1}H NMR spectra are shown in Figure 4, and the assignments are shown in Table III. The numbering schemes used to label the carbon and hydrogen atoms are indicated in Figure 5. The position and splitting pattern of the signals prove the structure of the compounds. It is noteworthy that all experimental chemical shift values are larger (i.e., more downfield) than those calculated from standard chemical shift increments.[18] This discrepancy suggests a somewhat diminished electron density at the periphery of the molecules where the hydrogen nuclei are situated.

Comparison of the experimental shifts of dialdehydes 1_1, 1_2, and 1_3 with the experimental shifts of dialdehydes of type **3** (δ(Ca) ~ 9.85 ppm in compounds 1_x versus δ(Ca) = 9.92 ppm in compounds 3_x; δ(2) = 7.10 ppm in 1_x versus δ(2) = 7.15 ppm in 3_x; δ(Me) ~ 3.88 ppm in 1_x versus δ(Me) = 3.88 ppm in 3_x (see ref 14)) shows a qualitative correlation with the Hammett σ-values of O-alkyl and OCO-alkyl groups, i.e., and OCH_2CH_2– chain appears to be less electron withdrawing than an $OCOCH_2CH_2$– chain.



dialdehydes of type 3

^{13}C NMR spectra and their assignments are presented in Figure 6 and Table IV. These results confirm the proposed structure. As expected, the chemical shifts remain unchanged when the length of the ethylene oxide chain is varied. This observation facilitates the assignments of C(X1) and C(X2) in dialdehyde 1_2. In 1_3 the shifts of C(X2) and C(X3) are very close. In order to distinguish these peaks, a heteronuclear correlation two-dimensional NMR (HETCOR 2D-NMR) study was made, and the results are shown in Figure 7. This information together with the unambiguous assignment of the ^{1}H spectrum allowed us to assign with certainty δ = 70.4 ppm to C(X2) and δ = 70.6 ppm to C(X3).

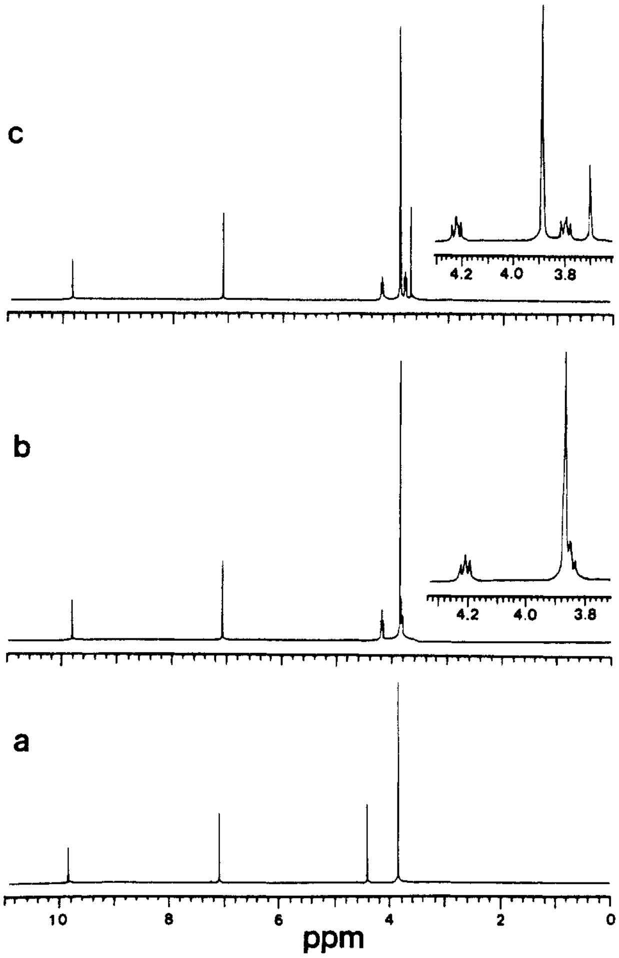


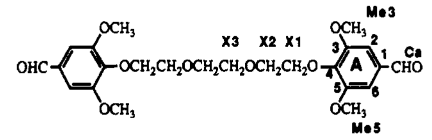
Figure 4. ^{1}H NMR spectra of the dialdehydes in $CDCl_3$: (a) compound 1_1; (b) compound 1_2; (c) compound 1_3. The atom numbering scheme is given in Figure 5.

