Electrical properties of anionically synthesized conducting block copolymer from the precursor polystyrene-*block*-poly(phenyl vinyl sulfoxide)

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A series of styrene–phenyl vinyl sulfoxide diblock copolymers was prepared using the 'living' anionic polymerization technique. The thermally labile phenyl vinyl sulfoxides undergo an elimination process to yield acetylene moieties at 150°C. The weight and volume of the iodine-doped conducting fractions were adjusted by changing the length of the styrene block. A sigmoidal composition-dependent conductivity and a maximum in the dielectric constant measurement near the threshold composition suggested a 'percolation-like' conducting process. In addition to electrical measurement, the block copolymers were also characterized by infra-red spectroscopy, thermal analysis, ^{1}H n.m.r., and size exclusion chromatography.

(Keywords: anionic polymerization; block copolymer; electrical properties)

Introduction

Various methods have been used to improve the processability of usually infusible conjugated conducting polymers. Soluble bulky pendent groups, such as n-butyl, n-butoxy and higher carbon number moieties, attached to the repeating unit structure have been found to enhance the solubility of the conjugated polymer in organic solvents[1,2]. This method usually requires the preparation of speciality monomers. Another extensively studied method is the precursor route for the synthesis of conjugated polymers. Swager *et al.*[3] and Feast *et al.*[4] have used ring-opening metathesis polymerization of the precursor for polyacetylene (PA). Water-soluble sulfonium salts of the precursor to poly(*p*-phenylene vinylene) have also been studied by various groups[5–7]. Copolymerization and grafting with a soluble polymer component can also increase the solubility of a conducting polymer in its conjugated form[8–11]. The solubility of the copolymer, however, is limited by the fraction of soluble material that has been grafted or copolymerized. The requirement of a large soluble non-conducting fraction has usually resulted in low conductivity of the copolymer. An interesting morphology may result, however, for a microphase-separated block or graft copolymer[8,11].

A recent series of studies by Kanga *et al.*[12,13] and the present authors[14,15] has demonstrated the feasibility of preparing yet another PA precursor through anionic polymerization. The polymer prepared, poly(phenyl vinyl sulfoxide) (PVSO), can be polymerized by electron transfer initiators such as lithium naphthalide and delocalized carbanion initiators such as (diphenylmethyl)lithium and (triphenylmethyl)lithium, etc. The molecular weight of the polymer can be readily controlled by the monomer-to-initiator ratio, with polydispersity index usually below 1.3. Without termination, the 'living' anions can be propagated further to produce completely soluble A–B or A–B–A type block copolymers. The thermally labile phenyl vinyl sulfoxide (VSO) can be readily eliminated by heating to a high temperature to yield a benzenesulfenic acid (PhSOH) and an acetylene moiety. Details of the elimination process and its side-reaction products have been given in recent publications by Kanga *et al.*[13] and Reibel *et al.*[16]. The electrical properties of the PVSO homopolymer, as well as its thermal and environmental stability, have been studied using different redox doping agents[14].

For the series of A–B type conducting diblock copolymers prepared in this study, the chemical linkage between the conducting and the non-conducting blocks prohibited macroscopic phase segregation between the two likely incompatible components. Conductivity results when charge carriers are allowed to hop between the microphase-separated domains or when a continuous conducting phase is established. The electrical properties of the conducting block copolymer are reported for the frequency range of 11.7 Hz to 100 kHz and are compared to the results from the blend and random copolymer systems reported previously.

Experimental

Synthesis and preparation of the monomer and polymers. VSO was prepared in our laboratory from thiophenol and 1,2-dibromoethane (Fluka) following the method suggested by Paquette and Carr[17], with some modifications. Details of the monomer synthesis have been presented in a previous publication[14]. The VSO collected was further purified by a three-fold vacuum distillation over calcium hydride. Styrene (Aldrich) was washed first with a 10% NaOH solution to remove the inhibitor and then in deionized water to remove excess base. It was predried in anhydrous sodium sulfate and then vacuum distilled over calcium hydride once. A 1 M fluoroyl lithium in tetrahydrofuran (THF) solution was added dropwise to the styrene monomer until a permanent deep red colour appeared. The thoroughly dried styrene was

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distilled from the coloured mixture under vacuum before polymerization. The purity of the monomers was monitored by i.r. spectrometry and ^{1}H n.m.r.

THF was purified and dried using the conventional method[14]. The initiator employed for the anionic polymerization was 0.5 M sec-butyl lithium (sec-BuLi) in THF. The initiator was prepared in our laboratory by stirring a four to six times molar excess of lithium metal and 2-butyl chloride in dried THF under argon for 72 h. The concentration of the filtered initiator was determined by the Gilmen double titration method[18].

All polymerization reactions were carried out under inert gas atmosphere in a glass manifold purged with high purity nitrogen or argon gas (above 99.96%). The gas was purified after passing through a 4 Å molecular sieve (RDH) column and a BTS (Fluka) catalytic oxygen trap. The solvent, monomers and initiator were all transferred by syringe. The reaction flask and other glassware were all dried in an oven at about 130°C overnight. After connecting the predried reaction flask to the glass manifold, the flask was flame-dried while the manifold underwent a few cycles of evacuation and inert gas filling. A slightly positive pressure of inert gas was maintained during the reactions.

The reactions leading to the formation of the diblock copolymer are shown in *Figure 1*. In a typical copolymerization reaction, 50 ml of dried THF was first injected into the reaction flask followed by 0.6–0.8 ml of the sec-BuLi initiator solution. The mixture was then lowered to −78°C by an acetone/dry ice bath. After reaching −78°C, 0.5–3 ml freshly distilled styrene was injected quickly into the reaction flask. An orange–red colour appeared immediately, indicating the formation of living lithiostyrene anions. After reacting for 10 min, a 5 ml sample solution was withdrawn and terminated in methanol for later molecular weight characterization. Then an amount, approximately 1.2 to 1.5 times in excess of the remaining initiator, of vacuum distilled 1,1-diphenylethylene (1,1-DPE, Fluka) was added to reduce the nucleophilicity of the living lithiostyrene anions. The solution turned to a deep red colour immediately. VSO (2–3 ml) was then injected into the well-stirred reaction mixture as soon as possible. The solution became pale-green, indicating successful initiation of the sulfoxide monomer. The reaction was terminated by degassed methanol after 30 min reaction time. A mixed diethyl ether and methanol (70/30 to 90/10 v/v, depending on the styrene content) non-solvent was used to collect the copolymers by precipitation. The white to pale yellow diblock copolymers were purified by additional reprecipitation and then vacuum dried at room temperature. The yellowness of the copolymers increased with the percentage of VSO. Since VSO is unstable at room temperature[12], the copolymer was stored at −20°C under an inert gas blanket before use.