Table III. ^{1}H NMR Spectra of the Dialdehydes in $CDCl_3$ Solution

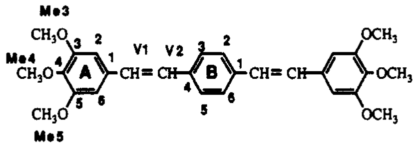
proton[a]	chemical shift (ppm) monomer 1_1	monomer 1_2	monomer 1_3
H(Ca)	9.86	9.83	9.84
H(2)	7.11	7.08	7.10
H(Me)	3.88	3.87	3.89
H(X1)	4.43	4.22[b]	4.22[b]
H(X2)		3.85[b]	3.80[b]
H(X3)			3.70

[a] See Figure 5 for the atomic numbering scheme. [b] Triplet, with ^3J = 5 Hz.

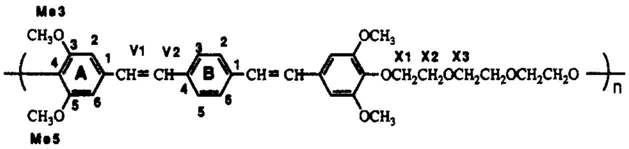
Characterization of the Polymers. In the IR spectra of the copolymers (see Figure 3b) the band at 1682–1695 cm^{-1}, which was assigned to the C=O stretching vibration in the dialdehydes, is no longer present, but a new band at 957–959 cm^{-1} has emerged. This new band is attributed to the out-of-plane bending vibration of the *trans* –CH=CH– moieties, which are formed from the C=O in



monomer labels for NMR assignment



model compound labels for NMR assignment



polymer labels for NMR assignment

Figure 5. Atom numbering scheme used in NMR assignments.

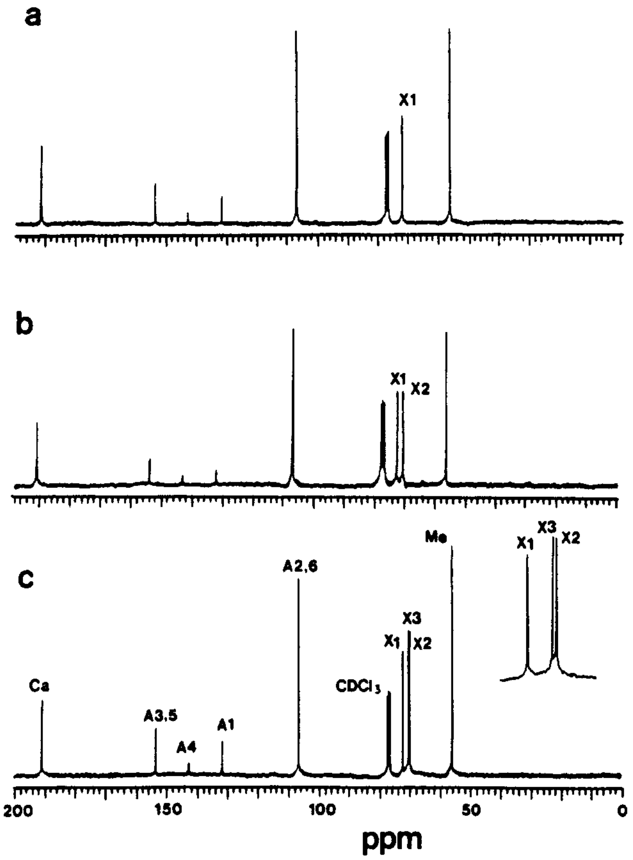


Figure 6. ^{13}C NMR spectra of the dialdehydes in CDCl$_3$: (a) compound 1_1; (b) compound 1_2; (c) compound 1_3. See Figure 5 for the atom numbering scheme.

the Wittig polymerization and subsequent isomerization processes.

The assignments made on the basis of ^{13}C NMR spectra of the copolymers in Figure 8 are compared with that of M in Table V. The differences between the chemical shifts of M and the copolymers are less than 0.3 ppm, except for C(A4). This exception is anticipated. In M, C(A4) is connected to a methoxy group, whereas it is connected to at least one ethylene oxide group in the copolymers. In contrast, the other carbon atoms of M and the copolymers all have very similar chemical surroundings. The assignments in the phenylenevinylene moieties follow those given by Nouwen et al.[19] in an extensive NMR study of alkoxy-substituted PPV derivatives and by Yang et al.[20] in a HETCOR 2D-NMR study of M. The carbon atom shifts in the ethylene oxide blocks of the copolymers are assigned as were those in the dialdehyde monomers because of the great similarity in chemical shift values and the high degree of certainty of the dialdehyde assignment. The following conclusions can be drawn. First, the spectra confirm the correctness of the proposed structures 2_1, 2_2, and 2_3. Second, the configuration around the olefinic bonds in the polymers is *trans*; no significant *cis* chemical shifts were observed. This finding indicates that the conventional method for isomerization to the *all-trans* form (refluxing the sample in toluene with a catalytic amount of iodine) is applicable to the polymers containing EO blocks. This behavior contrasts with that of similar copolymers with the same rigid blocks but with flexible alkyl blocks connected via ester bonds.[14]