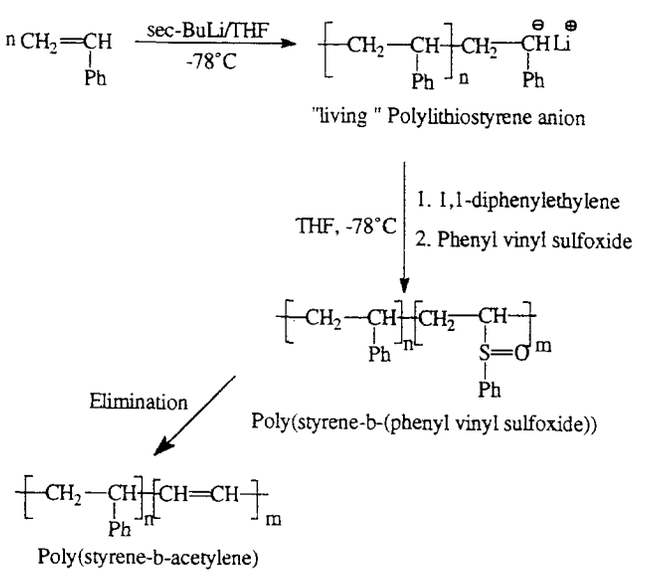

Figure 1 Synthetic routes for the conducting block copolymers

Elimination and doping. Samples of the purified diblock copolymer powders (50–100 mg) were compressed into pellets, 0.5 inch in diameter, using a 12 ton laboratory press. The pellets obtained were clear, smooth films with thicknesses in the range 3×10^{-3} to 1.1×10^{-2} cm. The sample for elimination was placed in a glass reactor connected to a cold trap and a vacuum source. The pressure inside the reactor was kept in the range 10^{-3} to 10^{-4} mmHg at all times. The glass reactor was then heated in a tubular furnace from room temperature to 80°C at a rate of 1°C min^{-1}. After maintaining the temperature at 80°C for 1 h, the reactor temperature was again raised to 150°C at 1°C min^{-1}. The sample was held at the maximum elimination temperature for 4 h. The samples appeared black in colour. To completely remove the elimination product (PhSOH) the pellet was extracted with n-hexane for 12 h. The vacuum-dried sample was then subjected[14] to vapour-phase iodine doping at 50°C for 24 h.

Characterization. The apparent molecular weight and the molecular weight distribution of the copolymers were determined by gel-permeation chromatography (g.p.c.) using a Waters HPLC (model 590) equipped with r.i. detector (model R401) and a Polymer Laboratories PLgel-5μMix column. The eluent was THF running at a rate of 1 ml min^{-1}. A series of polystyrene (PS) standards (Polymer Lab) was used for calibrating the molecular weight (MW). The composition of the copolymers was analysed by FTn.m.r. (270 MHz, Jeol JNM-EX270) and i.r. (Hitachi model 27-30 with data processor) spectrometers. Thermal analysis was performed on a Shimadzu TGA-40 thermogravimetric analyser heating from room temperature to 600°C at 5°C min^{-1} under nitrogen atmosphere. Electrical properties were measured on a GenRad 1693 RLC digibridge using a four-point probe with wedge-shaped contacts for conductivity measurement and parallel plates for dissipation factor measurement. All metallic contacting points were gold-plated. Test frequencies from 11.7 Hz to 100 kHz were employed. Electrical measurement on the copolymers was performed under ambient conditions (18–20°C, 50–60% r.h., 1 atm).

Results and discussion

Characterization of the diblock copolymers. The styrene–phenyl vinyl sulfoxide diblock copolymers are labelled as PSVSOXX. The XX represents the molar percentage of VSO determined experimentally, which varied from 34 to 78%. The formation of diblock copolymers was confirmed by g.p.c. (see *Figure 2*). A single elution peak is obtained for both the styrene block collected after the first polymerization step and the

diblock copolymer after the addition of VSO. A PS standard ($\bar{M}_n = 28\,000$, $\bar{M}_w/\bar{M}_n = 1.07$) is also shown in *Figure 2* for comparison. The polydispersity of the styrene block is less than 1.14 in all cases and is typical for anionically prepared low-*MW* PS. A low-*MW* tail on the chromatogram, however, was detected after the addition of VSO. The low-*MW* fraction increased the polydispersity of the diblock copolymer and is an indication that termination occurred as soon as VSO was added to the reacting mixture. A similar situation was observed when t-butyllithium was employed as the initiator instead of the sec-BuLi used in this study[12]. Termination of the 'living' anions may be due to decomposition products from the unstable VSO, although freshly distilled monomer was used for polymerization. Base-promoted elimination of PVSO by the growing carbanion is also known to terminate the anions during the propagating step[12]. The polydispersity index obtained for all copolymers, however, is still below 1.20 and is comparable to PVSO homopolymers obtained earlier[12,14]. Past experiences have indicated that the polydispersity increased with the molar ratio of VSO monomer to initiator, owing to the side reactions already mentioned[12]. An effort was therefore made to maintain a constant ratio of initiator to VSO monomer.

In order to study the effects of the conducting volume and weight fractions on the overall electrical properties, the styrene block length was varied while the precursor block maintained its length. The *MW* of the styrene block was determined from g.p.c. using PS standards for calibration. The PS blocks have $\bar{M}_n$ below 15000 with some of the lower-*MW* PS blocks beyond the resolution of the g.p.c. column employed. Both the theoretically calculated and experimentally determined *MW* for the styrene block and the copolymer are given in *Table 1*. The *MW* of the diblock copolymers has also been measured by g.p.c. using the same set of PS standards. The results were much lower than theoretically predicted M_n values. This is because the hydrodynamic volume of the VSO repeating unit is different from styrene, and also because of the contribution from low-*MW* species. In order to accurately determine the *MW* of the diblock copolymer, ^{1}H n.m.r. was used to establish the molar ratio of the styrene ($\delta = 7.0$ and 6.5) and VSO ($\delta = 7.5$) repeating units in the copolymers, according to their aromatic proton absorption ratios[12]. From this ratio, the number-average number of repeating units for styrene and VSO was calculated. The overall $\bar{M}_n$ for the diblock

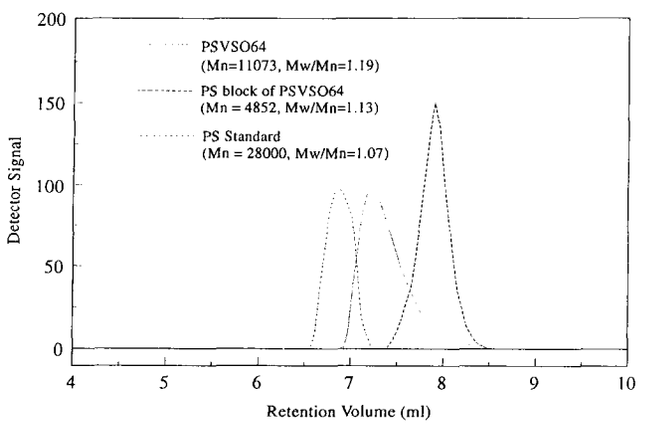

Figure 2 G.p.c. chromatograms of a PS standard, a diblock precursor copolymer (PSVSO64) and its PS block before copolymerization

Table 1 Molecular weight and composition of the diblock copolymers

Sample	Styrene ($\text{mol} \times 10^3$)	sec-BuLi ($\text{mol} \times 10^3$)	PS block			VSO ($\text{mol} \times 10^3$)	PVSO block	Diblock copolymer			PVSO (mol%)		No. styrene units[c]	No. VSO units[c]	Overall M_n[d]
			M_n (calcd)	M_n (g.p.c.)	M_w/M_n (g.p.c.)		M_n (calcd)[a]	M_n (calcd)	M_n (g.p.c.)	M_w/M_n (g.p.c.)	Calculated	Experimental[b]			
PSVSO34	26.10	0.17	15988	14802	1.13	15.18	14824	30812	19599	1.15	38.81	33.71	142.12	72.27	25803
PSVSO55	17.40	0.17	10659	8324	1.13	15.18	15529	26188	15214	1.15	49.92	54.79	79.92	96.86	23068
PSVSO64	8.70	0.17	5329	4852	1.12	15.18	14824	20153	11073	1.19	65.55	63.56	46.59	81.26	17221
PSVSO67	8.70	0.255	3553			22.76	15529	19082	10881	1.19	74.94	66.67			
PSVSO74	4.35	0.17	2665			15.18	14824	17488	9541	1.15	79.19	74.18			
PSVSO78	4.35	0.255	1776			22.76	13588	15365	11474	1.17	83.96	78.63			

[a] $\bar{M}_n$ determined from g.p.c. using THF as solvent and PS standards for calibration
[b] From ^{1}H n.m.r.
[c] Calculated from molar ratio of styrene and VSO
[d] Sum of number of styrene and VSO units multiplied by their formula weight

copolymers can be obtained by multiplying the number of repeating units by their formula weights (see *Table 1*). Owing to reduction in the length of the styrene block, the overall $\bar{M}_n$ of the copolymers decreased with increase in the VSO content.