Table IV. ^{13}C NMR Spectra of the Dialdehydes in CDCl$_3$ Solution

	chemical shift (ppm)		
carbon atom[a]	dialdehyde 1_1	dialdehyde 1_2	dialdehyde 1_3
C(A1)	131.6	131.8	131.7
C(A2, A6)	106.8	106.6	106.7
C(A3, A5)	153.5	153.8	153.7
C(A4)	142.4	142.4	142.4
C(Ca)	191.0	191.0	191.0
C(M3, M5)	56.3	56.2	56.2
C(X1)	72.0	72.4	72.4
C(X2)		70.4	70.4
C(X3)			70.7

[a] See Figure 5 for the atom numbering scheme.

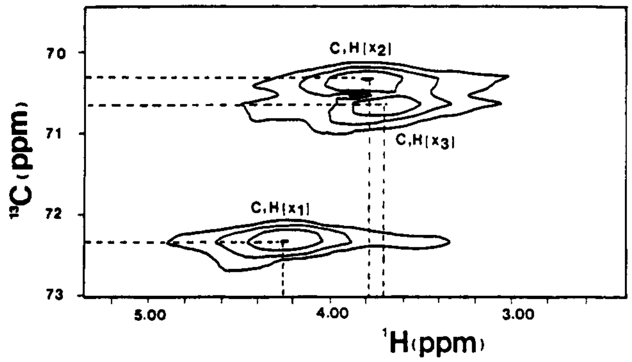


Figure 7. Short-range coupling in the heteronuclear correlation 2D-NMR spectrum of compound 1_3.

Gel permeation chromatography shows (see Table II) that polystyrene-relative molecular weights (M_w) of the copolymers are 23 000–29 000. Molecular weight distributions are rather broad because of the limitation of the Wittig condensation reaction. The use of chloroform as a cosolvent in the polymerization process helps to increase the molecular weights. When the polymerizations were carried out in pure ethanol, the relative molecular weights of the polymers were between 10 000 and 20 000. Chloroform, which is a good solvent of the polymer, keeps the growing oligomers in solution and prevents termination of the polymerization by early precipitation. Normally, when the polymer is not soluble in the medium, Wittig condensation polymerizations yield polymers with lower molecular weights.[5,10]

The UV–vis spectra of the copolymers are identical to that of the M in the range 200–600 nm. A similar phenomenon has been observed in another series of polymers.[15]

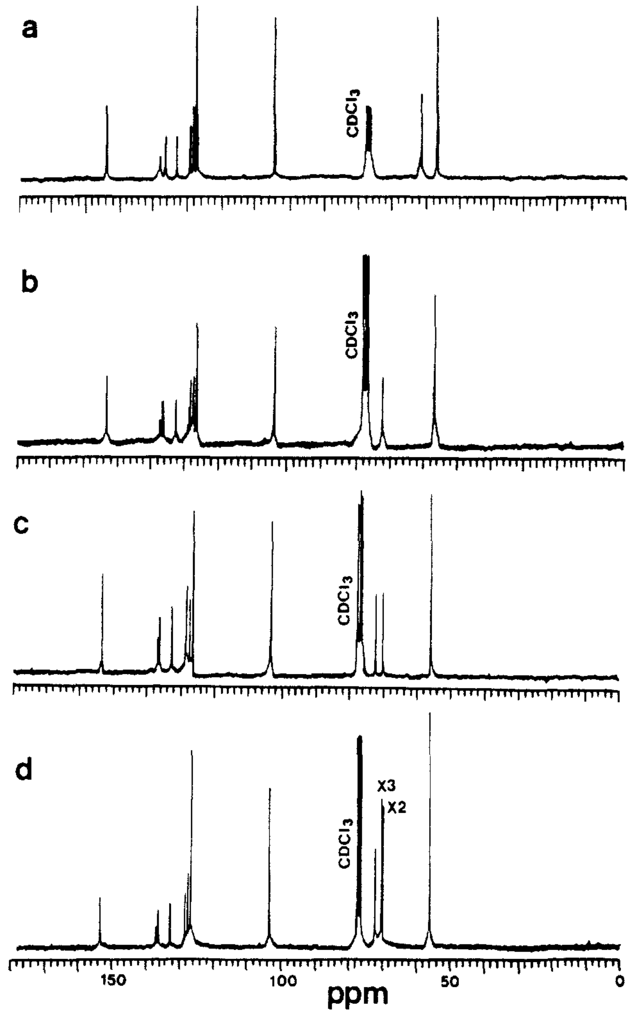


Figure 8. ^{13}C NMR spectra from $CDCl_3$ solution: (a) model compound (M); (b) copolymer 2_1; (c) copolymer 2_2; (d) polymer 2_3.

Table V. ^{13}C NMR Spectra of the Copolymers and the Model Compound in $CDCl_3$

	chemical shift (ppm)			
carbon atom[a]	model compound	copolymer 2_1	copolymer 2_2	copolymer 2_3
C(A1)	133.1	132.9	133.0	133.1
C(A2, A6)	103.8	103.8	103.5	103.6
C(A3, A5)	153.5	153.5	153.5	153.5
C(A4)	138.0	137.4	137.0	136.9
C(V1)	128.6	128.6	128.6	128.6
C(V2)	127.7	127.7	127.6	127.6
C(B1, B4)	136.6	136.6	136.5	136.5
C(B2, B3, B5, B6)	126.8	126.8	126.8	126.8
C(Me3, Me5)	56.1	56.2	56.1	56.1
C(Me4)	60.9			
C(X1)		71.8	72.3	72.3
C(X2)			70.3	70.4
C(X3)				70.6

[a] See Figure 5 for the atom numbering scheme.

DSC of the Copolymers and Blends. DSC results, shown in Figure 9 and Table II, indicate that each copolymer displays a T_g in the measurment range between -120 and +220 °C. (The figure only shows a part of the temperature range from 0 to 200 °C.) Neither a melting peak nor any transition attributable to liquid crystal behavior was found in the heating and cooling cycles in this temperature range. When the copolymers were heated up to their glass transition temperatures, they softened and eventually turned into a viscous fluid. These results and the transparency of the copolymer films establish that the copolymers are amorphous, homogeneous, and fusible. It is noted (Table II) that, as the PEO block is lengthened, the T_g decreases. This is consistent with the premise that the glass transition results from motion in the flexible EO blocks with values modified by the rigid end-group anchoring units.

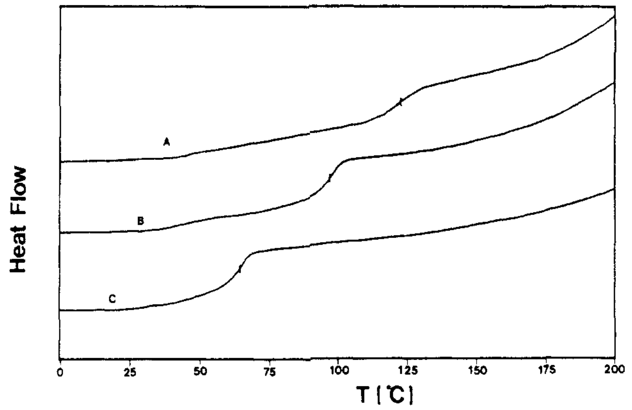


Figure 9. DSC of the copolymers: (A) copolymer 2_1; (B) copolymer 2_2; (C) copolymer 2_3.

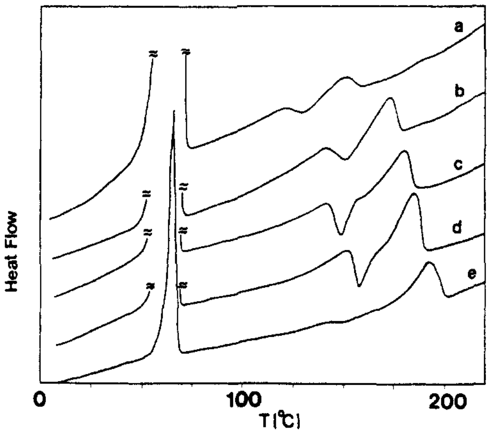


Figure 10. DSC of blends of the model compound (M) and PEO (P) with weight ratios M/PEO of (a) 1/10, (b) 1/3, (c) 1/2, (d) 2/3, and (e) 1/1.