Thermal elimination and doping. Thermal properties of the PVSO homopolymer have been discussed in length in previous publications[12–16]. The unstable VSO has been known to undergo a concerted, cyclic, sigmatropic elimination process to produce acetylene and PhSOH upon heating[12,13]. The PhSOH may react further to produce a series of side products, such as its acid anhydride. The rate of elimination increases with temperature but undesirable side reactions, such as homolytic cleavage of the sulfur–carbon bond and cross-linking, can also result at high temperature. Usually, elimination at 150°C, which is the maximum elimination rate temperature as determined by d.s.c., has been found to produce samples with the highest extent of elimination and conductivity after doping[14]. A milder elimination condition using a slower heating programme was selected for the diblock copolymer series in order to minimize the number of defects retained. The extent of elimination, however, was always less than 100%, especially when a second component was present. The extent of elimination determined from gravimetric techniques is between 87 and 92%. This is slighly lower than the 90–95% elimination for PVSO homopolymers, but higher than the 83–93% obtained for PS/PVSO blends[15].

The uneliminated copolymers are all soluble in common organic solvents, such as chloroform, methylene chloride or THF. However, solvent-cast thin films with a high VSO content become brittle after thermal elimination and cannot be used for electrical measurement. Instead, room temperature compression-moulded sample pellets were used. The eliminated pellets may be porous in nature; the method used to determine the void fraction and to correct for volume conductivity has been reported in an earlier study[14]. The eliminated samples appeared black in colour, irrespective of the VSO content, which indicates that a high degree of conjugation has resulted. The volume and weight fractions of acetylene units in the copolymer can be calculated from the relative density of the eliminated sample, PA and PS after correcting for the uneliminated VSO[14].

The PA obtained by this precursor method can be doped by either n- or p-type dopant (p-PA). Vapour-phase iodine doping was found to provide samples with the optimal balance of electrical properties and environmental stability under ambient conditions[14]. The doping level for the eliminated product is given as $(CHD_y)_x$, where y is the molar ratio of the dopant D to a CH unit. Since the phenyl moieties in PS and uneliminated VSO may also absorb some of the iodine dopant, the actual amount of iodine reacted to the conjugated CH unit is obtained by subtracting the equivalent amount of iodine that may have been absorbed by the PS block under the same doping conditions[15]. The corrected doping level (y') is between 0.36 to 0.48 and is well above the saturation doping limit. Conductivity is known to be independent of the doping level above the saturation point[19]. The relatively high doping level is also due to the high doping temperature employed.

Electrical properties of the diblock copolymers. The volume conductivity (σ) of saturation iodine-doped p-PA homopolymer and its random copolymers has been reported to have a sigmoidal dependence on four calculated variables over the full conducting composition range[14]. The variables are: the number of defects, the weight and volume fraction of acetylene units, and the mean conjugation length (*MCL*). For the diblock copolymers, the *MCL* and the number of defects remained almost constant owing to a similar VSO block length and the elimination conditions applied. The *MCL* of the conducting block is calculated to be in the range of 7–8 (based on copolymers with known VSO block length). Extrapolating from previous data[14], the conductivity (11.7 Hz) corresponding to p-PA with the same *MCL* is 6×10^{-2} to 2×10^{-1} S cm^{-1}. However, the measured conductivity (at 11.7 Hz) of all the diblock copolymers is well below 10^{-2} S cm^{-1} and the largest reported value is 8×10^{-3} S cm^{-1}. The lower conductivity indicates that the presence of the PS block has somehow hampered the charge transport process, even at high conducting volume fractions. The failure to achieve 'metal-like' conductivity at high conducting volume fractions matches results from the frequency-dependent conductivity study, to be discussed later. The PS block may also have affected homogeneous distribution of the dopant, even though y' is well above the saturation concentration. For a p-PA homopolymer with the highest degree of elimination[14] (at 95%, $y = 0.17$), its conductivity (at 11.7 Hz) is 4.4 S cm^{-1}. This is the upper conductivity limit for the block copolymer system and is comparable to iodine-doped PA obtained by other precursor methods, such as the Durham route ($\sigma = 10$ S cm^{-1}, $y = 0.27$)[19]. The datum, however, is substantially lower than 160 S cm^{-1} ($y = 0.4$) reported for crystalline *trans*-PA prepared according to Shirakawa's method[20].