For comparison, several blends of the conjugated model compound M with PEO were prepared (see the Experimental Section) and investigated by DSC (Figure 10). At 64 °C the PEO matrix melts while at higher temperatures, the viscosity of the matrix decreases, and the low molar mass M molecules develop greater motional freedom and recrystallize. Indeed, an exothermic crystallization peak is often seen, followed by an endothermic melting peak. The enthalpy of crystallization (ΔH_c) and of melting (ΔH_m) should be equal if the crystalline exotherm originated from an amorphous mixture, i.e., if at the beginning of the heating process the low molar mass M molecules were randomly distributed in the PEO matrix. Figure 10 shows that this prediction is essentially true for a blend with a M/PEO = 1/10 weight ratio. Rapid evaporation of the solvent in the preparation of the blends left behind a nonequilibrium system. Therefore, at a low concentration of the M molecules the latter can be completely dispersed in PEO. It is found that the melting enthalpy becomes larger than the crystallization enthalpy when the M/PEO ratio exceeds 1/3. This suggests that increasing the ratio M/PEO to values greater than 1/3 permits a fraction of M to crystallize in the PEO matrix during the preparation of the blend from solution. A similar behavior for the same model compound was previously observed in a blend with poly(methyl methacrylate) using solid-state NMR.[13]

As the M/PEO ratio increases, the $|\Delta H_c|/\Delta H_m|$ ratio decreases. As the ratio M/PEO is increased to 1/1, $|\Delta H_c|/|\Delta H_m|$ became so small that most of the crystalline material melting in the DSC experiment originates from the blend preparation process. In the copolymers, however, the weight ratio of the rigid block to flexible block (ratio R/F) is 6.67 for copolymer 2_1, 3.85 for copolymer 2_2, and 2.70 for copolymer 2_3. Thus in contrast to the blends, the copolymers do not show heterogeneous behavior, despite a high R/F ratio. Neither crystalline nor liquid crystalline behavior was observed for the copolymers even though their aspects of their molecular structure resembles main-chain liquid crystalline polymers.

Pure M has a melting point of 205–206 °C. In the blends, however, the melting point is 20–45 °C lower. This behavior is caused by the interaction between M and PEO molecules and mostly by excessive defects in the crystal.

Doping and Electrical Conductivities. Alkoxy-substituted PPVs are electrically conducting upon doping with iodine.[21,22] The copolymers presented here are analogues of alkoxy-substituted PPV even though the conjugation length of the rigid block is relatively short. However, it is known that a short conjugation length may also result in doped species.[12,23] The copolymer films were doped in iodine vapor; the highest electrical conductivities reached after the doping process were about 10^{-3} S cm^{-1} at iodine uptakes of 140–170 wt %. The copolymers gradually assumed a black color over 2 days. A preliminary ESR study suggests the formation of a charge-transfer complex between the conjugated blocks and the iodine, as occurs in the case of the model compound.[24] This is different from the mainly ionic species present in the PEO/NaI/I_2 system studied by Hardy and Shriver.[25] In addition, blends of M/PEO (1/5) and a control pure PEO film were also doped in the same way in an iodine chamber. In both cases, the films became brown within a few hours and reached conductivity limits in the range of 10^{-6}–10^{-5} S cm^{-1}. Further doping resulted in a black paste rather than a highly conductive film. Similar copolymers with methylenes as flexible blocks and the same conjugated blocks show similar conductivity.[14,24] In combination with the results in ref 12, these results imply that I_2-doped conjugated blocks rather than EO blocks are responsible for the conductivity of the copolymers. The conductivity of the doped copolymer does not vary significantly as the length of the flexible block of the copolymer changes, which is similar to the conductivity behavior of the blends.[12] The conductivity of the blends reaches a plateau as the active component ratio increases to a certain level. The conductivity and the black color is maintained for at least several months when the doped films are stored in a sealed bottle. When stored in ambient air, the iodine evaporated gradually and the conductivity decreased to insulator levels; the film itself became transparent but dark brown. The present copolymers were also doped in solution as described in the Experimental Section. The resulting conductivities were also about 10^{-3} S cm^{-1}. No precipitate was formed when the copolymer and iodine were mixed in chloroform; when the solvent was gradually evaporated in the film-casting process, the newly formed film became black. This behavior is unlike that of model compound blends.[12] In the latter a black precipitate formed immediately upon mixing the chloroform solution of M with a chloroform solution of iodine. Precipitates were also formed in a related series of similar copolymers[14] with ester bonds as linkages between the substituted PV rigid blocks and ethylene flexible blocks.

It is noteworthy that the copolymers 2_1, 2_2, and 2_3 become conducting after doping even though the conjugation length is only $2^1/_2$ PPV units long. The charge transport process in this case must be dominated by interblock and interchain hopping mechanisms.

Conclusion

Well-defined copolymers with alternating substituted PV and EO short blocks were synthesized using the Wittig reaction and are intrinsically soluble and fusible. Homogeneous free-standing transparent films can be cast from the copolymer solution. After doping with iodine, either from the vapor or solution, the copolymers are electrically conducting even though the conjugation length of the phenylenevinylene moieties is only $2^1/_2$ units.

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