By changing the length of the PS block in the copolymer while keeping the PVSO block length constant, the conducting volume fraction is varied and its effects on the overall electrical properties can be observed. In *Figure 3*, volume conductivities (from 11.7 Hz to 100 kHz) of the saturation-doped conducting diblock copolymers are found to have a sigmoidal dependence on the volume fraction of the acetylene units. The maximum and minimum conductivities are the

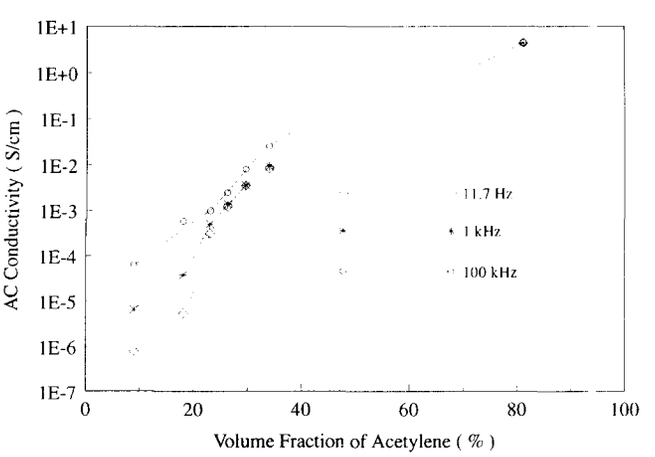

Figure 3 Volume conductivity (at 11.7 Hz, 1 kHz and 100 kHz) of the iodine-doped conducting diblock copolymers as a function of the calculated acetylene volume fraction

conductivity of a p-PA homopolymer and a PS saturation-doped with iodine ($y=0.66$, $\sigma=10^{-8}$ S cm^{-1}). The threshold composition, at which the 11.7 Hz conductivity started to increase rapidly, is found to be about 18 vol% of acetylene units. This threshold onset value shifted to a higher volume fraction with increase in the measuring frequency. The threshold transition was verified by a maximum in the dielectric constant measurement detected near the transition region with the maximum slope change. Disregarding the absolute magnitude of conductivity, the transition threshold matched closely with the result of 16 ± 2 vol% PA for a series of styrene–acetylene block copolymers prepared by anionic-to-Zielger–Natta catalysis[8]. PA prepared from catalytic methods is known to have crystalline fibrillar morphology, whereas precursor-derived p-PA is amorphous in nature[19]. The catalysed products also have higher molecular weight and polydispersity. The differences in morphology and molecular weight of the PA block did not affect the transition range, which indicates that charge transport is affected more by the dispersion of the conducting phase than by the microstructure of the PA chains within the conducting microdomain. Diblock copolymers of 2-vinylpyridine and either butadiene or styrene have also been prepared[11]. The percolation threshold detected at 40–60 mol% of the conducting element is again within the range of 55 mol% VSO reported here. The 2-vinylpyridine samples with high conductivity were reported to have a 'worm-like' conducting domain or bicontinuous two-phase structure using electron microscopy. The similarity in the threshold transition composition for the different block copolymer systems suggested that there may be an equilibrium microphase structure for the rigid rod and random coil diblock copolymer.

As found in earlier studies[14,15], the conductivity increased with frequency for samples with a conducting volume below the threshold composition. This is due to polarization coupling between the dispersed conducting microdomains and the continuous insulating PS matrix[21]. The frequency dependence in conductivity for a conducting composite, however, diminished with increase in conducting fraction and became constant as 'metal-like' conductivity was established. Although the block copolymer become less frequency-dependent above the percolation conducting threshold, their conductivities continue to increase above 1 kHz. Increase in conductivity with frequency is characteristic of the hopping mechanism of conduction[22]. The frequency dependence suggests that conduction is not truly metallic but rather the result of charge carrier hopping along the paths with least resistance.

Conclusions

With the known and narrow MW distribution for the anionically prepared precursor, a scheme to regulate the efficiency of intrachain, interchain and interdomain (or interparticle) charge transport can be effected by modifying the chemical structure and composition of the precursor polymer. Compared to conducting diblock copolymers prepared by different methods, the threshold transition composition is found to be independent of the microstructure and MW of the conducting block, but dependent on the volume fraction of the conducting elements. The results of studies on distribution in the conjugated units and variation in the mean conjugation length will be reported in a forthcoming study in which the electrical properties of the diblock copolymers, polymer blends containing the precursor and random copolymers of the presursor are compared.

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